Mononuclear and Polynuclear Chain Complexes of a Series of Multinucleating N/S Donor Ligands

Tanya K. Ronson,[a] Harry Adams,[a] and Michael D. Ward*[a]

Keywords: Chelates / Coordination chemistry / Copper / Silver / Helical structures

We have prepared a series of five ligands with potentially N,S-bidentate chelating arms derived from 3-[2-(methylsulfanyl)phenyl]pyrazole linked to central aromatic spacers by methylene units. Complexes with a variety of architectures have been obtained, including simple mononuclear complexes and polynuclear chain complexes. The *p*-xylyl-spaced ligand L^1 forms one-dimensional helical coordination polymers with copper(I) and silver(I) ions. These polymers display interligand aromatic stacking interactions within each helical chain. The *m*-xylyl-spaced ligand L^2 forms a coordination polymer with copper(I) but a mononuclear complex with the larger silver(I) ion in which the central phenyl ring is involved in an η^1 π-type Ag···C interaction with the Ag^I. The 3,3′-biphenyl-spaced ligand L^3 also forms one-dimensional polymers with silver(I) and copper(I) ions, but in this case the sequence of bridging ligands between one metal centre and the next follows a zig-zag path rather than being helical. The 1,8-naphthyl-spaced ligand L^4 only forms mononuclear complexes with copper(I) and silver(I) ions showing that this spacer is not large enough to enforce a bridging coordination mode. The three-armed ligand L^5, prepared from 2,4,6-tris(bromomethyl)mesitylene, also forms a mononuclear complex with silver(I) ions, where one of the three arms is pendant. However, when excess silver(I) ions are present two of these mononuclear complexes can be assembled into the trinuclear complex $[Ag_3(L^5)_2](ClO_4)_3$.

Introduction

Metal-directed self assembly of elaborate polynuclear complexes relies in part on a good match between the stereoelectronic properties of the metal ion and the arrangement and type of donor sites on the bridging ligand.[1] With respect to the ligands, a minimum condition is that the binding sites must be arranged so that they bridge two or more metal centres, otherwise simple mononuclear complexes will result. If a bridging ligand is conformationally flexible, the competition between bridging and chelating coordination modes is an important factor in determining the course of a self-assembly reaction. To this end we have been investigating the coordination chemistry of ligands in which two N,N-bidentate, chelating pyrazolylpyridine groups are connected by a range of different spacer groups, which results in different separations between the two metal-ion binding sites. Depending on the nature of the spacer (a phenyl group, a biphenyl group, 1,8-naphthyl, and so on) and the coordination preferences of the metal ion, complexes have been isolated ranging in complexity from simple mononuclear species to dodecanuclear truncated-tetrahedral cages.[2]

In this paper we describe the synthesis and coordination behaviour of a related series of ligands based on N,S-donor chelating (pyrazolyl/thioether) fragments, the structures of whose complexes depend on the nature of the spacer separating the two chelating components. Potentially bridging N,S-donor ligands of this general type have been of some interest recently with respect to coordination with soft metal ions such as Cu^I and Ag^I; the combination of flexible bridging ligands with metal ions, which are tolerant of a wide range of coordination geometries has led to a remarkable collection of oligomeric and polymeric structures.[3] The complexes described in this paper illustrate in particular the propensity of the N,S-donor bridging ligands to afford one-dimensional helical coordination polymers, in contrast to the discrete M_2L_2 dinuclear double helicates which tend to form with the analogous N,O-donor ligands containing pyrazolylphenolate donor sites that we described recently.[4]

Results and Discussion

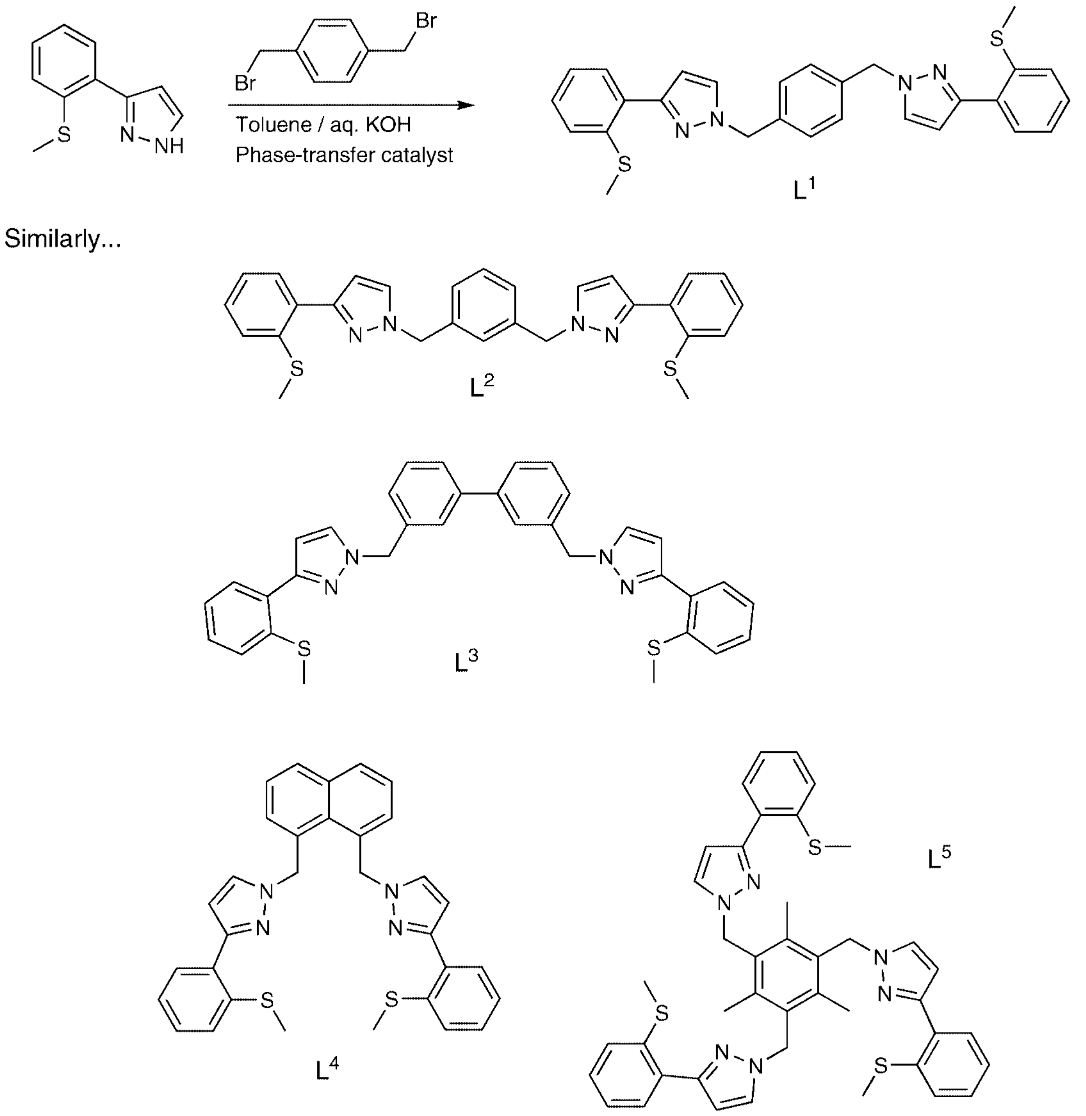
Syntheses and Structures of the Ligands

The ligands are shown in Scheme 1. 3-[2(Methylsulfanyl)phenyl]pyrazole was prepared as described earlier,[5] and was treated with an appropriate bromomethylated aromatic compound under phase-transfer conditions[2] to give the new ligands L^1–L^5. The ligands L^1, L^2, L^3 and L^4 contain two potentially bidentate N,S-chelating units, with pyrazolyl and thioether donors, but differ in length due to variation in the length of the spacer unit. In contrast ligand L^5 is a

---

[a] Department of Chemistry, University of Sheffield,
Sheffield S3 7HF, UK
E-mail: m.d.ward@sheffield.ac.uk

DOI: 10.1002/ejic.200500704



Scheme 1.

potentially hexadentate tripodal ligand with three bidentate arms linked to a central aromatic unit though methylene groups. The ligands were characterised by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and elemental analyses. Ligands L^{1}, L^{4} and L^{5} were also characterised by X-ray crystallography and their structures are shown in Figure 1, Figure 2, and Figure 3.

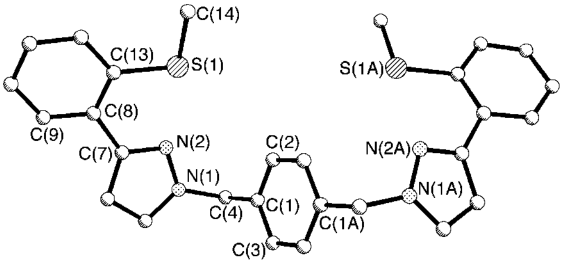


Figure 1. Molecular structure of L^{1}. Symmetry operation to generate equivalent atoms: (–x, y, 3/2 – z).

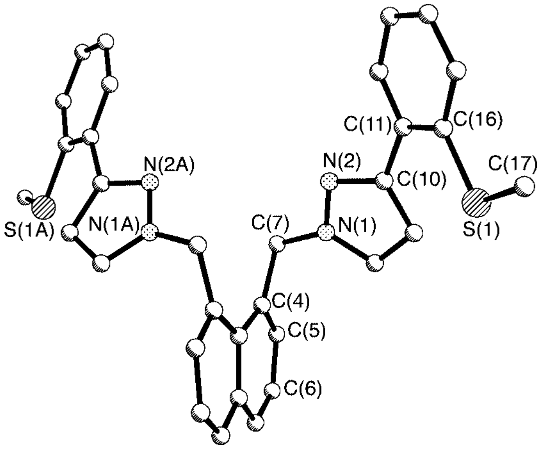


Figure 2. Molecular structure of L^{4}. Symmetry operation to generate equivalent atoms: (1–x, y, 1/2 – z).

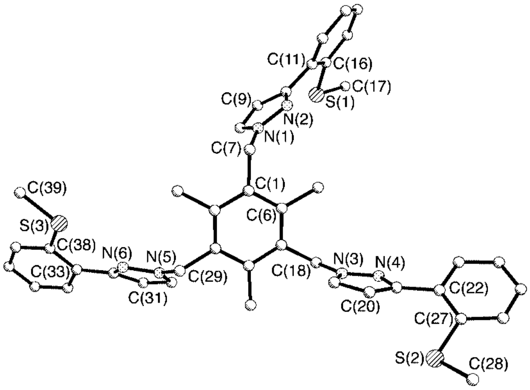


Figure 3. Molecular structure of L^5.

For L^1 the molecule lies astride a twofold axis of symmetry through the centre of the phenyl spacer, such that the two halves are crystallographically equivalent. The (methylsulfanylphenyl)pyrazole units adopt a *cisoid* configuration with the methyl group pointing away from the lone pairs of the pyrazole nitrogen atoms. The chelating units show a significant deviation from planarity with an angle of 26.6° between the methylsulfanylphenyl and pyrazole rings. The *cisoid* arrangement of the rings is, on the face of it, surprising because it brings the lone pairs of electrons on N(2) and S(1) into proximity; in polypyridyl ligands such as 2,2′-bipyridine, and the higher oligomers by contrast, adjacent pyridyl rings are always *transoid* so that the nitrogen lone pairs can avoid each other.[6] In fact the non-bonded N(2)···S(1) distance of 2.863(2) Å is in agreement with the known propensity of divalent S (and Se) atoms to become involved in relatively short contacts with nucleophilic atoms.[7] The nucleophile [here, pyrazolyl N(2)] tends to approach the S atom of an S–X bond in a direction corresponding to elongation of that bond, because of the involvement of the S–X σ* orbital in the interaction; in consequence the N···S–C angle should be nearly linear, consistent with other steric constraints, and in fact the angle N(2)–S(1)–C(14) is almost perfectly linear at 177.9(1)°.

L^4 also lies astride a twofold axis of symmetry which lies through the centre of the naphthyl spacer. The (methylsulfanylphenyl)pyrazole units this time adopt a *transoid* configuration, unlike the *cisoid* configuration observed in L^1; the chelating units show a significant deviation from planarity with an angle of 34.7° between the methylsulfanylphenyl and pyrazole rings. The two chelating arms are arranged on opposite sides of the plane of the central naphthyl spacer, and rotation of the methylsulfanylphenyl rings would be required in order for both arms to chelate to a single metal ion. It is clear from these structures that in L^1 the bidentate units are too far apart from one another to coordinate to a single metal ion, and L^1 must necessarily act as a bridging ligand. However, this is not the case for L^4 where a tetradentate chelating mode is also possible. There is no evidence for any inter- or intramolecular N···S interactions of the type seen for L^1.

Molecules of L^5 have no internal symmetry in the crystal. The chelating units show a significant deviation from planarity with angles of 39.5, 38.5 and 23.9° between the methylsulfanylphenyl and pyrazole rings. One of the (methylsulfanylphenyl)pyrazole units [involving atoms S(3) and N(6)] adopts a *cisoid* conformation, resulting again (as in L^1, above) in a relatively short N(6)···S(3) separation of 2.832 Å, and a near-linear N(6)···S(3)–C(39) angle of 175.7°, both consistent with an intermolecular donor-acceptor interaction involving the lone pair of N(3) and the S–C σ* orbital.[7] The torsion angle between these pyrazolyl and sulfanylphenyl rings is 23.9°. The other two methylsulfanylphenyl-pyrazole units, which have approximately *transoid* conformations, have a greater degree of twist between the aromatic rings (39.5 and 38.5°) because there is no N···S interaction which tends to keep the rings concerned more coplanar. Sulfur atoms S(1) and S(2) are not involved in any intermolecular N···S contacts comparable to that seen for S(3).

Complexes with L^1

The reaction of L^1 with one equivalent of $[Cu(CH_3CN)_4]PF_6$ in dry acetonitrile under nitrogen resulted in a pale yellow solution. Diethyl ether diffusion into the reaction mixture gave pale yellow crystals whose elemental analysis indicates the stochiometry $[CuL^1][PF_6]$, i.e. a 1:1 metal/ligand ratio as expected for a complex between a tetradentate ligand and a metal ion with preference for tetrahedral geometry. The presence of the PF_6^- anion was confirmed by the presence of peaks at 839 and 558 cm^{-1} in the IR spectrum,[8] and the electrospray mass spectrum showed a molecular ion peak at $m/z = 545$ for $\{CuL^1\}^+$.

