DALTON
FULL PAPER

Complexes of late transition metals containing the mixed donor ligands $2,6\text{-}(RSCH_2)_2C_5H_3N$ (R = Ph, Me): Crystal structures of $[\{Cu(2,6\text{-}(PhSCH_2)_2C_5H_3N)(\mu\text{-}X)\}_2]$ (X = Cl, Br) and $[Ni(2,6\text{-}(PhSCH_2)_2C_5H_3N)Br_2]$

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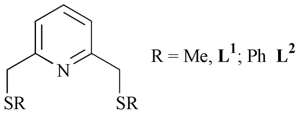
A range of NiX_2 and CuX (X = halide) complexes containing the tridentate NS_2 ligands 2,6-bis(methylthiomethyl)-pyridine ($\mathbf{L}^1$) and 2,6-bis(phenylthiomethyl)pyridine ($\mathbf{L}^2$) were prepared. Reaction of CuX with 1 molar equivalent of $\mathbf{L}^1$ or $\mathbf{L}^2$ afforded the binuclear species $[\{CuL(\mu\text{-}X)\}_2]$ (L = $\mathbf{L}^1$, X = Cl; L = $\mathbf{L}^2$, X = Cl, Br, I). These compounds have been characterised by IR and ^1H NMR spectroscopies, mass spectrometry and microanalysis. Crystal structure determinations of $[\{Cu\mathbf{L}^2(\mu\text{-}X)\}_2]$ (X = Cl, Br) confirm the dimeric nature of these complexes through bridging halide centres, with the NS_2 ligands coordinated through their pyridyl nitrogens and one of the sulfur atoms in a bidentate manner. Reaction of NiX_2 with 1 molar equivalent of $\mathbf{L}^1$ or $\mathbf{L}^2$ afforded mononuclear species for $[NiLX_2]$ (L = $\mathbf{L}^1$, X = I; L = $\mathbf{L}^2$, X = Br, I) and binuclear species for $[NiLX_2]_2$ (L = $\mathbf{L}^1$, X = Cl, Br; L = $\mathbf{L}^2$, X = Cl). These compounds have limited solubility and were characterised through IR and UV-Vis reflectance spectroscopies and microanalysis. The crystal structure determination of $[Ni\mathbf{L}^2Br_2]$ confirms the compound to be monomeric with a five-coordinate, square pyramidal nickel centre.

Introduction

Extensive studies into the bonding and structural features of transition metal complexes containing multidentate thioether ligands have been conducted.[1] Similarly, studies of mixed multidentate phosphine/thioether ligand containing complexes have also been reported.[2] The structures of complexes containing these multidentate ligands vary from mononuclear compounds which have not contributed to supramolecular motifs within the infinite structure,[1b–e] to complexes which form ion channels and two-dimensional sheets.[3] Solution studies of a large number of these complexes have also been reported with significant conclusions being drawn concerning bonding patterns within groups of metals as well as ligands.

Complexes containing nitrogen/sulfur mixed donor ligands have recently attracted increasing interest. Ligands such as these are used for the preparation of complexes designed as enzyme mimics.[4] Enzymes such as nickel hydrogenase and copper proteins have the metal centres surrounded by histidine (N-donor) and cysteine (S-donor) groups.[5,6] Related to this, complexes containing multidentate mixed donor ligands consisting of hard N-donor and softer S-donor atoms have been investigated as catalysts for a number of catalytic reactions.[7] 2,6-(Rthiomethyl)pyridine ligands (**I**) (R = alkyl, aryl) have been studied less. Their applications include metal selectivity such as the selective extraction of palladium from mixtures of palladium(II) and copper(II) in aqueous solutions by polymer bound 2,6-bis(methylthiomethyl)-3-hydroxypyridine.[8] This application can also extend to the preparation of sensors.[9] This ligand type contains three donor atoms, allowing for the ligand to act as a tridentate (**II**) or bidentate ligand (**III**). In the solid-state, these ligands generally behave as tridentate ligands, bonding to metal centres through the pyridyl nitrogen centre and both sulfur atoms,[10–16] with one exception where bidentate ligation is observed.[17] In solution, although the ligand can behave as a bidentate, chelating metal centres through the pyridyl nitrogen and one sulfur atom, it can readily undergo fluxional processes.[18–20] Very few reports of complexes containing these ligands have considered bonding comparisons between ligands containing alkyl-thioethers and aryl-thioether groups, and even fewer have made comparisons between different halide complexes of the same metal. One study of $CuCl_2$ complexes containing NS_2 ligands have shown that alkyl-thioether ligands are less π-acidic than aryl-thioether ligands and that the latter ligand has a higher ability to stabilise low oxidation state metals.[14]



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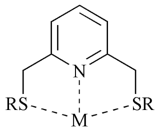

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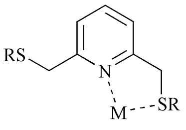

III

Herein we report the preparation of a number of Ni(II) and Cu(I) halide complexes containing the ligands 2,6-bis(methylthiomethyl)pyridine ($\mathbf{L}^1$) and 2,6-bis(phenylthiomethyl)-pyridine ($\mathbf{L}^2$). We show that for nickel(II) complexes, changing both the ligand and halide results in a change in structure of the complexes, through spectral characterisation as well as single crystal X-ray diffraction studies. We also illustrate a difference

