View Article Online / Journal Homepage / Table of Contents for this issue

DALTON
FULL PAPER

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

Pyridine-2-thione derivatives of silver(I) and mercury(II): crystal structures of dimeric [bis(diphenylphosphino)methane][(1-oxopyridine-2-thionato)silver(I), [2-(benzylsulfanyl)pyridine 1-oxide]dichloromercury(II) and phenyl(pyridine-2-thionato)mercury(II) †

Tarlok S. Lobana,*[a] Seema Paul[a] and Alfonso Castineiras[b]

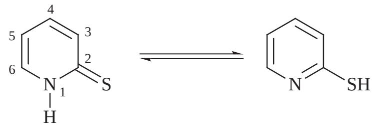
[a] *Department of Chemistry, Guru Nanak Dev University, Punjab, Amritsar-143 005, India*
[b] *Departamento de Quimica Inorganica, Universidade de Santiago, 15706-Santiago, Spain*

Received 14th January 1999, Accepted 9th April 1999

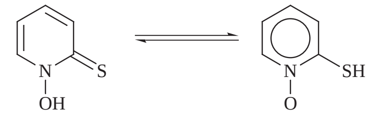
Silver(I) complexes, [Ag(O,S-C_5H_4NOS)(L)] [L = $Ph_2PCH_2PPh_2$ (dppm) **1**, $Ph_2P(CH_2)_4PPh_2$ (dppb) **2**, PPh_3 **3** or $P(C_6H_4Me\text{-}m)_3$ **4**] were obtained from silver(I) acetate and neutral 1-hydroxypyridine-2-thione(C_5H_5NOS) in water–ethanol medium followed by addition of tertiary phosphines. Direct reaction of mercury(II) halides with 2-benzylsulfanyl)pyridine 1-oxide[$C_5H_4NO(SCH_2C_6H_5)$] in ethanol formed [$HgX_2\{C_5H_4NO(SCH_2C_6H_5\}$] [X = Cl **5** or Br **6**]. Similarly, organomercury(II) derivatives, Hg(R)L [R = m-$O_2NC_6H_4$, L = $C_5H_4NS^-$ **7** or $C_5H_4NOS^-$ **8**; R = p-ClC_6H_4, L = $C_5H_4NS^-$ **9** or $C_5H_4NOS^-$ **10**; R = C_6H_5, L = $C_5H_4NS^-$ **11** or $C_5H_4NOS^-$ **12**] were prepared from Hg(R)(O_2CCH_3) and neutral pyridine-2-thiones(C_5H_5NS or C_5H_5NOS). All these have been characterised using analytical data, IR, far-IR, NMR (^1H, ^{13}C or ^{31}P) spectroscopy and for **1**, **5** and **11** X-ray crystallography. Complex **1** exists as a dimer with dppm bridging the two Ag atoms leading to the formation of an eight membered metallacyclic ring with $C_5H_4NOS^-$ moieties chelating to each Ag atom *via* O,S-donor atoms. The geometry about each Ag is highly distorted tetrahedral with bond angles varying from 72.85(7) to 137.92(4)°. Compounds **5** and **11** acquire formally dimeric structures *via* weaker interactions. For example, in **5**, Hg binds strongly to one O, two Cl and weakly to one Cl and one S atom of a second ligand molecule. The geometry about each Hg is formally highly distorted trigonal bipyramidal with Cl(1)–Hg–Cl(2) and O(1)–Hg–S(1*) bond angles of 172.84(5) and 151.70(9)° respectively. Finally in **11** Hg is bonded strongly to one C and one S atom, relatively weakly to N{Hg–N 2.795(10), 2.879(9) Å} and very weakly to a second S atom of a second ligand molecule {Hg–S 3.312(3), 3.365(3) Å}. If secondary interactions are ignored the geometry about Hg is formally distorted T-shaped.

The co-ordination chemistry of heterocyclic thiones is of immense interest because such compounds mimic (a) cysteine sulfur co-ordination in metalloenzymes, (b) electronic and structural properties of the active sites in copper "blue" proteins involving S,N co-ordination, (c) the environment for molybdenum in nitrogenase where S,N-chelated molybdenum is believed to be relevant to the reduction of nitrogen by nitrogenase, (d) interactions of nucleotides and nucleic acid and bases with metals,[1,2] *etc.* In addition, the use of sulfur-co-ordinated gold(I) complexes in the treatment of rheumatoid arthritis, platinum complexes in anticancer activity and a variety of biochemical applications have stimulated interest in heterocyclic thiones and their derivatives.[3–6] Using the simplest molecules, pyridine-2-thione (**I**, C_5H_5NS) and its *N*-oxide derivative, namely 1-hydroxypyridine-2-thione (**II**, C_5H_5NOS), several investigations have been made by others[4–6] and our laboratory.[7–16] Compound **I** and its anion $C_5H_4NS^-$ bind in several ways[4–6] while C_5H_5NOS co-ordinates only in its anionic form *via* its O,S-donor atoms in a chelating mode.[7]