The X-ray crystal structure (Figure 4) shows that the crystalline material is an infinite one-dimensional helical coordination polymer $\{[CuL^1](PF_6)\}_\infty$; helical chains have become well known recently with examples based on N,S-chelating[4] and other[9] bridging ligands. The Cu^I ion and the phosphorus atom of the PF_6^- are at special positions such that the asymmetric unit contains half a Cu^I ion, half a ligand and half a PF_6^- ion. Each Cu^I ion is in a four-coordinate environment, coordinated by an N,S-chelating arm from each of two separate ligands. Each ligand therefore bridges two metal ions. The Cu···Cu separation between metals linked by the same bridging ligand is 9.85 Å. The geometry around the Cu^I ion is distorted tetrahedral with an angle of 75.5° between the two Cu(NS) planes (Figure 4, a); the twist angle within each bidentate (methylsulfanylphenyl)pyrazole unit is 28.7°. The ligands are arranged around the Cu^I ions such that each polymeric chain is helical with equal amounts of each enantiomer in the crystal. There are interligand aromatic stacking interactions within each helical strand, which is a common feature of helical complexes.[10] Each central phenyl spacer is stacked to a (methylsulfanyl)phenyl ring from a ligand on each side of it, with the stacked rings inclined at 6.7° to each other. The distance between these stacked rings (distance of atoms in one from the mean plane of the other) is in the range 3.2–3.7 Å. The angle between the planes of alternating central

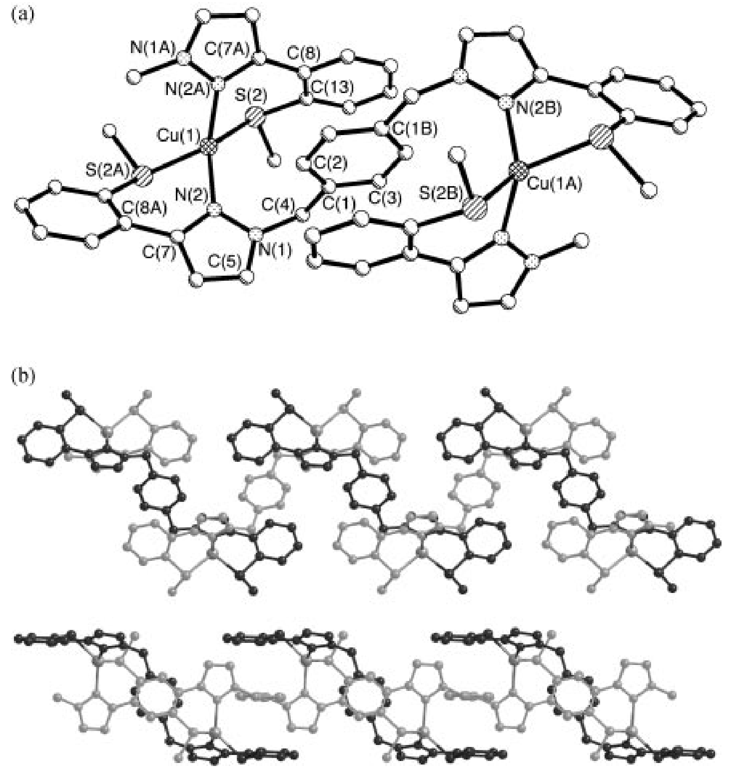


Figure 4. (a) Structure of the metal complex unit of $\{[CuL^1](PF_6)\}_\infty$ showing the coordination geometry around the Cu^I centres. (b) Two views of the one-dimensional helical chain of $\{[CuL^1](PF_6)\}_\infty$, with alternate ligands shaded differently for clarity. The bottom view shows the interligand aromatic stacking interactions within each chain.

phenyl rings is 73.6°, hence stacking can be seen in two almost perpendicular directions (Figure 4, b) (Table 1).

Table 1. Selected bond lengths [Å] and angles [°] for $\{[CuL^1](PF_6)\}_\infty$.

Cu(1)–N(2A)	2.014(2)
Cu(1)–N(2)	2.014(2)
Cu(1)–S(2A)	2.2933(8)
Cu(1)–S(2)	2.2933(8)
N(2A)–Cu(1)–N(2)	118.65(12)
N(2A)–Cu(1)–S(2A)	129.48(7)
N(2)–Cu(1)–S(2A)	87.61(6)
N(2A)–Cu(1)–S(2)	87.61(6)
N(2)–Cu(1)–S(2)	129.48(7)
S(2A)–Cu(1)–S(2)	108.80(4)

Symmetry transformations used to generate equivalent atoms: $-x$, y, $-z + 1/2$.

Reaction of L^1 in methanol with a solution of one equivalent of $AgNO_3$ in H_2O gave a white powder after filtration, whose elemental analysis indicated the composition $\{[AgL^1](NO_3)\}_\infty$. The IR spectrum confirmed the presence of the NO_3^- counterion with a broad band centred around 1339 cm^{-1}, and the FAB mass spectrum (see Experimental Section) showed peaks arising from 1:1, 2:1 and 2:1 Ag/L^1 fragments.

X-ray quality crystals were grown from slow evaporation of the filtrate; the structure of the complex (Figure 5) shows it to be an infinite helical polymer $\{[AgL^1](NO_3)\cdot MeOH\}_\infty$, with a similar structure to $\{[CuL^1](PF_6)\}_\infty$. Each Ag^I ion is in a four-coordinate N_2S_2 environment, coordinated by a N,S-chelating arm from two separate ligands. The nitrate counterions are non-coordinating. The Ag···Ag separation is 7.62 Å, significantly shorter than the inter-metal separation in $\{[CuL^1](PF_6)\}_\infty$. The geometry around the Ag^I ion is almost tetrahedral with an angle of 80.2° between the two Ag(NS) planes. The bidentate (methylsulfanylphenyl)pyrazole unit show large deviations from planarity with twist angles between the two rings of 43.5 and 47.8°. The central phenyl spacers of successive ligands in the chain are oriented at 72.5° to each other. Unlike in $\{[CuL^1](PF_6)\}_\infty$, only every second phenyl spacer is involved in interligand stacking interactions, being sandwiched between pyrazolyl rings on either side of it to which it is near-parallel (6.9° between planes); the distance between the stacked rings is 3.1–3.5 Å (Table 2).

Table 2. Selected bond lengths [Å] and angles [°] for $\{[AgL^1](NO_3)\}_\infty$.

Ag(1)–N(4)	2.231(5)
Ag(1)–N(2)	2.410(5)
Ag(1)–S(1)	2.4782(18)
Ag(1)–S(2)	2.6950(18)
N(4)–Ag(1)–N(2)	120.82(17)
N(4)–Ag(1)–S(1)	150.59(13)
N(2)–Ag(1)–S(1)	77.71(13)
N(4)–Ag(1)–S(2)	75.52(13)
N(2)–Ag(1)–S(2)	99.66(13)
S(1)–Ag(1)–S(2)	126.93(6)

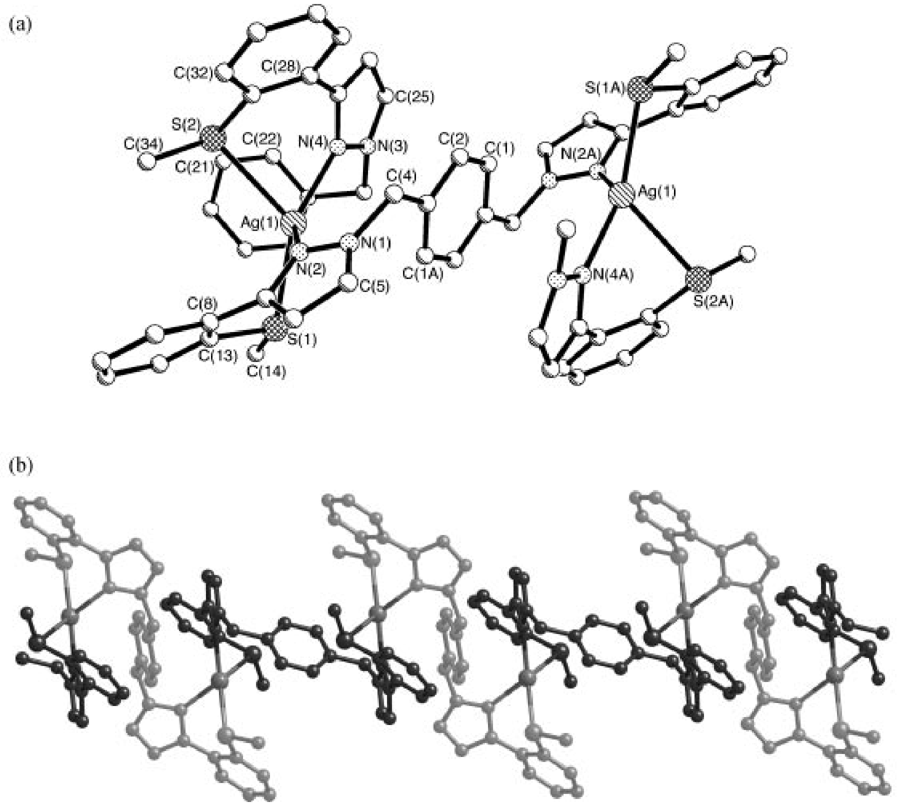


Figure 5. (a) Structure of the metal complex unit of $\{[AgL^1](NO_3)\}_\infty$ showing the coordination geometry around the Ag^I centres. (b) Structure of the one-dimensional helical chain of $\{[AgL^1](NO_3)\}_\infty$ with alternate ligands shaded differently for clarity.

Complexes with L^2

The reaction of L^2 with one equivalent of $[Cu(CH_3CN)_4]BF_4$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether diffusion into the reaction mixture gave almost colourless crystals whose elemental analysis indicates a 1:1 metal/ligand ratio. The IR spectrum confirms the presence of the BF_4^- counterion at 1056 cm^{-1}. The electrospray mass spectrum shows a peak at $m/z = 545$ for the mononuclear species $\{CuL^2\}^+$. The X-ray crystal structure (Figure 6) shows that the crystalline material is an infinite one-dimensional coordination polymer $\{[CuL^2](BF_4)\}_\infty$. However, unlike the structure of $\{[CuL^1](PF_6)\}_\infty$ the chains are not helical. Each ligand is folded back on itself with the two coordinating arms almost overlapping but pointing in opposite directions, coordinating to separate Cu^I ions.

The Cu^I ion and the boron atom of the BF_4^- are at special positions such that the asymmetric unit contains half a Cu^I ion, half a ligand and half of an anion, as well as fractions of two acetonitrile and a diethyl ether molecule which are also at special positions. Each Cu^I ion is in a four-coordinate environment, coordinated by an N,S-chelating arm from each of two separate ligands. The Cu···Cu separation between metals linked by the same bridging ligand is 6.17 Å, significantly shorter than that found in $\{[CuL^1](PF_6)\}_\infty$ (9.85 Å). The geometry around the Cu^I ion is distorted tetrahedral with an angle of 77.2° between the two Cu(NS) planes (Figure 6, a); the twist angle within each bidentate (methylsulfanylphenyl)pyrazole unit is 28.6°. There are no close π-π stacking interactions within each chain (Table 3).

The reaction of L^2 with one equivalent of $[Ag(CH_3CN)_4]BF_4$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether diffusion into the reaction mixture gave almost colourless crystals whose elemental analysis was consistent with the formulation $[Ag(L^2)](BF_4)$. The IR spectrum showed the presence of the BF_4^- counterion with a broad band at 1050 cm^{-1}. The electrospray mass spectrum showed a molecular ion peak at $m/z = 589$ for $\{AgL^2\}^+$ with no peaks for higher oligomers. The X-ray structure of the complex shows it to be the mononuclear complex $[Ag(L^2)](BF_4)$, in contrast to the infinite chain that was observed with Cu^I. There are two unique molecules in the asymmetric unit, which are associated into a dimer by face-to-face π-stacking between the phenyl rings of the aromatic spacers with an average distance of 3.60 Å between the overlapping rings.

The two complex molecules in the asymmetric unit display similar geometries. If only the N,S-donors are considered, both Ag^I ions are in a flattened tetrahedral environment [angles of 80.8° and 80.6° between the Ag(NS) planes], coordinated by an L^2 ligand acting as a tetradentate chelate. One of the bidentate arms shows a larger dihedral twist [44.9° and 49.3° for the molecules containing Ag(1) and Ag(2), respectively] between the two rings than the

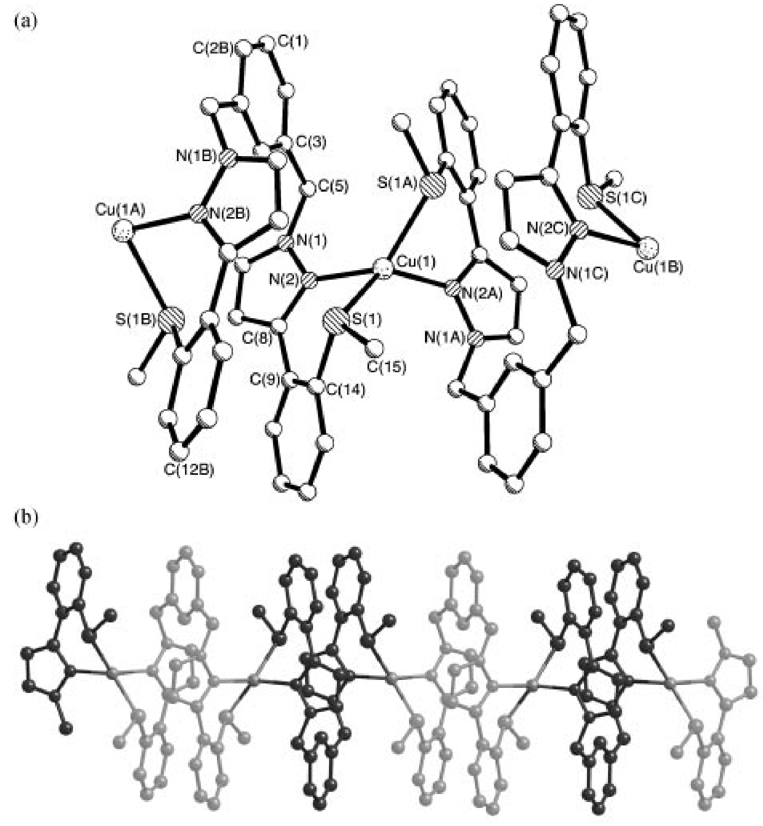


Figure 6. (a) Structure of the metal complex unit of $\{[CuL^2](BF_4)\}_\infty$ showing the coordination geometry around the Cu^I centres. (b) Structure of the one-dimensional chain of $\{[CuL^2](BF_4)\}_\infty$, with alternate ligands shaded differently for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for $\{[CuL^2](BF_4)\}_\infty$.