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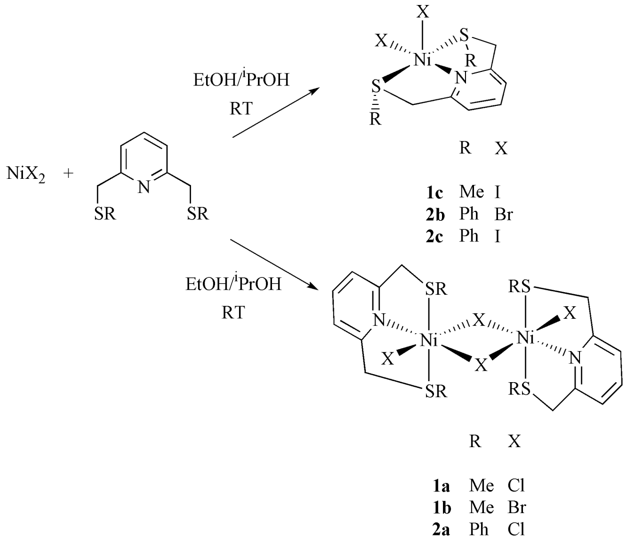
in the ability of the two ligands to stabilise low oxidation state complexes when the electron density of the metal is varied from our studies of copper(I) halide complexes. We also report the monomeric and dimeric structures of three metal complexes containing 2,6-bis(phenylthiomethyl)pyridine, the dimeric structure being the first reported for a Cu(I) metal complex containing this type of ligand.

Results and discussion

Nickel

The stoichiometric reaction of NiX_2 (X = Cl, Br, I) with ligands $\mathbf{L}^1$ or $\mathbf{L}^2$ in ethanol at ambient temperature affords the complexes $[NiLX_2]$ in low to good yield as green [L = $\mathbf{L}^1$, X = Cl (**1a**), Br (**1b**), I (**1c**); L = $\mathbf{L}^2$, X = Cl (**2a**)] or brown powders [L = $\mathbf{L}^2$, X = Br (**2b**), I (**2c**)], see Scheme 1. The nickel complexes are air stable but insoluble in most common solvents, thus limiting solution spectroscopic studies. FAB mass spectra for the complexes $[Ni\mathbf{L}^2X_2]$ (3-NOBA matrix) show fragments corresponding to the $[Ni\mathbf{L}^2X_2]$ ions, with further loss of halide and nickel leading to the observation of the $[Ni\mathbf{L}^2X]$ and $[\mathbf{L}^2]$ ions, respectively. The ion $[Ni\mathbf{L}^2Cl_3Ni]$ is also observed in the FAB mass spectrum of $[Ni\mathbf{L}^2Cl_2]_2$ suggesting that the compound is dinuclear. On heating the brown monomeric complex $[Ni\mathbf{L}^2Br_2]$ in acetonitrile for 30 min, a green solid is formed, presumably either an octahedral binuclear $[\{Ni\mathbf{L}^2Br_2\}_2]$ complex or an octahedral monomeric complex containing a coordinated MeCN molecule.



Scheme 1 Preparation of nickel(II) halide complexes **1a**–**c** and **2a**–**c**.

Solid-state electronic spectra were obtained for all nickel halide complexes. The reflectance UV/vis spectra of the dimeric complexes $[Ni\mathbf{L}^1Cl_2]_2$, $[Ni\mathbf{L}^1Br_2]_2$ and $[Ni\mathbf{L}^2Cl_2]_2$ show bands which are consistent with high spin d^8 metal centres with pseudo octahedral geometry, additional splitting being due to the loss of symmetry. The spectra exhibit two d–d transition bands in the regions 7900–11000 and 13100–14500 cm^{-1} with a third near the charge transfer bands corresponding to the $^3A_{2g}\longrightarrow{}^3T_{2g}$, $^3A_{2g}\longrightarrow{}^3T_{1g}$ and $^3A_{2g}\longrightarrow{}^3T_{1g}(P)$ allowed transitions, respectively.[21] In contrast, the UV-Vis spectra of $[Ni\mathbf{L}^1I_2]$, $[Ni\mathbf{L}^2Br_2]$ and $[Ni\mathbf{L}^2I_2]$ exhibit bands in the ranges 5400–6300, 8169–11100, 9328–13600, and 23000–24500 cm^{-1}, which can be assigned to $^3B_1\longrightarrow{}^3E$ (2 bands), $^3B_1\longrightarrow{}^3B_2$, $^3B_1\longrightarrow{}^3A_2(P)$ and $^3B_1\longrightarrow{}^3E(P)$ transitions, respectively, of a high spin pentacoordinate nickel species with square pyramidal geometry.[21] The difference in structure between the complexes suggests that the presence of the more bulky ligand imparts considerable steric constraints within the molecule as does the presence of the larger halide ion. The monomeric nature of the larger halide complexes also can be attributed to the decreased bridging ability of the halide.

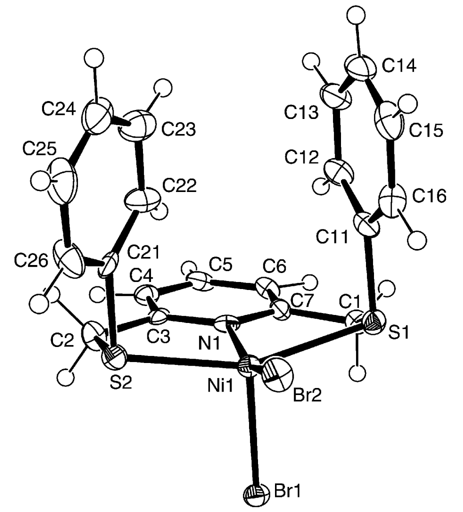


Fig. 1 Molecular projection of $[Ni\mathbf{L}^2Br_2]$, showing atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.

X-Ray structure determination of $[Ni\mathbf{L}^2Br_2]$ (2b)

Crystals suitable for X-ray diffraction studies were grown by the liquid diffusion of the two reagents using ethanol (containing $NiBr_2$) and isopropanol (containing $\mathbf{L}^2$) as solvent. $[Ni\mathbf{L}^2Br_2]$ crystallises as orange/brown plate-like crystals in the triclinic space group $P\bar{1}$ (no. 2) with the asymmetric unit comprised of a monomeric species containing a five-coordinate nickel centre with distorted square pyramidal geometry (Fig. 1). Crystallographic data of $[Ni\mathbf{L}^2Br_2]$ are listed in Table 1. Important bond distances and angles of $[Ni\mathbf{L}^2Br_2]$ are listed in Table 2. The ligand acts as a tridentate ligand, chelating the metal centre in a meridional fashion through the nitrogen and two sulfur centres, occupying three basal positions of the square pyramid. The two thioether moieties are coordinated to the nickel centre, *meso* relative to each other. The two bromine atoms occupy the remaining apical position and the axial position. These structural features are also observed in the copper(II) compound [Cu{2,6-bis(ethylthiomethyl)pyridine}Cl_2].[12] The related complex [Ni{2,6-bis(benzylthiomethyl)pyridine}Br(μ-Br)]$_2$ has a considerably different structure where the molecule is dimeric through bridging bromide atoms with octahedral nickel centres,[16] 2,6-bis(benzylthiomethyl)pyridine also acting as a tridentate ligand and coordinating to the metal centres in a meridional fashion. A terminally bound bromide atom occupies the remaining coordination site. In the case of [{Ni[2,6-bis(benzylthiomethyl)pyridine]Br(μ-Br)}$_2$], the methylene spacer reduces the effective bulk of the phenyl group in the vicinity of the sulfur, and hence, the nickel, thus accommodating the bridging bromide atoms, resulting in a dimeric stucture.[16]

The Ni–N bond distance of 2.057(5) Å in $[Ni\mathbf{L}^2Br_2]$ is comparable with that in [{Ni[bis(benzylthiomethyl)pyridine]Br(μ-Br)}$_2$] [2.057(5) Å][16] and similar to those found in $[Ni([18]aneN_2S_4)]^{2+}$ [2.065(13), 2.126(13) Å] {$[18]aneN_2S_4$ = 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane}, where the macrocyclic ligand coordinates to the octahedral nickel centre through all six donors.[22] The average Ni–N bond distance in (2,11-dithia[3,3](2,6)pyridinophane)nickel(II) of 2.08 Å[23] is slightly longer than that of $[Ni\mathbf{L}^2Br_2]$ which can be attributed to the increased strain within the macrocyclic ligands associated with the square planar nickel centre. The Ni–S bond distances found in $[Ni\mathbf{L}^2Br_2]$ are 2.370(2) and 2.397(2) Å, similar Ni–S bond distances being observed in (2,11-dithia[3,3](2,6)-pyridinophane)nickel(II) [2.385(1), 2.407(1) Å].[23] Longer Ni–S

Table 1 Crystallographic data for [NiL^{2}Br$_2$] and [{CuL^2(μ-X)}$_2$]

	[NiL^{2}Br$_2$]	[{CuL^2(μ-Cl)}$_2$]	[{CuL^2(μ-Br)}$_2$]
Formula	$C_{19}H_{17}NS_2NiBr_2$	$C_{38}H_{34}N_2S_4Cu_2Cl_2$	$C_{38}H_{34}N_2S_4Cu_2Br_2$
M	541.98	844.97	933.84
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.294(3)	7.8258(5)	10.035(2)
b/Å	17.025(4)	9.7175(6)	13.133(6)
c/Å	7.520(4)	12.9919(8)	7.866(2)
α/°	95.86(3)	105.981(1)	105.25(3)
β/°	109.48(3)	105.008(1)	96.69(2)
γ/°	99.24(2)	95.913(1)	106.58(3)
U/Å^3	974.2(6)	901.1(2)	937.8(6)
D_c/g cm^{-3}	1.848	1.557	1.653
Z	2	1	1
μ/cm^{-1}	52.7	15.9	35.2
$T_{(\mathrm{min,\ max})}$[a]	0.35, 0.73	0.66, 0.83	0.21, 0.35
$2\theta_{\mathrm{max}}$/°	50.0	75.0	50.0
No. unique reflections	3412	9279[a]	3302
No. observed data	2275	7335	2286
R	0.037	0.030	0.051
R'	0.041	0.035	0.082

[a] R_{int} = 0.025.