Cu(1)–N(2A)	2.057(2)
Cu(1)–N(2)	2.057(2)
Cu(1)–S(1A)	2.2992(7)
Cu(1)–S(1)	2.2992(7)
N(2A)–Cu(1)–N(2)	113.93(12)
N(2A)–Cu(1)–S(1A)	84.10(6)
N(2)–Cu(1)–S(1A)	130.48(6)
N(2A)–Cu(1)–S(1)	130.48(6)
N(2)–Cu(1)–S(1)	84.10(6)
S(1A)–Cu(1)–S(1)	119.85(4)

Symmetry transformations used to generate equivalent atoms: $x, -y + 2, -z$.

other [17.7° and 22.7° for the molecules containing Ag(1) and Ag(2), respectively]. The average Ag–N bond length is 2.39 Å and the average Ag–S bond length is 2.64 Å (Table 4). However, the near-linearity of the N–Ag–N angles [169° at each metal centre] results in a large gap in the Ag^I coordination sphere, which is filled by an interaction of each Ag^I ion with the "capping" phenyl ring. The Ag^I ions do not sit centrally above the phenyl rings but are slightly offset, such that they interact with just one C atom (dotted line in Figure 7). The Ag(1)···C(1) separation is 2.76 Å, and the corresponding Ag(2)···C(101) separation in the independent molecule is 2.74 Å. This type of η^1 interaction of an Ag^I ion with a phenyl ring, although less common than the η^2 π-type interaction in which the metal ion interacts with one edge of a phenyl ring,[11] is still well known[12] with many dozens of examples in the Cambridge Structural Database. It is characterised by a contact in the range 2.4–2.8 Å between the Ag^I ion and one C atom such that the Ag–C vector is near-perpendicular to the aromatic ring, as we see for $[Ag(L^2)](BF_4)$, where these angles are 77°

Table 4. Selected bond lengths [Å] and angles [°] for $[AgL^2](BF_4)$.

Ag(1)–N(1)	2.331(3)
Ag(1)–N(4)	2.408(3)
Ag(1)–S(2)	2.6311(10)
Ag(1)–S(1)	2.6602(11)
Ag(1)–C(1)	2.763(3)
Ag(2)–N(101)	2.367(3)
Ag(2)–N(104)	2.446(3)
Ag(2)–S(102)	2.6100(10)
Ag(2)–S(101)	2.6686(11)
Ag(2)–C(101)	2.737(3)
N(1)–Ag(1)–N(4)	169.09(10)
N(1)–Ag(1)–S(2)	116.08(7)
N(4)–Ag(1)–S(2)	70.66(7)
N(1)–Ag(1)–S(1)	76.45(8)
N(4)–Ag(1)–S(1)	110.44(8)
S(2)–Ag(1)–S(1)	107.77(3)
N(101)–Ag(2)–N(104)	168.91(10)
N(101)–Ag(2)–S(102)	114.65(7)
N(104)–Ag(2)–S(102)	72.36(7)
N(101)–Ag(2)–S(101)	74.70(8)
N(104)–Ag(2)–S(101)	112.09(8)
S(102)–Ag(2)–S(101)	108.22(3)

for Ag(1) and 83° for Ag(2). In this case, this results in a coordination geometry about the metal ions that is best described as trigonal bipyramidal, with the C and two S donors forming the trigonal plane and the two N donors being axial. The τ parameter for this complex is 0.67 [0.64 for the independent complex molecular containing Ag(2)], where 1.0 denotes a perfect trigonal bipyramid and 0.0 denotes a perfect square pyramid.[13]

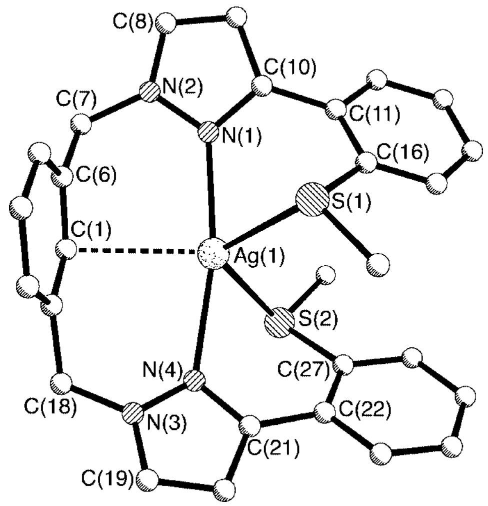


Figure 7. Structure of the metal complex unit of $[AgL^2](BF_4)$. The Ag···C interaction to the phenyl ring is shown with a dashed line.

The presence of this metal–carbon interaction with Ag^I, but not Cu^I, is likely to be an important factor in explaining why $\{[CuL^2](BF_4)\}_\infty$ forms an infinite chain whereas $[Ag(L^2)](BF_4)$ is mononuclear; the binding mode in $[Ag(L^2)](BF_4)$ in which both bidentate arms of L^2 coordinate to the same metal ion necessarily brings the phenyl spacer into close contact with the metal ion. In addition, this mononucleating, tetradentate coordination mode would be harder to achieve with the smaller Cu^I ions in any case.

Complexes with L^3

The reaction of L^3 with one equivalent of $[Cu(CH_3CN)_4]BF_4$ in ethanol resulted in a suspension from which an off-white solid was isolated after filtration. The infrared spectrum showed a broad band centred around 1083 cm^{-1} for the BF_4^- counterions and the FAB mass spectrum showed peaks consistent with 1:1, 1:2 and 2:2 Cu/L^3 fragments; the elemental analysis was consistent with a 1:1 metal/ligand ratio.

X-ray quality crystals were grown by diffusion of diethyl ether vapour into a solution of the complex in MeCN. The

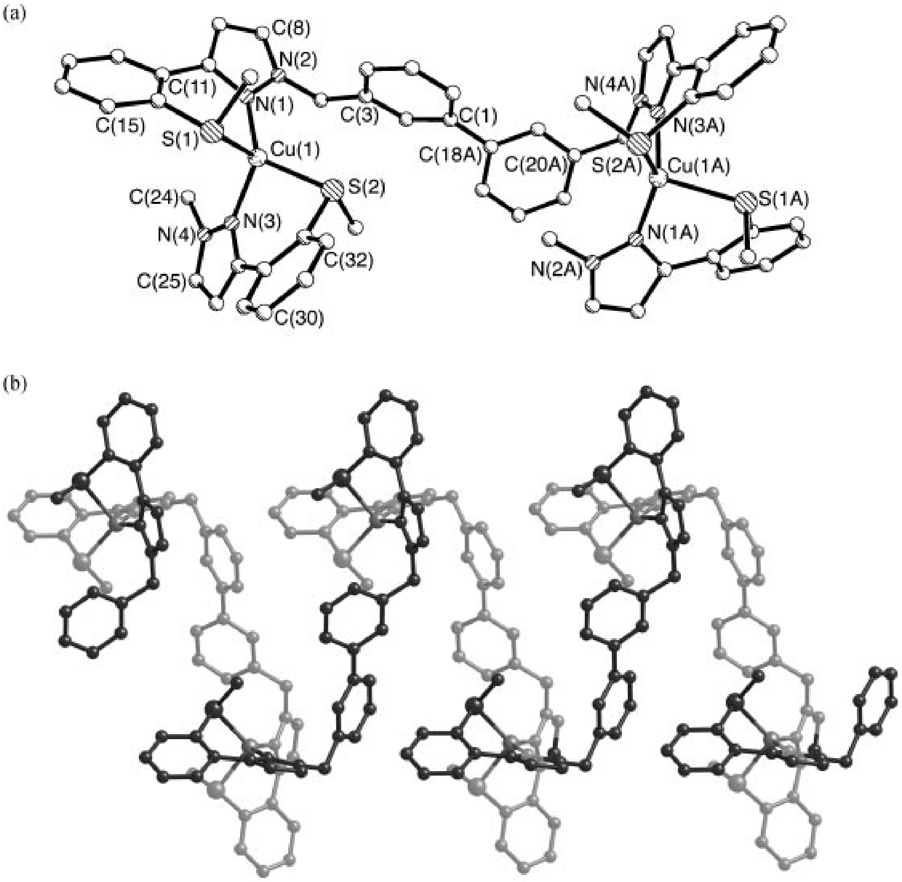


Figure 8. (a) Structure of the metal complex unit of $\{[CuL^3](BF_4)\}_\infty \cdot 1.53CH_3CN \cdot 0.47Et_2O$ showing the coordination geometry around the Cu^I centres. (b) Structure of the one-dimensional polymeric chain of $\{[CuL^3](BF_4)\}_\infty \cdot 1.53CH_3CN \cdot 0.47Et_2O$, with alternate ligands shaded differently for clarity.

structure of the complex (Figure 8) shows it to be the one-dimensional coordination polymer $\{[CuL^3](BF_4)\}_\infty$ with one Cu^I ion and one complete ligand in the asymmetric unit. Unlike the complexes of L^1, the structure of $\{[CuL^3](BF_4)\}_\infty$ is not helical. Rather, the sequence of bridging ligands between one ligand and the next follows a zig-zag path. The Cu^I ions are in a four-coordinate N_2S_2 environment with an almost tetrahedral geometry [angle of 87.2° between the Cu(NS) planes]. The Cu···Cu separation between metal atoms which are linked by the same bridging ligand is 10.645 Å, and the separation between alternate Cu^I centres is almost identical at 10.649 Å. The twist angle within the biphenyl spacer is 40.6° and the twist angles within each bidentate (methylsulfanylphenyl)pyrazole units are 34.7 and 36.7°. Unlike the structure of L^1 there is no face-to-face π-stacking within the polymer chains (Table 5).

Table 5. Selected bond lengths [Å] and angles [°] for $\{[CuL^3](BF_4)\}_\infty \cdot 1.53CH_3CN \cdot 0.47Et_2O$.

Cu(1)–N(1)	1.961(5)
Cu(1)–N(3)	1.996(5)
Cu(1)–S(2)	2.3045(17)
Cu(1)–S(1)	2.3567(18)
N(1)–Cu(1)–N(3)	127.27(18)
N(1)–Cu(1)–S(2)	128.63(14)
N(3)–Cu(1)–S(2)	92.35(14)
N(1)–Cu(1)–S(1)	94.48(15)
N(3)–Cu(1)–S(1)	107.71(14)
S(2)–Cu(1)–S(1)	103.55(6)

The reaction of L^3 with one equivalent of $[Ag(CH_3CN)_4]BF_4$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether diffusion into the reaction mixture gave almost colourless crystals whose elemental analysis indicates a 1:1 metal/ligand ratio. The IR spectrum confirms the presence of the BF_4^- counterion at 1061 cm^{-1}. The FAB mass spectrum shows peaks arising from 1:1, 1:2 and 2:2 Ag/L^3 fragments. The X-ray crystal structure (Figure 9) shows that the crystalline material is another infinite one-dimensional coordination polymer $\{[AgL^3](BF_4)\}_\infty$. One of the coordinating arms [containing S(4) and N(7)] is disordered and has been modelled over two sites; unless otherwise stated only the major component of this disorder will be discussed. Each metal/ligand chain shows a clear zig-zag (non-helical) structure, similar to that of $\{[CuL^3](BF_4)\}_\infty$. The Ag···Ag separations between metal atoms which are linked by the same bridging ligand are 8.95 and 9.05 Å, less than the equivalent distances in $\{[CuL^3](BF_4)\}_\infty$. The separations between alternate Ag^I centres are however greater at 11.97 Å.

The Ag^I ions in each chain alternate between being four-coordinate [Ag(1)] and three-coordinate [Ag(2)]. Ag(1) is in an almost tetrahedral N_2S_2 environment [angle of 87.2° between the Ag(NS) planes], coordinated by two bidentate arms from separate ligands. Ag(2) is in an N_2S environment approximating a T-shape, with the silver atom sitting ca. 0.1 Å above the plane of the donor atoms [N(4), N(5) and S(2)]. The remaining donor atom [S(3)] is too far from the

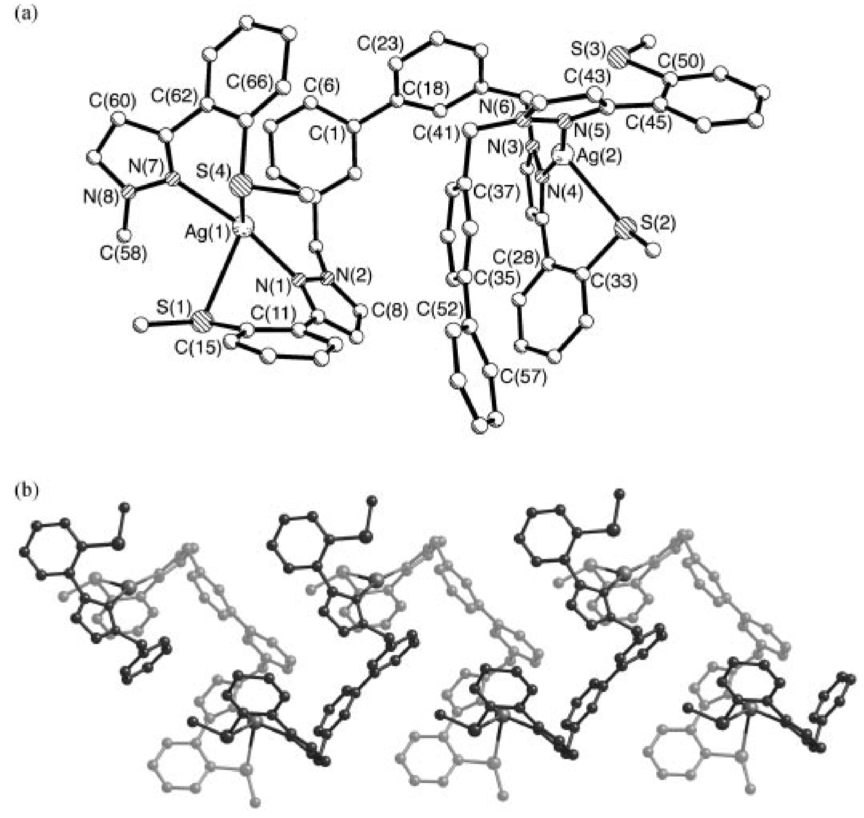


Figure 9. (a) Structure of the metal complex unit of $\{[AgL^3](BF_4)\}_\infty$ showing the asymmetric unit and the coordination geometry around the Ag^I centres. (b) Structure of the one-dimensional polymeric chain of $\{[AgL^3](BF_4)\}_\infty$, with alternate ligands shaded differently for clarity.

metal to be considered as forming a normal coordinate bond [Ag(2)···S(3), 3.02 Å compared to 2.6934(12) Å for Ag(2)–S(2), Table 6] but may interact weakly with Ag(2). The bonds to the N-donors are slightly shorter than those to Ag(1) [Ag(2)–N(4) 2.213(3) Å, Ag(2)–N(5) 2.191(3) Å] as a consequence of the lower coordination number. Despite the low coordination numer there is no evidence for additional Ag···C contacts of the type described above for $[Ag(L^2)](BF_4)$. The twist angles within the biphenyl spacers are 35.4 and 34.2° and the twist angles within each bidentate (methylsulfanyl)phenyl-pyrazole units are in the range 37.7–47.4°. There is no face-to-face π-stacking within the polymer chains. However there is a CH-π interaction between one of the rings of the biphenyl spacer and the CH in the 4-position of the next biphenyl spacer (separation of 2.78 Å between the H^4 of the biphenyl unit and the centroid of the relevant phenyl ring).