Table 2 Selected bond distances (Å) and angles (°) of [NiL^{2}Br$_2$]

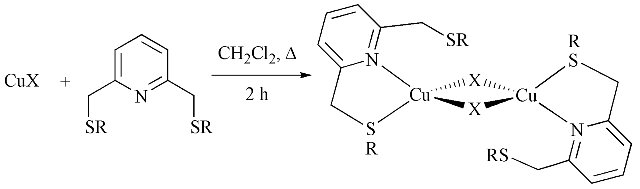
Ni–Br(1)	2.434(1)	S(1)–C(1)	1.807(6)
Ni–Br(2)	2.417(1)	S(1)–C(11)	1.772(7)
Ni–S(1)	2.397(2)	S(2)–C(2)	1.799(7)
Ni–S(2)	2.370(2)	S(2)–C(21)	1.765(7)
Ni–N	2.057(5)		
Br(1)–Ni–Br(2)	104.57(4)	Br(2)–Ni–S(1)	91.89(6)
Br(1)–Ni–S(1)	101.31(6)	Br(2)–Ni–S(2)	92.96(6)
Br(1)–Ni–S(2)	99.50(6)	Br(2)–Ni–N	160.9(2)
Br(1)–Ni–N	94.5(2)		
Torsion angles			
S(1)–C(1),C(7)–N(1)	−22.3(8)	S(2)–C(2),C(3)–N(1)	8.9(8)

bond distances are recorded for the dimeric complex [{Ni[2,6-bis(benzylthiomethyl)pyridine]Br(μ-Br)}$_2$] [2.427(2), 2.459(2) Å],[16] consistent with the increased coordination number of the nickel, while the significantly longer Ni–S bonds in [Ni([18]aneN$_2$S$_4$)]$^{2+}$ [2.403(6)–2.430(5) Å][22] and [Ni([9]aneN$_2$S)$_2$]$^{2+}$ [2.418(1) Å], {[9]aneN$_2$S = 1-thia-4,7-diazacyclononane},[24] which contain N-alkyl rather than N-aryl moieties within the ligand, suggest the thioether to be a stronger donor to nickel in the presence of aromatic nitrogen donor moieties. The Ni–Br bond distances of [NiL^{2}Br$_2$] are 2.434(1) and 2.417(1) Å where the longer bond distance is associated with the bromine atom occupying the apical position. These bond distances are significantly shorter than the distance involving the terminally bound bromide in [{Ni[2,6-bis(benzylthiomethyl)pyridine]Br(μ-Br)}$_2$] [2.529(1) Å], again consistent with the increased coordination number of the nickel centre.[16]

The least-square plane of best fit defined by the atoms Br(2), S(1), N(1) and S(2) has an r.m.s. deviation of 0.041 and the nickel centre is 0.409 Å out of the least-square plane inside the polyhedron. The angle between the least-square plane of best fit defined by the base atoms and S(1), Br(1), S(2) is 88.7°, and, with N(1), Br(1), Br(2), is also 88.7°. The angle between the two intersecting planes perpendicular to the base least-square plane is 89.9°. The distortion of the polyhedron can partly be attributed to the Br(1)···Br(2) repulsion [Br(1)–Ni–Br(2) = 104.57(4)°]. The bite angles of the ligand are also restrictive on the polyhedron [N–Ni–S = 83.3(2), 84.7(2)°]. The Br(2)–Ni–S bond angles of 92.96(6) and 91.89(6)° are slightly larger than ideal to help alleviate strain within the molecule. The phenyl groups are orientated away from the Br(1) atom, the *meso* arrangement of the phenyl groups blocking the sixth position of the octahedron, and preventing dimerisation through halide bridges.

Copper

Reaction of CuX (X = Cl, Br, I) with one molar equivalent of L (L = **L**^{1} or **L**^{2}) in refluxing CH$_2$Cl$_2$ for 2 hours gave green to brown coloured solutions. Addition of diethyl ether afforded [{CuLX}$_2$] as green [L = **L**^{1}, X = Cl (**3a**); L = **L**^{2}, X = Cl (**4a**), I (**4c**)] or yellow solids [L = **L**^{2}, X = Br (**4b**)] in low yields, see Scheme 2. Attempts to prepare the complexes [{CuL^{1}X}$_2$] (X = Br, I) only resulted in the isolation of the CuX reagent. Previous cyclic voltammetry studies on copper(II) chloride complexes containing NS$_2$ ligands indicated that complexes containing ligands with aryl-thioether moieties had enhanced capacity for stabilising low oxidation states of copper compared to ligands containing alkyl-thioether moieties.[14] The less π-acidic S-alkyl ligand is unable to compensate for the increased electron density of the copper(I) centre on varying the halide from chloride to iodide with consequent failure to prepare these heavier halide complexes. FAB mass spectra of [{CuL^{2}Cl}$_2$], [{CuL^{2}Br}$_2$] and [{CuL^{2}I}$_2$] show peaks at *m*/*z* 809, 853 and 901, respectively, with the correct isotopic pattern corresponding to [**L**^{2}–Cu–X–Cu–**L**^{2}]$^+$, suggesting the presence of dimeric species. Further loss of halide is observed with the peak corresponding to [CuL^2]$^+$ also present in all spectra.



	R	X
3a	Me	Cl
4a	Ph	Cl
4b	Ph	Br
4c	Ph	I

Scheme 2 Preparation of copper(I) halide complexes **3a** and **4a**–**c**.

The 297 K ^{1}H NMR spectra of the [{CuL^{2}X}$_2$] complexes show aromatic protons as multiplets at 6.8–7.7 ppm. The resonances are broadened, suggesting fluxionality and inversion of the ligand *via* κ^3-coordination of the ligand, when bound to

Table 3 Selected bond distances (Å) and angles (°) of [{Cu**L**^{2}(μ-X)}$_2$] [X = Cl (**4a**), X = Br (**4b**)]

	4a	**4b**
Cu–X(1)	2.2649(4)	2.3905(11)
Cu–X(1*)	2.4380(4)	2.5452(12)
Cu–S(1)	2.3501(3)	2.383(2)
Cu–N(1)	2.067(1)	2.074(4)
S(1)–C(1)	1.821(1)	1.820(6)
S(2)–C(2)	1.808(1)	1.791(7)
S(1)–C(11)	1.784(1)	1.778(6)
S(2)–C(21)	1.774(1)	1.783(8)
Cu–X(1)–Cu*	72.61(1)	67.03(4)
X(1*)–Cu–X(1)	107.39(1)	112.97(4)
X(1)–Cu–S(1)	124.41(1)	120.58(6)
X(1)–Cu–N(1)	126.23(3)	125.32(13)
X(1*)–Cu–S(1)	104.88(1)	103.59(6)
X(1*)–Cu–N(1)	104.59(3)	104.22(12)
S(1)–Cu–N(1)	86.02(3)	85.58(14)

the metal centre. The methylene proton resonances are also very broad and are non-observable for [{Cu**L**^{2}X}$_2$] and [{Cu**L**^{1}Cl}$_2$]. The resonance corresponding to the methyl protons of [{Cu**L**^{1}Cl}$_2$] is also broad. The spectrum of [{Cu**L**^{2}I}$_2$] shows the methylene protons to be equivalent as a single resonance at 4.64 ppm. The aromatic region is also better resolved but does not show inequivalence of the aromatic thioether rings. Low temperature NMR studies were carried out to investigate the intramolecular fluxional process but even at 220 K, the methylene resonances could not be resolved, with only a slight improvement in the resolution of the aromatic region. This contrasts with similar studies of rhenium carbonyl complexes containing **L**^{1} where the ambient temperature spectrum shows the presence of two non-exchanging invertomers, both having one coordinated and one non-coordinated MeS arm.[20] On heating the sample, the four resonances of the methyl protons exhibited exchange broadening and coalesced to a single resonance. Studies of the line shape changes suggested concurrent pyramidal sulfur inversion and intramolecular exchange of the uncoordinated and coordinated MeS groups.

X-Ray structure determinations of [{Cu**L**^{2}(μ-X)}$_2$] [X = Cl (4a), Br (4b)]

Crystallographic data for [{Cu**L**^{2}(μ-X)}$_2$] are listed in Table 1, important bond distances and angles being given in Table 3. Suitable crystals of [{Cu**L**^{2}(μ-X)}$_2$] crystallised in the triclinic space group $P\bar{1}$ (no. 2) with the molecules being dimeric through unsymmetrical halide bridges, containing two four-coordinate copper centres having distorted tetrahedral geometries (Fig. 2) (X = Br, that for X = Cl is similar). The asymmetric units are comprised of one half of each dimer, the second half being generated through a crystallographic inversion centre, the molecules having an obligate planar Cu$_2$X$_2$ four-membered ring core. The two remaining coordination sites on each copper centre are occupied by the pyridyl nitrogen and one sulfur atom of the ligand, forming a five-membered chelate ring. The two uncoordinated sulfur atoms arrange themselves *anti* with respect to the pyridyl ring and do not participate in any inter- or intra-molecular bonding.

The Cu–S bond distances of 2.3501(3) and 2.383(2) Å (**4a** and **4b**, respectively) are comparable to distances seen in related thiopyridyl complexes.[25] An elongation in the Cu–S bond distance from the chloride to bromide complex is concomitant with increased electron density on the copper centre imparted by the heavier halide. The Cu–S bond distances are significantly longer than those found in [Cu$_2$(Me$_2$[18]aneN$_2$S$_4$)-(NCMe)$_2$]$^{2+}$ [2.317(4), 2.286(4) Å] which is a dinuclear complex in which each Cu(I) centre is bound tetrahedrally by two sulfur and one nitrogen atoms of the macrocycle.[26] The difference in bond distances may be attributed to geometrical restrictions