Table 6. Selected bond lengths [Å] and angles [°] for $\{[AgL^3](BF_4)\}_\infty$.

Ag(1)–N(7′)	2.133(8)
Ag(1)–N(1)	2.215(3)
Ag(1)–N(7)	2.328(9)
Ag(1)–S(4)	2.632(3)
Ag(1)–S(4′)	2.810(3)
Ag(1)–S(1)	2.8543(13)
Ag(2)–N(5)	2.191(3)
Ag(2)–N(4)	2.213(3)
Ag(2)–S(2)	2.6934(12)
N(7′)–Ag(1)–N(1)	173.3(2)
N(1)–Ag(1)–N(7)	161.2(2)
N(1)–Ag(1)–S(4)	119.95(13)
N(7)–Ag(1)–S(4)	78.4(2)
N(7′)–Ag(1)–S(4′)	75.6(3)
N(1)–Ag(1)–S(4′)	110.28(12)
N(7′)–Ag(1)–S(1)	109.4(2)
N(1)–Ag(1)–S(1)	73.54(9)
N(7)–Ag(1)–S(1)	101.4(2)
S(4)–Ag(1)–S(1)	98.75(7)
S(4′)–Ag(1)–S(1)	97.49(7)
N(5)–Ag(2)–N(4)	164.86(12)
N(5)–Ag(2)–S(2)	115.06(9)
N(4)–Ag(2)–S(2)	79.00(9)

Complexes with L^4

Reaction of L^4 with one equivalent of $[Cu(CH_3CN)_4]PF_6$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether diffusion into the reaction mixture gave colourless crystals whose elemental analysis was consistent with a 1:1 metal/ligand ratio. The IR spectrum showed peaks at 841 and 557 cm^{-1} for the PF_6^- counterions. The FAB mass spectrum showed a molecular ion peak at $m/z = 595$ for $\{CuL^4\}^+$ but no peaks for higher oligomers. A subsequent X-ray crystal structure determination (Figure 10) showed that the crystalline material is the mononuclear complex $[Cu(L^4)](PF_6)$, in obvious contrast to the polymeric structures obtained with L^1, L^2 and L^3. The Cu^I ion is in a distorted tetrahedral N_2S_2 environment [angle of 85.6° between the Cu(NS) planes] with L^4 acting as a tetradentate chelate. The bond lengths to the Cu^I ion are typical for this series (average Cu–N 2.03 Å, average Cu–S 2.30 Å, Table 7). The bidentate arms are not individually coplanar with substantial dihedral twists of 38.7° and 36.5° between the pyrazolyl and methylsulfanylphenyl rings.

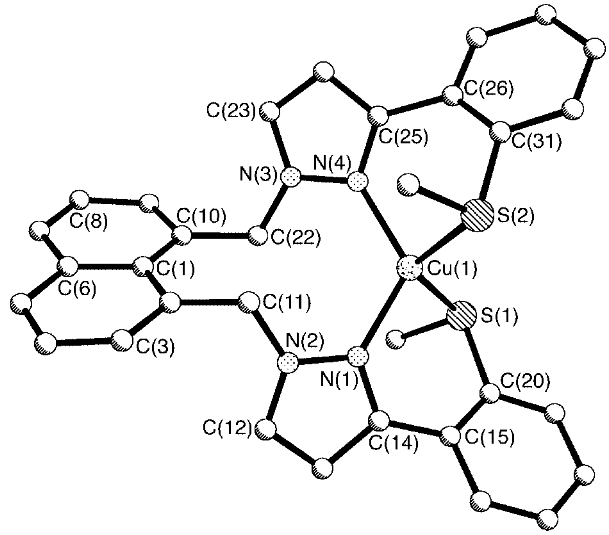


Figure 10. Molecular structure of the metal complex unit of $[CuL^4](PF_6)$.

Table 7. Selected bond lengths [Å] and angles [°] for $[CuL^4](PF_6)\cdot 2MeCN\cdot 2H_2O$.

Cu(1)–N(4)	2.020(4)
Cu(1)–N(1)	2.032(4)
Cu(1)–S(1)	2.2973(14)
Cu(1)–S(2)	2.2998(14)
N(4)–Cu(1)–N(1)	121.28(9)
N(4)–Cu(1)–S(1)	115.85(11)
N(1)–Cu(1)–S(1)	92.81(12)
N(4)–Cu(1)–S(2)	93.24(11)
N(1)–Cu(1)–S(2)	115.43(11)

The reaction of L^4 with one equivalent of $[Ag(CH_3CN)_4]BF_4$ in ethanol resulted in a suspension from which an off-white solid was isolated after filtration. The elemental analysis of the powder is consistent with the formulation $[AgL^4](BF_4)$. The IR spectrum showed the presence of the BF_4^- counterion with a broad band at 1071 cm^{-1}. The FAB mass spectrum showed a molecular ion peak at $m/z = 641$ for $\{AgL^4\}^+$ with no peaks for higher oligomers. The crystal structure of the complex shows it to be the mononuclear complex $[Ag(L^4)](BF_4)$ (Figure 11). There are two unique complex molecules in the unit cell which are associated into a dimer by weak, long-range Ag···N interactions (> 3 Å) between the Ag^I ion of one complex and the pyrazolyl N atoms of another. The two silver ions are 4.20 Å apart, which precludes any Ag···Ag interaction between them, and the two naphthalene spacers are at opposite sides of the dimer.

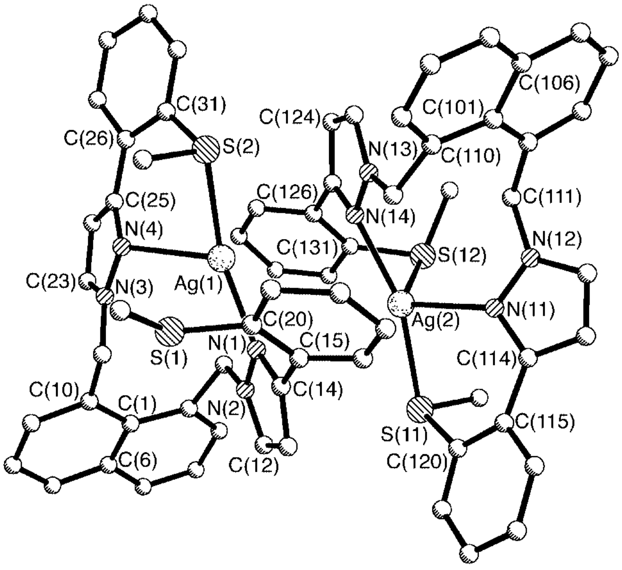


Figure 11. Molecular structure of the metal complex unit of $[AgL^4](BF_4)$ showing the stacking of two independent molecules in the unit cell.

One Ag^I ion [Ag(2)] is in a flattened tetrahedral environment [angle of 75.6° between the Ag(NS) planes] coordinated by an L^4 ligand acting as a tetradentate chelate. The Ag–N bonds are 2.246(10) and 2.367(9) Å and the Ag–S bonds are longer at 2.468(3) and 2.785(4) Å and are typical of the silver complexes in this series. One of the bidentate arms shows a larger dihedral twist between the two rings than the other [59.0° for the arm containing N(11) and S(11), and 22.8° for the arm containing N(14) and S(12)]. The other Ag^I ion is in a three-coordinate N_2S environment with all donor atoms coming from a single L^4 molecule. Here the remaining sulfur atom is too far from the metal to be considered as forming a normal coordinate bond [Ag(1)–S(1) = 3.02 Å compared to 2.445(3) Å for Ag(1)–S(2), Table 8]. The coordination environment is almost planar with the Ag(1) sitting ca. 0.1 Å above the plane of the donor atoms. The bond to one of the N-donors is significantly longer than that to the other N-donor [Ag(1)–N(1), 2.146(9) Å; Ag(1)–N(4), 2.446(9) Å]. The bidentate arm where the sulfur atom is not coordinated to the metal shows a greater dihedral angle between the pyrazole and methylsulfanylphenyl rings (58.0°) than the arm where both donor atoms are coordinated (21.5°).

Table 8. Selected bond lengths [Å] and angles [°] for $[AgL^4](BF_4)$.

Ag(1)–N(1)	2.146(9)
Ag(1)–S(2)	2.445(3)
Ag(1)–N(4)	2.446(9)
Ag(2)–N(14)	2.246(10)
Ag(2)–N(11)	2.367(9)
Ag(2)–S(11)	2.468(3)
Ag(2)–S(12)	2.785(4)
N(1)–Ag(1)–S(2)	161.3(3)
N(1)–Ag(1)–N(4)	114.0(3)
S(2)–Ag(1)–N(4)	83.6(2)
N(14)–Ag(2)–N(11)	110.5(3)
N(14)–Ag(2)–S(11)	162.7(3)
N(11)–Ag(2)–S(11)	85.3(2)
N(14)–Ag(2)–S(12)	81.5(3)
N(11)–Ag(2)–S(12)	108.8(2)
S(11)–Ag(2)–S(12)	100.35(13)

The NMR spectra of $[CuL^4](PF_6)$ and $[AgL^4](BF_4)$ show that the complexes have twofold symmetry in solution.

Complexes with L^5

The reaction of L^5 with 1.5 equivalents of $Ag(ClO_4)_4 \cdot H_2O$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether diffusion into the reaction mixture gave colourless crystals whose elemental analysis indicates the stochiometry $[AgL^5](ClO_4)$, i.e. a 1:1 metal/ligand ratio rather than the 3:2 ratio expected for a complex between a hexadentate ligand and a metal ion with preference for tetrahedral geometry. The IR spectrum showed the presence of the ClO_4^- counterions at 1091 and 623 cm^{-1}, and the FAB mass spectrum showed a molecular ion peak at m/z = 835 for the fragment $\{AgL^5\}^+$ all indicating formation of a 1:1 complex.

X-ray crystallography confirmed (Figure 12) that the complex is mononuclear, with some obvious structural similarities to $[AgL^2](BF_4)$ as a consequence of the *meta* substitution pattern of the central phenyl spacer. The Ag^I ion is bound by two of the bidentate N,S-donor arms of L^5 with the third arm pendant. As we saw with $[AgL^2](BF_4)$, the orientation of the two chelating bidentate arms to the same face of the phenyl spacer necessarily results in a close contact between the metal ion and the phenyl ring, resulting in an η^1 π-type interaction with C(2) of the phenyl ring [Ag(1)···C(2), 2.70 Å (dotted line in Figure 12; Table 9), with the angle between the Ag–C vector and the phenyl plane being 89°]. The Ag^I centre is therefore five coordinate; the τ parameter of 0.12 indicates that the geometry is best described as square-based pyramidal, with S(2) being the "axial" donor. Although the third pendant arm is directed

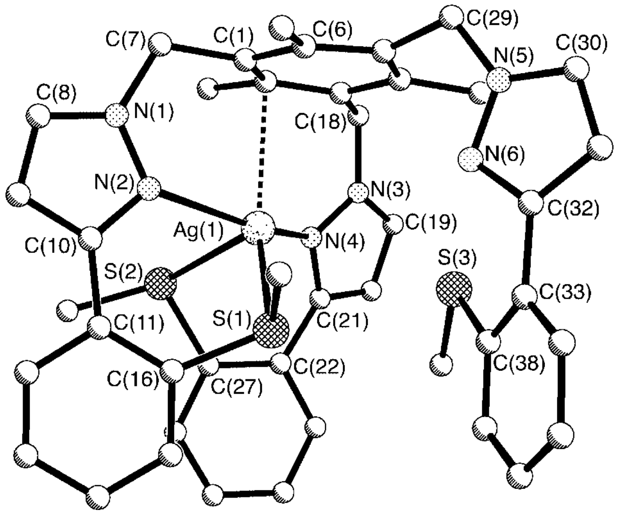


Figure 12. Molecular structure of the metal complex unit of $[AgL^5](ClO_4)$. The Ag···C interaction to the phenyl ring is shown with a dashed line.

towards the same face of the aromatic spacer as the two other arms, the remaining donor atoms are not interacting with the Ag^I centre [Ag(1)–N(6), 4.69 Å; Ag(1)–S(3), 3.71 Å]. All three bidentate arms show substantial deviations from planarity (twist angles of 17.7 and 33.5° between the pyrazolyl and methylsulfanylphenyl rings for the coordinated arms and 34.6° for the non-coordinated arm).

Table 9. Selected bond lengths [Å] and angles [°] for $[AgL^5](ClO_4)$.

Ag(1)–N(4)	2.3172(19)
Ag(1)–N(2)	2.436(2)
Ag(1)–S(1)	2.5201(7)
Ag(1)–S(2)	2.8347(7)
Ag(1)–C(2)	2.701(2)
N(4)–Ag(1)–N(2)	151.66(7)
N(4)–Ag(1)–S(1)	124.95(5)
N(2)–Ag(1)–S(1)	79.22(5)
N(4)–Ag(1)–S(2)	69.23(5)
N(2)–Ag(1)–S(2)	90.61(5)
S(1)–Ag(1)–S(2)	107.53(2)

Despite the asymmetry of the complex in the solid state, the ^1H NMR spectrum of $[AgL^5](ClO_4)$ showed that all three arms of the ligand are equivalent in solution, indicating that the silver(I) ion is coordinated by all three arms or, more likely, that the structure is fluxional in solution.