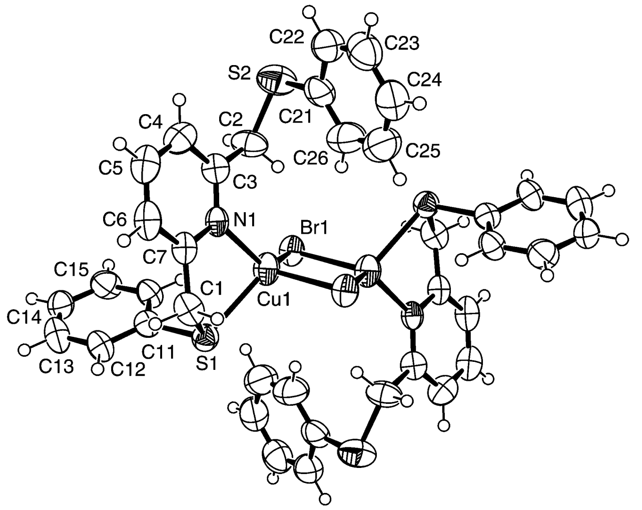


Fig. 2 Molecular projection of [{Cu**L**^{2}(μ-Br)}$_2$], showing atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level.

imposed on the copper centre in the latter by the macrocyclic ligand, as well as stronger bonds to the metal centre associated with the macrocyclic effect. The Cu–N bond distances for [{Cu**L**^{2}(μ-X)}$_2$] [2.067(1) (**4a**), 2.074(4) Å (**4b**)] are significantly shorter than the Cu–N bond in [Cu$_2$(Me$_2$[18]aneN$_2$S$_4$)-(NCMe)$_2$]$^{2+}$ [2.165(7) Å][26] but are comparable to that of Cu-[2-(*tert*-butylthiomethyl)pyridine]$_2$Br [2.109(9) Å],[25] suggesting that the pyridyl ring is a stronger donor than the sp^3 nitrogen centre of the macrocyclic ligand. The C–N bond distances in [{Cu**L**^{2}(μ-X}$_2$] are comparable to those in other four-coordinate Cu(I) complexes containing pyridine ligands, *e.g.* [Cu(pyr)$_4$]-[ClO$_4$] [2.05(1) Å].[27] The Cu–X bond distances for [{Cu**L**^{2}(μ-X}$_2$] [2.2649(4), 2.4380(4) Å (X = Cl), 2.3905(11), 2.5452(12) Å (X = Br)] are consistent with some degree of weak bonding through the bridging halide atoms to the second metal centre.

The bite angles (N–Cu–S) of the bidentate ligand in the two complexes of 86.02(3) (**4a**) and 85.58(14)° (**4b**) are similar to the bite angle of the chelating ligand in Cu[2-(*tert*-butylthiomethyl)pyridine]$_2$Br [N–Cu–S = 85.4(3)°],[25] these small angles contributing to the distortion from ideal tetrahedral geometry of the copper centres. The N–Cu–X (X = Cl, Br) bond angles are larger than ideal to compensate for the small bite angles, while the N–Cu–X(1*) and S–Cu–X(1*) bond angles for both compounds are close to ideal. The X(1)–Cu–X(1*) bond angles are also slightly larger than ideal.

Conclusions

A number of nickel(II) halide and copper(I) halide complexes containing the NS$_2$ ligands 2,6-bis(methylthiomethyl)pyridine (**L**^{1}) and 2,6-bis(phenylthiomethyl)pyridine (**L**^{2}) have been prepared from the stoichiometric reaction of the metal halide with the appropriate ligand.

Structural features vary between the nickel(II) complexes, depending on both the ligand used as well as the choice of halide. Green dimeric complexes, most probably through bridging halide atoms, are obtained when the ligand **L**^{1} is present, in both the chloride and bromide complexes. The analogous iodide complex, which is brown in colour, appears to be monomeric. When the more sterically demanding ligand, **L**^{2}, is used in conjunction with the larger halides, bromide and iodide, the brown compounds become monomeric in structure, most probably containing a five-coordinate, square pyramidal nickel centre, based on comparisons of the spectroscopic data of these complexes with that of the structurally authenticated complex Ni**L**^{2}Br$_2$. A dimeric complex is obtained containing this ligand when the smaller chloride ligand is present.

The copper(I) halide complexes obtained are dimeric in structure, by way of bridging halides. [{Cu**L**^{2}X}$_2$] complexes (X = Cl, Br, I) were prepared, while reactions of copper(I) bromide and copper(I) iodide with **L**^{1} only resulted in the isolation of the copper halide. The difference in reactivity between the two ligands illustrates the difference in their electronic properties, with the aryl-thioether ligand being able to stabilise low oxidation state metals more effectively than the alkyl-thioether ligand, the electron density on the metal centre increasing on varying the halide from chloride to iodide. The structures of [{Cu**L**^{2}X}$_2$] (X = Cl, Br) show the ligand to act as a bidentate ligand, the first showing the ligand type to behave in this fashion in the solid-state.

Experimental

Infrared spectra were measured as CsI discs using a Perkin-Elmer 983 spectrometer over the range 200–4000 cm^{-1}. Reflectance UV-Vis spectra were recorded using a Perkin-Elmer Lambda19 UV-Vis spectrometer. Mass spectra were run by fast-atom bombardment (FAB) using 3-NOBA (3-nitrobenzyl alcohol) as matrix on a VG Analytical 70-250-SE Normal Geometry Double Focusing Mass Spectrometer or by positive electrospray (ES$^+$) using a VG Biotech Platform. ^{1}H NMR spectra were recorded using Bruker AM300 or AM360 spectrometers operating at 300 and 360 MHz, respectively. Microanalyses were performed by the microanalytical service of Strathclyde University and the CSL Laboratory at the University of Tasmania. 2,6-Bis(methylthiomethyl)pyridine (**L**^{1})[8] and 2,6-bis(phenylthiomethyl)pyridine (**L**^{2})[14] were prepared using literature procedures.

Syntheses

[NiL^{2}Cl$_2$]$_2$. A colourless solution of **L**^{2} (110 mg, 0.34 mmol) in ^{i}PrOH (*ca.* 5 ml) was layered on a green solution of NiCl$_2$·6H$_2$O (80 mg, 0.51 mmol) in EtOH. The mixture was allowed to stand for 24 h at room temperature to afford a green precipitate. The solid was collected, washed with EtOH and dried (59 mg, 77%) (Found: C, 50.3; H, 3.7; N, 3.1. NiCl$_2$NS$_2$C$_{19}$H$_{17}$ requires C, 50.4; H, 3.8; N, 3.1%). $\bar{\nu}_{max}$/cm^{-1} 1598w, 1454w, 1359vs, 1089m, 996s, 740m, 690m, 566w, 322w, 208w (CsI); *m*/*z* 412 (M$^+$ − Cl), 377 (M$^+$ − 2Cl), 319 (**L**^{2}); λ_{max}/cm^{-1} (BaSO$_4$) 23800, 14500, 8000.

[NiL^{1}Cl$_2$]$_2$. Following the above procedure with **L**^{1} (51%) (Found: C, 32.7; H, 3.8; N, 3.9. NiCl$_2$NS$_2$C$_9$H$_{13}$ requires C, 32.9; H, 4.3; N, 4.0%); $\bar{\nu}_{max}$/cm^{-1} 3055vw, 2901vw, 1592s, 1570m, 1457s, 1420m, 1395m, 1358s, 1095m, 1019s, 991s, 870m, 796s, 698w, 254m, 207w (CsI); λ_{max}/cm^{-1} (BaSO$_4$) 27100, 13100, 10800.

[NiL^{2}Br$_2$]. Following the above procedure for [NiL^{2}Cl$_2$]$_2$ with NiBr$_2$ (65%) (Found: C, 42.1; H, 2.9; N, 2.2. NiBr$_2$NS$_2$C$_{19}$H$_{17}$ requires C, 42.1; H, 3.2; N, 2.6%); $\bar{\nu}_{max}$/cm^{-1} 3064vw, 2933vw, 2891vw, 1593w, 1570w, 1481w, 1458m, 1442w, 1358vs, 1106s, 1017s, 1000s, 887w, 834w, 802w, 745m, 734m, 683m, 613w, 476w, 319vw, 275vw, 203vw (CsI); *m*/*z* 461 (M$^+$ − Br), 382 (M$^+$ − 2Br), 319 (**L**^{2}); λ_{max}/cm^{-1} (BaSO$_4$) 24500, 21100, 13600, 10300, 5700.

[NiL^{1}Br$_2$]$_2$. Following the above procedure with **L**^{1} (41%) (Found: C, 26.8; H, 3.4; N, 3.2. NiCl$_2$NS$_2$C$_9$H$_{13}$ requires C, 25.9; H, 3.1; N, 3.4%); $\bar{\nu}_{max}$/cm^{-1} 3064vw, 1599m, 1571m, 1458m, 1410m, 1206w, 1172w, 1098m, 1018m, 984m, 961w, 871m, 797m, 763m, 697m, 589w, 557w, 382vw, 321vw, 273w, 240m, 225m (CsI); λ_{max}/cm^{-1} (BaSO$_4$) 23300, 14500, 9000.

[NiL^{2}I$_2$]. Following the above procedure for [NiL^{2}Cl$_2$]$_2$ with NiI$_2$ (74%) (Found: C, 32.8; H, 3.1; N, 2.3. NiCl$_2$NS$_2$C$_{19}$H$_{17}$·CH$_2$Cl$_2$ requires C, 33.3; H, 2.7; N, 1.9%); $\bar{\nu}_{max}$/cm^{-1} 1598w, 1481m, 1454m, 1441m, 1390s, 1359s, 1106w, 1019s, 999s, 885m, 834w, 795m, 744s, 733s, 683m, 613w, 476w, 423vw, 304vw, 257w, 228w, 212w (CsI); *m*/*z* 504 (M$^+$ − I), 377 (M$^+$ − 2I), 319 (**L**^{2}); λ_{max}/cm^{-1} (BaSO$_4$) 23000, 13100, 11100, 5400.

[NiL^{1}I$_2$]. Following the above procedure with **L**^{1} (31%) (Found: C, 26.5; H, 2.8; N, 3.4. NiCl$_2$NS$_2$C$_9$H$_{13}$ requires C, 21.1; H, 2.6; N, 2.7%); $\bar{\nu}_{max}$/cm^{-1} 3062vw, 2916vw, 1599s, 1570s, 1457vs, 1414s, 1358s, 1163m, 1094s, 1016s, 995m, 895w, 874w, 793m, 761w, 692vw, 235vw (CsI); λ_{max}/cm^{-1} (BaSO$_4$) 9300, 8200, 6300.