The structure of $[Ag(L^5)](ClO_4)$ suggested that the pendant arm would be able to coordinate a second metal ion, but only after the conformation of L^5 alters such that the pendant arm is rotated away from the metal ion. Reaction of L^5 with a 10 fold excess of $AgClO_4{\cdot}H_2O$ in dry acetonitrile under nitrogen resulted in a colourless solution. Diethyl ether vapour diffusion into this solution gave crystals of unreacted $[Ag(CH_3CN)_4]ClO_4$ in addition to crystals of the trinuclear complex $[Ag_3(L^5)_2](ClO_4)_3$. The FAB mass spectrum of these latter crystals shows a peak at $m/z = 835$ for $\{Ag(L^5)\}^+$ and additional peaks at $m/z = 1041$ for $\{Ag_2(L^5)(ClO_4)\}^+$ and 1768 for $\{Ag_2(L^5)_2(ClO_4)\}^+$. No peaks were observed for intact trinuclear $\{Ag_3(L^5)_2(ClO_4)_x\}$ species. The ^1H NMR spectrum showed a symmetrical structure in solution with identical chemical shifts to that of $[AgL^5](ClO_4)$, suggesting that $[Ag_3(L^5)_2]^{3+}$ only exists in the solid state. Attempts to isolate pure $[Ag_3(L^5)_2](ClO_4)_3$ by using a smaller excess of $Ag(ClO_4)_4{\cdot}H_2O$ were unsuccessful resulting in a mixture of $[Ag_3(L^5)_2](ClO_4)_3$ and $[Ag(L^5)_2](ClO_4)$.

In the crystal structure of $[Ag_3(L^5)_2](ClO_4)_3$ (Figure 13), the pendant arms of two mononuclear $\{Ag(L^5)\}^+$ units are coordinated to another Ag^I ion, linking two such units together via a third Ag^I centre. The two terminal Ag^I ions [Ag(1), Ag(3)] are in the familiar five-coordinate environments from two bidentate N,S-chelating ligand arms and an η^1 π-type interaction with the capping phenyl ring [Ag(1)···C(2), 2.79 Å; Ag(3)···C(102), 2.83 Å, Table 10; angles between Ag–C vectors and phenyl mean planes, 82° and 83° respectively; τ parameters 0.72 and 0.61 at Ag(1) and Ag(3) respectively]. The central Ag^I ion [Ag(2)] is in a five coordinate N_2SO_2 environment arising from an N,S bidentate arm from one ligand, just the pyrazolyl N-donor from the other ligand, and two oxygen atoms from one of the perchlorate anions [Ag–O distances, 2.85 and 2.87 Å]. The remaining non-coordinated S atom, S(103), is 3.82 Å away from Ag(2).

The two ligands are arranged such that the silver ions form a rough triangle. The inter-metallic distances between silver ions linked by the same ligand are 8.72 Å [Ag(1)···Ag(2)] and 7.47 Å [Ag(2)···Ag(3)]; the Ag(1)···Ag(3) separation is 9.58 Å. The bidentate arms show twist angles of 11.2–49.3° between pyrazolyl and methylsulfanylphenyl rings, whereas the arm where only the pyrazolyl donor is coordinated shows a larger twist angle of 78.2° in order to avoid unfavourable steric interactions between the thioether group and the nearby bidentate arm from the other ligand.

The reaction of L^5 with $[Cu(CH_3CN)_4]BF_4$ in a 2:3 ratio in dry ethanol resulted in an off-white precipitate which was isolated by filtration. The elemental analysis of the powder

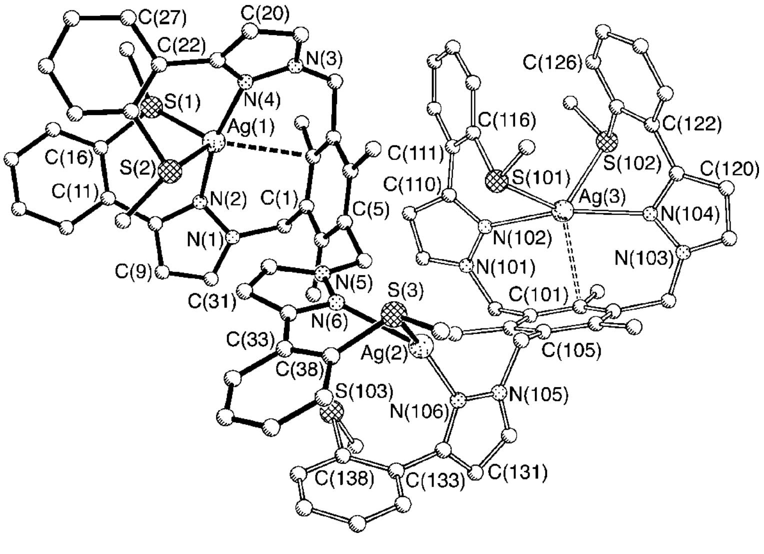


Figure 13. Molecular structure of the metal complex unit of $[Ag_3(L^5)_2](ClO_4)_3$; one ligand is shown with hollow bonds for clarity. The Ag···C interactions to the phenyl rings are shown with dashed lines.

Table 10. Selected bond lengths [Å] and angles [°] for $[Ag_2(L^5)_3](ClO_4)_3$.

Ag(1)–N(4)	2.308(6)
Ag(1)–N(2)	2.439(6)
Ag(1)–S(1)	2.586(2)
Ag(1)–S(2)	2.626(2)
Ag(1)–C(2)	2.785(6)
Ag(2)–N(106)	2.154(6)
Ag(2)–N(6)	2.336(6)
Ag(2)–S(3)	2.539(2)
Ag(2)–O(11)	2.848(7)
Ag(2)–O(12)	2.871(7)
Ag(3)–N(104)	2.375(6)
Ag(3)–N(102)	2.385(6)
Ag(3)–S(101)	2.603(2)
Ag(3)–S(102)	2.667(2)
Ag(3)–C(102)	2.823(6)
N(4)–Ag(1)–N(2)	168.2(2)
N(4)–Ag(1)–S(1)	114.18(16)
N(2)–Ag(1)–S(1)	71.62(15)
N(4)–Ag(1)–S(2)	78.16(16)
N(2)–Ag(1)–S(2)	109.53(14)
S(1)–Ag(1)–S(2)	113.54(7)
N(106)–Ag(2)–N(6)	129.7(2)
N(106)–Ag(2)–S(3)	152.01(16)
N(6)–Ag(2)–S(3)	72.58(15)
N(104)–Ag(3)–N(102)	162.7(2)
N(104)–Ag(3)–S(101)	120.34(15)
N(102)–Ag(3)–S(101)	75.28(14)
N(104)–Ag(3)–S(102)	72.05(15)
N(102)–Ag(3)–S(102)	109.47(15)
S(101)–Ag(3)–S(102)	115.13(6)

was consistent with a 1:1 metal/ligand ratio suggesting that the product is a mononuclear complex similar in structure to $[AgL^5](ClO_4)$. The IR spectrum is consistent with the presence of the BF_4^- anion with a broad band centred around 1064 cm^{-1}. The FAB mass spectrum shows a main peak at 789 for $\{CuL^5\}^+$ but also very weak peaks for 1006 ($\{Cu_2(L^5)$ + NOBA$\}^+$), 1515 ($\{Cu(L^5)_2\}^+$) and 1669 ($\{Cu(L^5)_2$ + NOBA$\}^+$) suggesting that a complex of higher nuclearity could have formed. The poor solubility of this complex did not permit study by NMR spectroscopy. All attempts to crystallise this complex have been unsuccessful.

Conclusions

Reaction of the bidentate N,S-donor fragment 3-[2-(methylsulfanyl)phenyl]pyrazole with a range of aromatic groups having two or three bromomethyl substituents allows two or three N,S-donor units to be linked to a central aromatic spacer. Depending on the separation between the N,S-donor units they can either each bind to a separate metal ion, giving one-dimensional (helical or zig-zag) chains with Ag^I and Cu^I, or can chelate to a single metal centre giving smaller mononuclear (metal/ligand, 1:1) or trinuclear (metal/ligand, 3:2) complexes. Whereas the Cu^I centres in these complexes are all four coordinate from two N,S-donor units, the Ag^I centres are sometimes three-coordinate due to incomplete coordination of the N,S-donor units. An additional factor responsible for the differences between Cu^I and Ag^I complexes with the same ligand is the presence of η^1 π-type Ag···C(phenyl) interactions which do not occur with Cu^I.

Experimental Section

General Details: 2′-(Methylthio)acetophenone,[14] 3,3′-bis(bromomethyl)biphenyl[15] and $[Cu(CH_3CN)_4]X$ (X = PF_6, BF_4)[16] were prepared according to literature methods. All other organic reagents and metal salts were purchased from Aldrich or Avocado and used as received. ^1H NMR spectra were recorded with a Bruker AC 250 or Bruker AMX2 400 spectrometer, and all mass spectra (FAB and EI) with a VG AutoSpec magnetic sector instrument. IR spectra were recorded with a Perkin–Elmer Spectrum One instrument. Samples for elemental analysis were vacuum-dried.

Preparation of 1,8-Bis(bromomethyl)naphthalene: This is a slight variant of a literature method.[17] PBr_3 (6.0 cm^3, 0.064 mol) was added to a suspension of 1,8-bis(hydroxymethyl)naphthalene (3.93 g, 0.0209 mol) in dry dichloromethane (50 cm^3) under nitrogen. The resulting clear solution was stirred at room temperature for 5 h. After this period water was carefully added dropwise until the evolution of gas ceased. The organic layer was separated, washed with water and dried ($MgSO_4$). Removal of the solvent afforded the crude product as an off-white solid. Recrystallisation from dichloromethane/hexane gave 5.29 g of off-white crystals (81%). All analytical data match those previously published.[17]

Preparation of 3-[(2-Methylthio)phenyl]pyrazole: This is a slight variant of the method published earlier.[5] A solution of 2′-(methylthio)acetophenone (4.28 g, 0.0257 mol) in dimethylformamide–dimethylacetal (10 cm^3, a large molar excess) was refluxed for 3 days under nitrogen to yield a dark brown solution. Removal of excess dimethylformamide-dimethylacetal in vacuo gave crude 3-(dimethylamino)-1-[2-(methylthio)phenyl]-2-propen-1-one as an orange/brown oil. To this was added ethanol (60 cm^3) and hydrazine hydrate (10 cm^3, a large molar excess), and the mixture refluxed in air for 2 h. The pale yellow solution was cooled and added to ice/water (300 cm^3) resulting in a pale yellow precipitate. The mixture was refrigerated overnight to complete the precipitation of the product. The solid was filtered off, washed with cold water (50 cm^3) and hexane (50 cm^3) and dried in vacuo. Subsequent recrystallisation from dichloromethane/hexane afforded 3-[(2-methylthio)phenyl]pyrazole as pale yellow needle crystals (4.35 g, 89%). EI MS: m/z = 190 [M^+]. ^1H NMR (250 MHz): $CDCl_3$: δ (ppm) = 7.63 (d, 1 H, pyrazolyl H^5), 7.50 (m, 1 H, phenyl H^3), 7.31–7.36 (m, 2 H, phenyl H^5, phenyl H^6), 7.21 (m, 1 H, phenyl H^4), 6.62 (d, 1 H, pyrazolyl H^4), 2.41 (s, 3 H, SCH_3). $C_{10}H_{10}N_2S$ (190.27): calcd. C 63.1, H 5.3, N, 14.7; found C 62.7, H 5.2, N 14.7.

Preparation of L^1: A two-phase mixture of 3-[(2-methylthio)phenyl]-pyrazole (1.26 g, 6.60 mmol), α,α′-dibromo-*p*-xylene (0.711 g, 2.70 mmol), toluene (90 cm^3), nBu_4NOH (0.10 cm^3) and aqueous 10 M NaOH (15 cm^3) was heated to 75 °C and stirred vigorously at this temperature for 24 h. After cooling the mixture was diluted with water (100 cm^3) and the aqueous layer extracted with toluene (2 × 100 cm^3). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (alumina, dichloromethane) to give 0.767 g of pale yellow solid (59%). FAB MS: m/z = 483 [MH^+]. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.55 (dd, 2 H, methylthiophenyl H^3), 7.38 (d, 2 H, pyrazolyl H^5), 7.23–7.35 (m, 8 H, phenyl, methylthiophenyl H^5, H^6), 7.17 (dd, 2 H, methylthiophenyl H^4), 6.63 (d, 2 H, pyrazolyl H^4), 5.36 (s, 4 H, CH_2), 2.42 (s, 6 H, SCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

150.6, 137.3, 136.5, 132.4, 129.7 (two closely spaced signals), 128.2, 128.1, 125.2, 124.6, 106.9, 55.7, 16.1 ppm. IR (KBr disk): ṽ = 2916 (w), 2854 (w), 1588 (w), 1514 (m), 1489 (m), 1426 (m), 1355 (m), 1322 (w), 1304 (w), 1261 (m), 1217 (w), 1065 (m), 1051 (s), 1000 (w), 952 (w), 861 (w), 777 (w), 754 (s), 722 (m), 705 (m), 946 (w), 629 (w), 521 (w) cm^{-1}. $C_{28}H_{26}N_4S_2$ (482.67): calcd. C 69.7, H 5.4, N 11.6; found C 69.6, H 5.4, N 11.2. X-ray quality crystals of L^1 were grown from slow evaporation of an acetonitrile solution.