[{CuL^{2}Cl}$_2$]. A solution of **L**^{2} (160 mg, 0.49 mmol) and CuCl (50 mg, 0.51 mmol) in degassed CH$_2$Cl$_2$ (20 ml) was refluxed for 2 hours. The green solution was cooled and the solvent volume was reduced *in vacuo* (*ca.* 2 ml). Addition of Et$_2$O afforded a light green precipitate, which was collected and recrystallised, from CH$_2$Cl$_2$ and Et$_2$O (10 mg, 25%) (Found: C, 53.6; H, 3.9; N, 3.3. CuClNS$_2$C$_{19}$H$_{17}$ requires C, 54.0; H, 4.1; N, 3.3%); $\bar{\nu}_{max}$/cm^{-1} 2918w, 2852w, 1596m, 1452w, 1359s, 1090s, 1022m, 885w, 796w, 740m, 690m, 612w, 488w, 204w (CsI); δ_H (CDCl$_3$) 7.7–6.5 (13H, m, C$_5$H$_3$N, C$_6$H$_5$); *m*/*z* 809 (M$^+$ − Cl), 427 (M$^+$ − Cu − **L**^{2} − 2Cl + MeCN), 386 (M$^+$ − Cu − **L**^{2} − 2Cl), 324 (**L**^{2}).

[{CuL^{1}Cl}$_2$]. Following the procedure for the preparation of [{CuL^{2}Cl}$_2$] using **L**^{1} (19%) (Found: C, 35.1; H, 4.6; N, 5.0. CuClNS$_2$C$_9$H$_{13}$ requires C, 36.2; H, 4.4; N, 4.7%); $\bar{\nu}_{max}$/cm^{-1} 2918w, 1596s, 1568m, 1453s, 1359s, 1261m, 1098vs, 805m, 614s, 303m, 251w (CsI); δ_H (CDCl$_3$) 7.7–7.3 (3H, m, C$_5$H$_3$N), 1.4 (6H, s, CH$_3$).

[{CuL^{2}Br}$_2$]. Following the above procedure with CuBr (28%) (Found: C, 48.9; H, 3.7; N, 3.0. CuBrNS$_2$C$_{19}$H$_{17}$ requires C, 48.3; H, 3.4; N, 2.8%); $\bar{\nu}_{max}$/cm^{-1} 1587w, 1432w, 1436w, 1359s, 1091s, 990m, 885w, 834w, 792w, 749m, 739vw, 690m, 614w, 342w, 202w, 189w (CsI); δ_H (CDCl$_3$) 7.5–7.0 (13H, m, C$_5$H$_3$N, C$_6$H$_5$); *m*/*z* 853 (M$^+$ − Br), 386 (M$^+$ − Cu − **L**^{2} − 2Br), 324 (**L**^{2}).

[{CuL^{2}I}$_2$]. Following the above procedure with CuI (20%) (Found: C, 44.4; H, 3.3; N, 2.7. CuINS$_2$C$_{19}$H$_{17}$ requires C, 44.0; H, 3.1; N, 2.6%); $\bar{\nu}_{max}$/cm^{-1} 1587m, 1452w, 1358s, 1091s, 988w, 885w, 835w, 749s, 690m, 540w, 484w (CsI); δ_H (CDCl$_3$) δ 7.6–7.1 (13H, m, C$_5$H$_3$N, C$_6$H$_5$), 4.65 (4H, s, CH$_2$); *m*/*z* 901 (M$^+$ − I), 386 (M$^+$ − Cu − **L**^{2} − 2I), 324 (**L**^{2}).

Structure determinations

Single crystals of [NiL^{2}Br$_2$] were grown from liquid diffusion of alcoholic solutions of the reagents at room temperature. Single crystals of [{CuL^2(μ-Br)}$_2$] were obtained from a solution of the complex in nitromethane at −30 °C. Single crystals of [{CuL^2(μ-Cl)}$_2$] were obtained from vapour diffusion of Et$_2$O into a solution of the complex in nitromethane. For each compound the selected crystal was coated with mineral oil and mounted on a glass fibre. Data collection for [NiL^{2}Br$_2$] and [{CuL^2(μ-Br)}$_2$] used a single counter Rigaku AFC7S diffractometer at 150 K (for [NiL^{2}Br$_2$]) or 297 K (for [{CuL^2(μ-Br)}$_2$]), (ω–2θ scans); for [{CuL^2(μ-Cl)}$_2$], a full sphere of data was measured using a Bruker AXS CCD instrument (18631 reflections; *T ca.* 153 K). “Empirical”/multiscan absorption corrections were applied, monochromatic Mo-Kα radiation being employed for all determinations. In the full matrix least-squares refinements, anisotropic thermal parameter forms were refined for the non-hydrogen atoms; for the Cu/Cl/**L**^{2} adduct, $(x, y, z, U_{iso})_H$ were refined, these parameters being included constrained at estimated values in the other two. Conventional R, R' on $|F|$ are quoted at convergence (statistical weights). Neutral atom complex scattering factors were employed within the context of SHELXL-97,[28] TEXSAN[29] or Xtal 3.7 program systems.[30] Pertinent results are given above and in the figures and tables.

CCDC reference numbers 164471, 164472 and 168826.

See http://www.rsc.org/suppdata/dt/b1/b104332n/ for crystallographic data in CIF or other electronic format.

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