Preparation of L^2: A two-phase mixture of 3-[(2-methylthio)phenyl]-pyrazole (1.00 g, 5.26 mmol), α,α′-dibromo-*m*-xylene (0.630 g, 2.39 mmol), toluene (100 cm^3), *n*Bu$_4$NOH (0.10 cm^3) and aqueous 10 M NaOH (15 cm^3) was heated to 65 °C and stirred vigorously at this temperature for 24 h. After cooling the mixture was diluted with water (100 cm^3) and the aqueous layer extracted with toluene (2 × 100 cm^3). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (alumina, dichloromethane) to give 0.691 g of colourless oil (60%). EI MS: *m*/*z* = 483 [MH$^+$]. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (dd, 2 H, methylthiophenyl H^3), 7.39 (d, 2 H, pyrazolyl H^5), 7.25–7.34 (m, 5 H, phenyl H^5, methylthiophenyl H^5, H^6), 7.15–7.22 (m, 5 H, phenyl H^2, H^4, methylthiophenyl H^4), 6.62 (d, 2 H, pyrazolyl H^4), 5.36 (s, 4 H, CH_2), 2.42 (s, 6 H, SCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.5, 137.4, 137.2, 132.3, 129.8 (two closely spaced signals), 129.2, 128.2, 127.3, 126.9, 125.2, 124.6, 106.9, 55.8, 16.0 ppm. IR (neat): ṽ = 3111 cm^{-1} (w), 3052 (w), 2979 (w), 2920 (m), 2854 (w), 1610 (w), 1591 (w), 1563 (w), 1516 (m), 1490 (s), 1453 (s), 1436 (s), 1400 (s), 1335 (s), 1259 (s), 1221 (s), 1164 (w), 1106 (w), 1064 (m), 1052 (s), 1002 (w), 967 (w), 947 (w), 753 (s), 710 (m), 654 (w) cm^{-1}. $C_{28}H_{26}N_4S_2$ (482.67): calcd. C 69.7, H 5.4, N 11.6; found C 69.4, H 5.8, N 11.4.

Preparation of L^3: A two-phase mixture of 3-[(2-methylthio)phenyl]-pyrazole (1.23 g, 6.46 mmol), 3,3′-bis(bromomethyl)biphenyl (1.00 g, 2.94 mmol), toluene (55 cm^3), *n*Bu$_4$NOH (0.03 cm^3) and aqueous 10 M NaOH (12 cm^3) was heated to 70 °C and stirred vigorously at this temperature for 24 h. After cooling the mixture was diluted with water (100 cm^3) and the aqueous layer extracted with toluene (2 × 100 cm^3). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (alumina, 20% hexane in dichloromethane) to give 0.701 g of white foam (43%). EI MS: *m*/*z* = 558 [M$^+$]. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.50–7.59 (m, 6 H), 7.43 (d, 2 H, pyrazolyl H^5), 7.23–7.42 (m, 8 H), 7.17 (ddd, 2 H, methylthiophenyl H^4), 6.62 (d, 2 H, pyrazolyl H^4), 5.43 (s, 4 H, CH_2), 2.39 (s, 6 H, SCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6, 141.2, 137.4, 137.2, 132.4, 129.8 (two closely spaced signals), 129.2, 128.2, 126.8 (two closely spaced signals), 126.6, 125.2, 124.6, 106.9, 56.0, 16.0 ppm. IR (KBr disk): ṽ 3050 (w), 2917 (m), 2853 (w), 1603 (w), 1588 (w), 1515 (w), 1488 (m), 1453 (m), 1434 (s), 1399 (m), 1334 (m), 1257 (m), 1220 (m), 1105 (w), 1063 (m), 1050 (m), 1000 (w), 946 (w), 751 (s), 732 (m), 695 (m), 654 (w) cm^{-1}. $C_{34}H_{30}N_4S_2$ (558.77): calcd. C 73.1, H 5.4, N 10.0; found C 72.8, H 5.6, N 9.6.

Preparation of L^4: A two-phase mixture of 3-[(2-methylthio)phenyl]-pyrazole (2.50 g, 13.1 mmol), 1,8-bis(bromomethyl)naphthalene (1.99 g, 6.34 mmol), toluene (120 cm^3), *n*Bu$_4$NOH (0.20 cm^3) and aqueous 10 M NaOH (26 cm^3) was heated to 65 °C and stirred vigorously at this temperature for 24 h. After cooling the mixture was diluted with water (100 cm^3) and the aqueous layer extracted with toluene (2 × 100 cm^3). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was recrystallised twice from dichloromethane/hexane to give 0.86 g of off-white needle crystals. A second crop of 1.17 g of off-white powder was obtained from the recrystallisation filtrates by column chromatography (alumina, 20% hexane in dichloromethane). Total yield: 2.03 g (60%). FAB MS: *m*/*z* = 533 [MH$^+$]. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.89 (dd, 2 H, napthyl H^4), 7.57 (ddd, 2 H, methylthiophenyl H^3), 7.45 (dd, 2 H, napthyl H^3), 7.24–7.32 (m, 4 H, methylthiophenyl H^5, H^6), 7.23 (dd, 2 H, naphthyl H^2), 7.20 (d, 2 H, pyrazolyl H^5), 7.16 (ddd, 2 H, methylthiophenyl H^4), 6.59 (d, 2 H, pyrazolyl H^4), 5.93 (s, 4 H, CH_2), 2.39 (s, 6 H, SCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_4$): δ (ppm) = 150.9, 137.4, 135.8, 132.4, 131.8, 130.8, 130.5, 130.4, 130.1, 129.7, 128.2, 125.5, 125.3, 124.5, 106.7, 56.7, 16.1. IR (KBr disk): ṽ 3117 (w), 2918 (w), 1586 (w), 1562 (w), 1509 (m), 1489 (m), 1454 (s), 1440 (m), 1399 (w), 1331 (m), 1258 (m), 1213 (m), 1170 (w), 1107 (w), 1052 (s), 976 (w), 960 (w), 944 (w), 844 (w), 782 (s), 769 (m), 753 (s), 737 (m), 676 (m), 622 (w) cm^{-1}. $C_{32}H_{28}N_4S_2$ (532.73): calcd. C 72.1, H 5.3, N 10.5; found C 72.0, H 5.3, N 10.5. X-ray quality crystals were grown from diethyl ether diffusion into an NMR sample of L^4 in $CDCl_3$.

Preparation of L^5: A two-phase mixture of 3-[(2-methylthio)phenyl]-pyrazole (1.54 g, 8.09 mmol), 2,4,6-tris(bromomethyl)mesitylene (0.981 g, 2.46 mmol), toluene (70 cm^3), *n*Bu$_4$NOH (0.10 cm^3) and aqueous 10 M NaOH (25 cm^3) was heated to 70 °C and stirred vigorously at this temperature for 24 h. After cooling the mixture was diluted with water (100 cm^3) and the aqueous layer extracted with toluene (2 × 100 cm^3). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (alumina, 1% methanol in dichloromethane) to give 0.551 g of off-white foam (31%). EI MS: *m*/*z* = 726 [M$^+$], 536 {M$^+$-[3-(2-methylthiophenyl)pyrazole]}, 347 {M$^+$ – 2[3-(2-methylthiophenyl)pyrazole]}. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.56 (dd, 3 H, methylthiophenyl H^3), 7.23–7.35 (m, 6 H, methylthiophenyl H^5, H^6), 7.17 (ddd, 3 H, methylthiophenyl H^4), 7.09 (d, 3 H, pyrazolyl H^5), 6.56 (d, 3 H, pyrazolyl H^4), 5.54 (s, 6 H, CH_2), 2.47 (s, 9 H, CH_3), 2.42 (s, 9 H, SCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.4, 139.7, 137.3, 132.2, 131.3, 129.6, 128.4, 128.2, 125.2, 124.6, 106.2, 50.9, 16.5, 16.1. IR (KBr disk): ṽ 3050 (w), 2977 (w), 2916 (m), 1589 (w), 1562 (w), 1514 (w), 1488 (m), 1453 (s), 1436 (s), 1398 (m), 1323 (m), 1256 (m), 1215 (s), 1106 (w), 1063 (m), 1051 (s), 998 (w), 944 (m), 752 (s), 732 (s), 654 (w), 618 (w) cm^{-1}. $C_{42}H_{42}N_6S_3$ (727.03): calcd. C 69.4, H 5.8, N 11.6; found C 69.2, H 5.9, N 11.5. X-ray quality crystals were grown from the diffusion of pentane vapour into an acetonitrile solution of L^5.

Preparation of {[CuL^1](PF$_6$)}$_\infty$: A solution of $[Cu(CH_3CN)_4]PF_6$ (62 mg, 0.17 mmol) in MeCN (5 cm^3) was added to a solution of L^1 (80 mg, 0.17 mmol) in MeCN (20 cm^3). The colourless solution was stirred for 4 h and the volume reduced to ca. 10 cm^3. Diethyl ether diffusion into the solution gave off-white crystals of {[CuL^1](PF$_6$)}$_\infty$ which were suitable for X-ray crystallography. Yield: 86 mg, 75%. ES MS: *m*/*z* = 545 [CuL^1]$^+$. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.69 (d, 2 H, pyrazolyl H^5), 7.48 (m, 2 H, methylthiophenyl H^3), 7.30-7.75 (m, 4 H, methylthiophenyl H^5, H^6), 7.18–7.25 (m, 2 H, methylthiophenyl H^4), 7.12 (s, 4 H, phenyl), 6.62 (d, 2 H, pyrazolyl H^4), 5.27 (s, 4 H, CH_2), 2.32 (s, 6 H, SMe). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 151.4, 137.8, 136.2, 132.8, 132.5, 131.1 129.7, 128.6, 127.8, 126.7, 107.6, 55.9, 17.3 ppm. IR (KBr disk): ṽ 3156 (w), 3138 (w), 3052 (w), 2997 (w), 2925 (w), 1631 (w), 1589 (w), 1564 (w), 1518 (s), 1501 (s), 1462 (w), 1425 (s), 1401 (w), 1357 (s), 1325 (s), 1277 (w), 1225 (m), 1075 (s), 1020 (w), 971 (m), 954 (m), 879 (m), 839 (s), 786 (s), 760 (s), 729 (m), 649 (w), 619 (w), 558 (s) cm^{-1}. $C_{28}H_{26}CuF_6N_4PS_2$ (691.18): calcd. C 48.7, H 3.8, N 8.1; found C 48.8, H 3.7, N 8.0.

Preparation of $\{[AgL^1](NO_3)\}_\infty$: A solution of $AgNO_3$ (29 mg, 0.17 mmol) in H_2O (3 cm^3) was added to a solution of L^1 (81 mg, 0.17 mmol) in hot MeOH (10 cm^3). The colourless solution was stirred for 4 h and the volume reduced to ca. 5 cm^3. The mixture was filtered to give $\{[AgL^1](NO_3)\}_\infty$ as a white powder. Yield: 71 mg, 65%. X-ray quality crystals were obtained from slow evaporation of the filtrate. FAB MS: *m*/*z* = 591 $[AgL^1]$, 651 $[Ag(L^1)(NO_3)]$, 697 $[Ag_2(L^1)]$, 760 $[Ag_2(L^1)(NO_3)]$, 850 $[Ag_2(L^1)$ + NOBA], 1179 $[Ag_2(L^1)_2]$, 1242 $[Ag_2(L^1)_2(NO_3)]$, 1333 $[Ag_2(L^1)_2$ + NOBA]. ^1H NMR (250 MHz, CD_3CN): δ (ppm) = 7.69 (d, 2 H, pyrazolyl H^5), 7.42 (dd, 2 H, methylthiophenyl H^3), 7.33 (ddd, 2 H, methylthiophenyl H^5), 7.25 (dd, 2 H, methylthiophenyl H^6), 7.19 (td, 2 H, methylthiophenyl H^4), 7.10 (s, 4 H, phenyl), 6.56 (d, 2 H, pyrazolyl H^4), 5.22 (s, 4 H, CH_2), 2.28 (s, 6 H, SMe); (500 MHz, CD_3NO_2): δ (ppm) = 7.80 (d, 2 H, pyrazolyl H^5), 7.37–7.42 (m, 4 H, methylthiophenyl H^3, H^5), 7.29 (td, 2 H, methylthiophenyl H^4), 7.28 (d, 2 H, methylthiophenyl H^6), 6.86 (s, 4 H, phenyl), 6.61 (d, 2 H, pyrazolyl H^4), 5.17 (s, 4 H, CH_2), 2.24 (s, 6 H, SMe). IR (KBr disk): $\tilde{\nu}$ 3108 (w), 2920 (w), 1624 (w), 1590 (w), 1519 (m), 1495 (m), 1430 (s), 1384 (s), 1339 (s), 1321 (s), 1259 (m), 1226 (m), 1065 (m), 1038 (w), 963 (m), 948 (m), 758 (s), 734 (m), 705 (w) cm^{-1}. $C_{28}H_{26}AgN_5O_3S_2$ (652.54): calcd. C 51.5, H 4.2, N 10.7; found C 51.4, H 4.1, N 10.6.

Preparation of $\{[CuL^2](BF_4)\}_\infty$: $[Cu(CH_3CN)_4]BF_4$ (61 mg, 0.19 mmol) was added to a solution of L^2 (94 mg, 0.19 mmol) in dry MeCN (20 cm^3). The colourless solution was stirred overnight under nitrogen and the volume reduced to ca. 10 cm^3. Diethyl ether diffusion into the solution gave off-white crystals of $[CuL^2](BF_4)$ which were suitable for X-ray crystallography. Yield: 70 mg, 56%. ES MS: *m*/*z* = 545 $[CuL^2]^+$. ^1H NMR (500 MHz, CD_3CN): δ = 7.68 (br. s, 2 H, pyrazolyl H^5), 7.47 (d, 2 H), 7.29–7.36 (m, 5 H), 7.11–7.23 (m, 4 H), 7.07 (s, 1 H), 6.61 (br. s, 2 H, pyrazolyl H^4), 5.32 (s, 4 H, CH_2), 2.34 (br. s, 6 H, SMe) ppm. IR (KBr disk): $\tilde{\nu}$ = 3135 (w), 3057 (w), 2975 (w), 2924 (w), 1610 (w), 1590 (w), 1567 (w), 1518 (m), 1500 (m), 1433 (s), 1406 (m), 1385 (w), 1356 (m), 1327 (w), 1280 (w), 1223 (w), 1169 (w), 1056 (s), 951 (w), 877 (w), 757 (s), 729 (m), 709 (w), 651 (w), 631 (w), 520 (w) cm^{-1}. $C_{28}H_{26}BCuF_4N_4S_2$ (633.02): calcd. C 53.1, H 4.1, N 8.9; found C 52.7, H 4.3, N 8.7.

Preparation of $[AgL^2](BF_4)$: $[Ag(CH_3CN)_4]BF_4$ (71 mg, 0.20 mmol) was added to a solution of L^2 (96 mg, 0.20 mmol) in dry MeCN (20 cm^3). The colourless solution was stirred overnight protected from light and the volume reduced to ca. 10 cm^3. Diethyl ether diffusion into the solution gave off-white crystals of $[AgL^2](BF_4)$ which were suitable for X-ray crystallography. Yield: 98 mg, 73%. ES MS: *m*/*z* = 589 $[AgL^2]^+$. ^1H NMR (500 MHz, CD_3CN): δ = 7.88 (d, 2 H, pyrazolyl H^5), 7.70 (s, 1 H, phenyl H^2), 7.45–7.49 (m, 4 H), 7.34–7.39 (m, 4 H), 7.28 (td, 2 H), 6.95 (dd, 2 H), 6.53 (d, 2 H, pyrazolyl H^4), 5.38 (s, 4 H, CH_2), 1.89 (s, 6 H, SMe) ppm. IR (KBr disk): $\tilde{\nu}$ = 3140 (w), 3127 (w), 3054 (w), 3007 (w), 2926 (w), 1590 (w), 1566 (w), 1516 (m), 1497 (s), 1456 (m), 1431 (s), 1410 (m), 1366 (w), 1351 (m), 1296 (w), 1273 (w), 1260 (w), 1217 (s), 1050 (s), 949 (m), 896 (m), 777 (m), 760 (s), 740 (s), 707 (m), 650 (w), 620 (w), 521 (s) cm^{-1}. $C_{28}H_{26}AgBF_4N_4S_2$ (677.34): calcd. C 49.7, H 3.9, N 8.3; found C 49.6, H 3.6, N 8.2.

Preparation of $\{[CuL^3](BF_4)\}_\infty$: $[Cu(CH_3CN)_4]BF_4$ (50 mg, 0.16 mmol) was added to a suspension of L^3 (89 mg, 0.16 mmol) in dry MeOH (20 cm^3). The resulting suspension was sonicated for 10 min then stirred overnight under nitrogen. Filtration gave $\{[CuL^3](BF_4)\}_\infty$ as an off-white solid which was dried in vacuo. Yield: 86 mg, 76%. FAB MS: *m*/*z* = 621 $[CuL^3]$, 1179 $[Cu(L^3)_2]$, 1331 $[Cu_2(L^3)_2(BF_4)$ and/or $Cu(L^3)_2$ + NOBA]. ^1H NMR (500 MHz, CD_3CN): δ (ppm) = 7.71 (br. s, 2 H, pyrazolyl H^5), 7.46–7.55 (m, 6 H), 7.41 (t, 2 H), 7.27–7.35 (m, 4 H), 7.25 (d, 2 H), 7.21 (m, 1 H), 6.58 (d, 2 H, pyrazolyl H^4), 5.40 (s, 4 H, CH_2), 2.28 (s, 6 H, SCH_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3143 (w), 2925 (w), 1602 (w), 1519 (w), 1502 (m), 1435 (m), 1412 (m), 1360 (w), 1329 (w), 1232 (m), 1083 (s, br), 1060 (s), 785 (m), 771 (m), 756 (s), 732 (w), 699 (m), 623 (w), 520 (w) cm^{-1}. $C_{34}H_{30}BCuF_4N_4S_2$ (709.12): calcd. C 57.6, H 4.3, N 7.9; found C 57.3, H 4.2, N 7.9. X-ray quality crystals were grown from diethyl ether diffusion into an acetonitrile solution of the complex.

Preparation of $\{[AgL^3](BF_4)\}_\infty$: $[Ag(CH_3CN)_4]BF_4$ (61 mg, 0.17 mmol) was added to a suspension of L^3 (95 mg, 0.17 mmol) in dry MeCN (20 cm^3). The colourless solution was protected from light and stirred overnight. The volume was then reduced to ca. 10 cm^3 in vacuo. Diethyl ether diffusion into the resulting solution gave off-white crystals of $\{[AgL^3](BF_4)\}_\infty$ which were suitable for X-ray crystallography. Yield: 114 mg, 89%. FAB MS: *m*/*z* = 667 $[Ag(L^3)]$, 1225 $[Ag(L^3)_2]$, 1332 $[Ag_2(L^3)_2]$, 1378 $[Ag(L^3)_2$ + NOBA], 1419 $[Ag_2(L^3)_2(BF_4)]$, 1485 $[Ag_2(L^3)_2$ + NOBA]. ^1H NMR (500 MHz, CD_3CN): δ (ppm) = 7.78 (d, 2 H, pyrazolyl H^5), 7.43–7.47 (m, 4 H), 7.40 (ddd, 2 H), 7.37 (td, 2 H), 7.30 (ddd, 2 H), 7.22 (td, 2 H), 7.18 (ddd, 2 H), 7.09 (dd, 2 H), 6.51 (d, 2 H, pyrazolyl H^4), 5.30 (s, 4 H, CH_2), 2.04 (s, 6 H, SMe). IR (KBr disk): $\tilde{\nu}$ = 3139 (w), 2924(w), 1604 (w), 1589 (w), 1519 (w), 1497 (m), 1432 (m), 1410 (m), 1356 (m), 1324 (w), 1262 (w), 1220 (m), 1061 (s, br), 786 (m), 757 (s), 728 (m), 703 (w), 520 (w) cm^{-1}. $C_{34}H_{30}AgBF_4N_4S_2$ (753.43): calcd. C 54.2, H 4.0, N 7.4; found C 54.1, H 3.9, N 7.4.

Preparation of $[CuL^4](PF_6)$: $[Cu(CH_3CN)_4]PF_6$ (57 mg, 0.15 mmol) was added to a suspension of L^4 (82 mg, 0.15 mmol) in dry MeCN (20 cm^3) and the colourless solution was stirred overnight. The volume was then reduced to ca. 10 cm^3 in vacuo and the solution filtered to remove a small amount of solid. Diethyl ether diffusion into the resulting solution gave off-white crystals of $[CuL^4](PF_6)$ which were suitable for X-ray crystallography. Yield: 57 mg, 50%. FAB MS: *m*/*z* = 595 $[Cu(L^4)]$. ^1H NMR (500 MHz, CD_3CN): δ (ppm) = 8.17 (dd, 2 H), 7.75 (dd, 2 H), 7.60–7.70 (m, 6 H), 7.42–7.49 (m, 6 H), 6.72 (d, 2 H, pyrazolyl H^4), 5.64 (s, 4 H, CH_2), 2.42 (s, 6 H, SMe). IR (KBr disk): $\tilde{\nu}$ = 2923 (w), 1624 (w), 1515 (w), 1499 (w), 1487 (w), 1431 (m), 1371 (m), 1325 (m), 1211 (m), 1065 (m), 841 (s), 781 (m), 760 (s), 685 (w), 557 (s) cm^{-1}. $C_{32}H_{28}CuF_6N_4PS_2$ (741.24): calcd. C 51.9, H 3.8, N, 7.6; found C 51.5, H 3.8, N, 7.7.

Preparation of $[AgL^4](BF_4)$: $[Ag(CH_3CN)_4]BF_4$ (137 mg, 0.38 mmol) was added to a suspension of L^4 (204 mg, 0.38 mmol) in EtOH (20 cm^3) protected from light and the mixture was stirred overnight. The off-white solid was collected by filtration and dried in vacuo. Yield: 247 mg, 89%. FAB MS: *m*/*z* = 641 $[Ag(L^4)]$. ^1H NMR (400 MHz, CD_3CN): δ (ppm) = 8.15 (dd, 2 H), 7.69 (dd, 2 H), 7.63 (dd, 2 H), 7.49 (m, 2 H), 7.41–7.45 (m, 4 H), 7.31 (m, 2 H), 7.16 (d, 2 H, pyrazolyl H^5), 6.47 (d, 2 H, pyrazolyl H^4), 5.78 (s, 4 H, CH_2), 2.50 (s, 6 H, SMe). ^{13}C NMR (100 MHz, CD_3CN): δ (ppm) = 152.6, 137.6, 135.7, 135.4, 133.3, 132.1, 131.7 (2 closely spaced signals), 131.1, 130.3, 129.8, 127.0 (2 closely spaced signals), 126.7, 107.9, 57.7, 16.9. IR (KBr disk): $\tilde{\nu}$ = 3144 (w), 2924 (w), 1590 (w), 1515 (w), 1496 (w), 1485 (w), 1429 (m), 1362 (w), 1324 (m), 1212 (m), 1103 (m), 1070 (s, br), 1048 (s), 849 (w), 825 (w), 779 (m), 765 (s), 684 (w), 520 (w) cm^{-1}. $C_{32}H_{28}AgBF_4N_4S_2$ (727.40): calcd. C 52.8, H 3.9, N 7.7; found C 52.3, H 3.8, N 7.6. X-ray quality crystals were obtained from slow evaporation of the filtrate when the reaction was carried out in methanol.

Preparation of $[CuL^5](BF_4)$: $[Cu(CH_3CN)_4]BF_4$ (54 mg, 0.17 mmol) was added to a suspension of L^5 (84 mg, 0.12 mmol) in dry and degassed EtOH (20 cm^3) and the suspension was stirred overnight under nitrogen. The volume was then reduced to ca. 10 cm^3 in vacuo and the off-white powder filtered off. Yield: 90 mg, 89%. FAB MS: *m*/*z* = 789 [Cu(L^5)], 1006 [Cu$_2$(L^5) + NOBA], 1515 [Cu(L^5)$_2$], 1669 [Cu(L^5)$_2$ + NOBA]. IR (KBr disk): ṽ =3134 (w), 2978 (w), 2918 (w), 1630 (w), 1588 (w), 1563 (w), 1486 (m), 1454 (m), 1433 (s), 1399 (m), 1326 (m), 1256 (w), 1216 (m), 1083 (s), 1064 (s), 1048 (s), 945 (w), 753 (s), 733 (m), 652 (w), 617 (w) cm^{-1}. $C_{42}H_{42}BCuF_4N_6S_3$ (877.38): calcd. C 57.5, H 4.8, N 9.6; found C 57.2, H 5.0, N 9.4.

Preparation of [AgL^5](ClO$_4$): ***Caution: Perchlorate salts are potentially explosive and should only be prepared in small quantities and handled with care!*** $AgClO_4 \cdot H_2O$ (38 mg, 0.18 mmol) was added to a suspension of L^5 (90 mg, 0.12 mmol) in dry MeCN (20 cm^3) and the colourless solution was stirred overnight while protected from light. The volume was then reduced to ca. 10 cm^3 in vacuo. Diethyl ether diffusion into the resulting solution gave colourless crystals of [AgL^5](ClO$_4$) which were suitable for X-ray crystallography. Yield: 93 mg, 80%. FAB MS: *m*/*z* = 835 {Ag(L^5)}. ^{1}H NMR (250 MHz, CD$_3$CN): δ (ppm) 7.79 (d, 3 H, pyrazolyl H^5), 7.44 (dd, 3 H, meth-

Table 11. Crystallographic data for the ligands L^1, L^4 and L^5.

Ligand	L^1	L^4	L^5
Formula	$C_{28}H_{26}N_4S_2$	$C_{32}H_{28}N_4S_2$	$C_{42}H_{42}N_6S_3$
Formula weight	482.65	532.70	727.00
T [K]	150(2)	150(2)	150(2)
Crystal system, space group	orthorhombic, *Pbcn*	monoclinic, *P*2/*c*	triclinic, $P\bar{1}$
a [Å]	30.251(5)	12.548(4)	8.5155(11)
b [Å]	8.8015(14)	8.423(2)	15.452(2)
c [Å]	9.2578(15)	12.579(4)	16.190(2)
α [°]	90	90	62.058(2)
β [°]	90	94.604(5)	82.603(2)
γ [°]	90	90	84.463(2)
V [Å^3]	2464.9(7)	1325.3(6)	1864.7(4)
Z	4	2	2
$D_{calcd.}$ [mg/m^3]	1.301	1.335	1.295
μ [mm^{-1}]	0.240	0.231	0.238
Crystal size [mm]	0.50 × 0.48 × 0.39	0.50 × 0.41 × 0.07	0.41 × 0.20 × 0.10
Reflections collected	25818	14511	21704
Independent reflections	2821 [*R*(int) = 0.0283]	3018 [*R*(int) = 0.0521]	8385 [*R*(int) = 0.0434]
Data/restraints/parameters	2821/0/155	3018/0/174	8385/2/467
Final *R* indices[a]	R_1 = 0.0377 wR_2 = 0.1138	R_1 = 0.0413 wR_2 = 0.1009	R_1 = 0.0590 wR_2 = 0.1677
Largest diff. peak and hole [e·Å^{-3}]	0.228 and –0.233	0.273 and –0.282	1.857 and –0.585

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

Table 12. Crystallographic data for Cu$^+$ and Ag$^+$ complexes with L^1 and L^2.

Ligand	$\{[Cu(L^1)](PF_6)\}_\infty$	$\{[AgL^1](NO_3) \cdot MeOH\}_\infty$	$\{[CuL^2](BF_4)\}_\infty \cdot 1.5MeCN \cdot 0.5Et_2O$	$[AgL^2](BF_4)$
Formula	$C_{28}H_{26}CuF_6N_4PS_2$	$C_{29}H_{30}AgN_5O_4S_2$	$C_{33}H_{37}BCuF_4N_{5.5}O_{0.5}S_2$	$C_{28}H_{26}AgBF_4N_4S_2$
Formula weight	691.16	684.57	733.15	677.33
T [K]	150(2)	150(2)	150(2)	150(2)
Crystal system, space group	monoclinic, *C*2/*c*	monoclinic, *P*21/*c*	orthorhombic, *Pmna*	orthorhombic, *P*2(1)2(1)2(1)
a [Å]	14.310(3)	12.963(3)	21.129(2)	12.794(3)
b [Å]	21.062(5)	12.529(3)	13.7026(15)	18.763(4)
c [Å]	11.250(3)	17.935(4)	11.7024(13)	23.184(5)
α [°]	90	90	90	90
β [°]	121.070(4)	93.948(4)	90	90
γ [°]	90	90	90	90
V [Å^3]	2904.2(12)	2906.0(11)	3388.1(6)	5566(2)
Z	4	4	4	8
$D_{calcd.}$ [mg/m^3]	1.581	1.565	1.437	1.617
μ [mm^{-1}]	1.016	0.882	0.824	0.928
Crystal size [mm]	0.48 × 0.38 × 0.30	0.36 × 0.24 × 0.10	0.41 × 0.20 × 0.20	0.23 × 0.22 × 0.10
Reflections collected	16217	17458	36991	62930
Independent reflections	3322 [*R*(int) = 0.0649]	4043 [*R*(int) = 0.1387]	4034 [*R*(int) = 0.0725]	12643 [*R*(int) = 0.0544]
Data/restraints/parameters	3322/0/192	4043/0/375	4034/7/242	12643/26/722
Final *R* indices[a]	R_1 = 0.0403 wR_2 = 0.1025	R_1 = 0.0555 wR_2 = 0.1489	R_1 = 0.0456 wR_2 = 0.1340	R_1 = 0.0360 wR_2 = 0.0777
Largest diff. peak and hole [e·Å^{-3}]	0.519 and –0.408	1.926 and –1.375	0.597 and –0.315	0.942 and –0.490

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

ylthiophenyl H^3), 7.32 (td, 3 H, methylthiophenyl H^5), 7.23 (td, 3 H, methylthiophenyl H^4), 6.83 (dd, 3 H, methylthiophenyl H^6), 6.55 (d, 3 H, pyrazolyl H^4), 5.58 (s, 6 H, CH$_2$), 2.47 (s, 9 H, CH$_3$), 1.77 (s, 9 H, SCH$_3$) ppm. IR (KBr disk): $\tilde{\nu}$ = 3127 (w), 3112 (w), 2970 (w), 2911 (w), 1625 (w), 1589 (w), 1563 (w), 1515 (w), 1492 (m), 1440 (m), 1429 (s), 1409 (m), 1348 (m), 1270 (w), 1258 (w), 1210 (s), 1091 (s, br), 980 (w), 961 (w), 946 (w), 802 (m), 754 (s), 733 (m), 623 (s), 613 (m) cm^{-1}. $C_{42}H_{42}AgClN_6O_4S_3$ (934.35): calcd. C 54.0, H 4.5, N 9.0; found C 53.9, H 4.3, N 8.9.

X-ray Crystallography: X-ray crystallographic data are summarised in Table 11, Table 12, Table 13 and Table 14. For each compound a suitable crystal was coated with hydrocarbon oil and attached to the tip of a glass fibre and transferred to Bruker-SMART diffractometer under a stream of cold N$_2$. Data were collected using a Siemens SMART CCD area diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å) with an Oxford Cryosystems low temperature system. The data were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods (SADABS)[18] based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods or heavy atom Patterson methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. Structures were solved and refined using the SHELX suite of programs.[19] Selected

Table 13. Crystallographic data for Cu$^+$ and Ag$^+$ complexes with L^3 and a Cu$^+$ complex with L^4.

Complex	$\{[CuL^3](BF_4)\}_\infty \cdot 1.53CH_3CN \cdot 0.47Et_2O$	$\{[AgL^3](BF_4)\}_\infty$	$[CuL^4](PF_6) \cdot 2MeCN \cdot 2H_2O$
Formula	$C_{38.95}H_{39.33}BCuF_4N_{5.53}O_{0.47}S_2$	$C_{34}H_{30}AgBF_4N_4S_2$	$C_{36}H_{38}CuF_6N_6O_2PS_2$
Formula weight	806.90	753.42	859.35
T [K]	150(2)	150(2)	150(2)
Crystal system	monoclinic, *P*21/*n*	triclinic, $P\bar{1}$	monoclinic, *Cc*
a [Å]	11.607(3)	11.666(2)	17.757(3)
b [Å]	10.649(2)	11.973(2)	22.728(4)
c [Å]	31.565(6)	24.485(5)	13.059(2)
α [°]	90	89.231(4)	90
β [°]	97.547(5)	81.743(4)	132.495(2)
γ [°]	90	71.756(3)	90
V [Å^3]	3867.6(14)	3212.6(11)	3886.0(12)
Z	4	4	4
$D_{calcd.}$ [mg/m^3]	1.386	1.558	1.469
μ [mm^{-1}]	0.729	0.812	0.781
Crystal size [mm]	0.38 × 0.21 × 0.06	0.45 × 0.38 × 0.23	0.38 × 0.32 × 0.21
Reflections collected	18589	36999	21450
Independent reflections	6456	14378	4408
	[*R*(int) = 0.1053]	[*R*(int) = 0.0543]	[*R*(int) = 0.0321]
Data/restraints/parameters	6456/4/477	14378/78/817	4408/74/549
Final *R* indices[a]	R_1 = 0.0647	R_1 = 0.0516	R_1 = 0.0337
	wR_2 = 0.1790	wR_2 = 0.1298	wR_2 = 0.0894
Largest diff. peak and hole [e·Å^{-3}]	0.630 and –0.896	1.076 and –0.661	0.575 and –0.328

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

Table 14. Crystallographic data for Ag$^+$ complexes with L^4 and L^5.

Ligand	$[Ag(L^4)](BF_4)$	$[AgL^5](ClO_4)$	$[Ag_3(L^5)_2](ClO_4)_3$
Formula	$C_{32}H_{28}AgBF_4N_4S_2$	$C_{42}H_{42}AgClN_6O_4S_3$	$C_{84}H_{85}Ag_3Cl_3N_{12}O_{12}S_6$
Formula weight	727.38	934.32	2076.96
T [K]	150(2)	150(2)	120(2)
Crystal system, space group	orthorhombic, *P*2(1)2(1)2(1)	orthorhombic, *Pbca*	triclinic, $P\bar{1}$
a [Å]	11.430(4)	12.3282(14)	11.666(4)
b [Å]	21.880(8)	21.611(3)	15.388(5)
c [Å]	23.840(8)	30.241(3)	25.033(9)
α [°]	90	90	72.435(8)
β [°]	90	90	89.156(7)
γ [°]	90	90	85.591(7)
V [Å^3]	5962(4)	8056.7(16)	4272(3)
Z	8	8	2
$D_{calcd.}$ [mg/m^3]	1.621	1.541	1.615
μ [mm^{-1}]	0.872	0.774	0.990
Crystal size [mm]	0.20 × 0.17 × 0.08	0.41 × 0.32 × 0.21	0.32 × 0.21 × 0.12
Reflections collected	58451	87723	41978
Independent reflections	10523	9248	15010
	[*R*(int) = 0.2292]	[*R*(int) = 0.0479]	[*R*(int) = 0.1254]
Data/restraints/parameters	10523/0/799	9248/0/520	15010/0/1093
Final *R* indices[a]	R_1 = 0.0816	R_1 = 0.0345	R_1 = 0.0569
	wR_2 = 0.2343	wR_2 = 0.0943	wR_2 = 0.1193
Largest diff. peak and hole [e·Å^{-3}]	1.506 and –1.323	1.016 and –0.705	0.860 and –1.212

[a] The value of R_1 is based on selected data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.

bond lengths and angles for the structures of the metal complexes are in Tables 1–10.

Acknowledgments

We thank the New Zealand Tertiary Education Commission for a Top Achiever Doctoral scholarship to T. K. R.

---

[1] a) D. L. Caulder, K. N. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975; b) G. F. Swiegers, T. J. Malefetse, *Chem. Eur. J.* **2001**, *7*, 3637; c) B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022; d) D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1155; e) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; f) S. R. Seidel, P. J. Stang, *Acc. Chem. Res.* **2002**, *35*, 972; g) L. K. Thompson, *Coord. Chem. Rev.* **2002**, *233*, 193.

[2] a) M. D. Ward, J. A. McCleverty, J. C. Jeffery, *Coord. Chem. Rev.* **2001**, *222*, 251; b) R. L. Paul, S. P. Argent, J. C. Jeffery, L. P. Harding, J. M. Lynam, M. D. Ward, *Dalton Trans.* **2004**, 3453; c) Z. R. Bell, L. P. Harding, M. D. Ward, *Chem. Commun.* **2003**, 2432; d) Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Angew. Chem. Int. Ed.* **2002**, *41*, 2515; e) R. L. Paul, Z. R. Bell, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4883.

[3] a) M. C. Hong, W. P. Su, R. Cao, M. Fujita, J. X. Lu, *Chem. Eur. J.* **2000**, *6*, 427; b) C. Y. Su, S. Liao, H. L. Zhu, B. S. Kang, X. M. Chen, H. Q. Liu, *J. Chem. Soc., Dalton Trans.* **2000**, 1985; c) S. Liao, C. Y. Su, H. X. Zhang, J. L. Shi, Z. Y. Zhou, H. Q. Liu, A. S. C. Chan, B. S. Kang, *Inorg. Chim. Acta* **2002**, *336*, 151; d) S. Tavacoli, T. A. Miller, R. L. Paul, J. C. Jeffery, M. D. Ward, *Polyhedron* **2003**, *22*, 507; e) Y. Zheng, M. Du, J.-R. Li, R.-H. Zhang, X.-H. Bu, *Dalton Trans.* **2003**, 1509; f) M. Oh, C. L. Stern, C. A. Mirkin, *Chem. Commun.* **2004**, 2684; g) Y.-B. Xie, C. Zhang, J.-R. Li, X.-H. Bu, *Dalton Trans.* **2004**, 562; h) D. A. McMorran, C. M. Hartshorn, P. J. Steel, *Polyhedron* **2004**, *23*, 1055.

[4] T. K. Ronson, H. Adams, M. D. Ward, *Inorg. Chim. Acta* **2005**, *358*, 1943.

[5] E. R. Humphrey, K. L. V. Mann, Z. R. Reeves, A. Behrendt, J. C. Jeffery, J. P. Maher, J. A. McCleverty, M. D. Ward, *New J. Chem.* **1999**, *23*, 417.

[6] a) E. C. Constable, S. M. Elder, J. V. Walker, P. D. Wood, D. A. Tocher, *J. Chem. Soc., Chem. Commun.* **1992**, 229; b) K. T. Potts, K. A. G. Rayford, M. Keshavarz-K, *J. Am. Chem. Soc.* **1993**, *115*, 2793; c) R. L. Cleary, D. A. Bardwell, M. Murray, J. C. Jeffery, M. D. Ward, *J. Chem. Soc., Perkin Trans. 2* **1997**, 2179.

[7] a) A. M. W. Cargill Thompson, D. A. Bardwell, J. C. Jeffery, L. H. Rees, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1997**, 721; b) R. E. Rosenfeld, Jr., R. Parthasarathy, J. D. Dunitz, *J. Am. Chem. Soc.* **1977**, *99*, 4860; c) F. T. Burling, B. M. Goldstein, *J. Am. Chem. Soc.* **1992**, *114*, 2313; d) F. T. Burling, B. M. Goldstein, *Acta Crystallogr., Sect. B* **1993**, *49*, 738; e) G. R. Desiraju, V. Nalini, *J. Mater. Chem.* **1991**, *1*, 201; f) D. Britton, J. D. Dunitz, *Helv. Chim. Acta* **1980**, *63*, 1068; g) M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* **1996**, *118*, 8077; h) M. Iwaoka, S. Takemoto, M. Okada, S. Tomoda, *Bull. Chem. Soc. Japan* **2002**, *75*, 1611; i) I. Vargas-Baca, T. Chivers, *Phosphorus, Sulfur, Silicon and the Related Elements* **2000**, *164*, 207; j) R. M. Minyaev, V. I. Minkin, *Can. J. Chem.* **1998**, *76*, 776.

[8] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**.

[9] a) Y.-P. Cai, H.-X. Zhang, A.-W. Xu, C.-Y. Su, C.-L. Chen, H.-Q. Liu, L. Zhang, B.-S. Kang, *J. Chem. Soc., Dalton Trans.* **2001**, 2429; b) E. Psillakis, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1997**, 1645; c) X. Meng, B. Xiao, Y. Fan, H. Hou, G. Li, *Inorg. Chim. Acta* **2004**, *357*, 1471; d) L. Carlucci, G. Ciani, D. W. von Gudenberg, D. M. Proserpio, *Inorg. Chem.* **1997**, *36*, 3812; e) R. Horikoshi, T. Mochida, H. Moriyama, *Inorg. Chem.* **2002**, *41*, 3017; f) P. L. Caradoc-Davies, L. R. Hanton, *Chem. Commun.* **2001**, 1098; g) Y. Kang, S. S. Lee, K.-M. Park, S. J. Lee, S. O. Kang, J. Ko, *Inorg. Chem.* **2001**, *40*, 7027.

[10] a) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; b) E. C. Constable, *Prog. Inorg. Chem.* **1994**, *42*, 67; c) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457.

[11] a) J. M. Baumeister, R. Alberto, K. Ortner, B. Spingler, P. A. Schubiger, T. A. Kaden, *J. Chem. Soc., Dalton Trans.* **2002**, 4143; b) H. C. Kang, A. W. Hanson, B. Eaton, V. Boekelheide, *J. Am. Chem. Soc.* **1985**, *107*, 1979; c) Y.-B. Dong, G.-X. Jin, M. D. Smith, R.-Q. Huang, B. Tang, H.-C. zur Loye, *Inorg. Chem.* **2002**, *41*, 4909; d) D. Song, S. Wang, *Eur. J. Inorg. Chem.* **2003**, 3774; e) Y.-B. Dong, Z. Zhao, G.-X. Jin, R.-Q. Huang, M. D. Smith, *Eur. J. Inorg. Chem.* **2003**, 4017; f) J. Budka, P. Lhotak, I. Stibor, J. Sykora, I. Cisarova, *Supramol. Chem.* **2003**, *15*, 353; g) C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, Z. Xie, *Inorg. Chem.* **2000**, *39*, 5851.

[12] a) D. Eisler, R. J. Puddephatt, *Inorg. Chem.* **2005**, *44*, 4666; b) W. Xu, R. J. Puddephatt, K. W. Muir, A. A. Torabi, *Organometallics* **1994**, *13*, 3054; c) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, G. L. Ning, T. Kojima, *J. Am. Chem. Soc.* **1998**, *120*, 8610.

[13] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

[14] a) S. H. Pines, *J. Org. Chem.* **1976**, *41*, 884; b) D. V. Griffiths, P. A. Griffiths, K. Karim, B. J. Whitehead, *J. Chem. Res.* **1996**, *176*, 901.

[15] M. Asakawa, P. R. Ashton, S. E. Boyd, C. L. Brown, S. Menzer, D. Pasini, J. F. Stoddart, M. S. Tolley, A. J. P. White, D. J. Williams, P. G. Wyatt, *Chem. Eur. J.* **1997**, *3*, 463.

[16] G. J. Kubas, *Inorg. Synth.* **1976**, *19*, 90.

[17] U. Azzena, S. Demartis, L. Pilo, E. Piras, *Tetrahedron* **2000**, *56*, 8375.

[18] G. M. Sheldrick, SADABS, A program for absorption correction with the Siemens SMART area-detector system; University of Göttingen, **1996**.

[19] a) Siemens SHELXTL, An integrated system for solving and refining crystal structures from diffraction data, revision 5.1; Siemens Analytical X-ray Instruments Ltd, Madison, WI, **1996**; b) G. M. Sheldrick, SHELXS-97, a Program for Automatic Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, **1997**; c) G. M. Sheldrick, SHELXL-97, a Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, **1997**.

Received: August 4, 2005