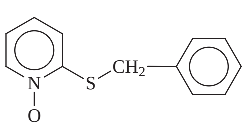
Silver(I) is known to form mono-, di-, hexa- and octa-nuclear complexes with neutral C_5H_5NS or its derivatives containing substituents in the pyridyl ring.[17–20] Similarly, there are a few reports on the use of organic substituents on sulfur which can significantly modulate the co-ordination properties of C_5H_5NOS.[21] Further, the co-ordination chemistry of organomercury(II) cations, RHg^+ (R = CH_3, Ph, *etc.*) is important in view of their toxicity to living systems by binding to cysteine thiolate groups and thus there is need for detoxification of mercury similar to metallothioneins.[22] There are limited reports on the interaction of heterocyclic thiones with organomercury(II) substrates.[3–6,23]



Ia **Ib**



IIa **IIb**



III

In this paper we report (a) complexes of silver(I) containing 2-thioxopyridine-1-one and tertiary phosphines as co-ligands, (b) 2-(benzylsulfanyl)pyridine 1-oxide **III** complexes with mercury(II) halides and (c) arylmercury(II) derivatives containing m-C_6H_4, p-ClC_6H_4 and Ph as organic moieties and $C_5H_4NS^-$, $C_5H_4NOS^-$ anions.[24]

Experimental

General materials

Mercury(II) chloride, bromide (used after recrystallisation from ethyl alcohol), silver acetate, silver carbonate and triphenyl-

---

† The chemistry of pyridinethiols and related ligands. Part 10.[24a]

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

phosphine were from M/s Sisco Laboratories, Bombay, tri-*m*-tolylphosphine and $Ph_2PCH_2PPh_2$ from Pressure Chemicals Co. Ltd., Pittsburg, USA; other materials were prepared as reported.[8,9] The compound C_5H_5NS was prepared by heating 2-hydroxypyridine with P_2S_5, C_5H_5NOS by oxidation of 2-chloropyridine using H_2O_2 followed by reaction with a mixture of NaSH (prepared by passing H_2S gas through NaOEt in EtOH)[7–9] and Na_2S. Sodium salts, $Na^+C_5H_4NS^-$ and $Na^+C_5H_4NOS^-$, were prepared by treating neutral C_5H_5NS and C_5H_5NOS with NaOEt prepared *in situ*.[7] $C_5H_4NO(SCH_2C_6H_5)$ was prepared by treating the sodium salt of C_5H_5NOS with benzyl chloride in 1 : 1 mole ratio (mp 158–59 °C).[24a] Phenylmercury(II) chloride (Fluka chemika, Switzerland) was used after recrystallisation from ethanol; *m*-nitrophenyl- and *p*-chlorophenyl-mercury(II) chlorides were prepared by literature methods.[25–27]

Preparations

$[Ag(C_5H_4NOS)(dppm)]$ 1. To a solution of silver(I) acetate (0.100 g, 0.6 mmol) in distilled water (20 ml) was added an ethanolic solution of C_5H_5NOS (0.076 g, 0.6 mmol) dropwise under magnetic stirring. After 0.5 h was added an ethanolic solution of dppm (0.230 g, 0.6 mmol) dropwise and stirred overnight. The white precipitates formed were filtered off, washed with water and dried *in vacuo*. Crystals were grown from ethanol–benzene–dichloromethane by slow evaporation at room temperature. Yield 60%, mp, 120–123 °C (Found: C, 57.3; N, 2.31. Required for $C_{30}H_{26}AgNOP_2S$: C, 58.0; N, 2.34%). IR (cm^{-1}): 1215m, 1190m, ν(C=S); 1100m, ν(P–C); 1080m, ν(N–O); 830m, δ(N–O). NMR (see structure **Ia** for numbering scheme): ^{1}H, δ 8.18 [d, $J(H^5H^6)$ 6.4, H^6], 6.84 [td, $J(H^4H^{3,5})$ 7.6, $J(H^4H^6)$ 1.4, H^4], 7.57 [d, $J(H^3H^4)$ 8.4, H^3] and 6.65 [td, $J(H^5H^{4,6})$ 6.8, $J(H^3H^5)$ 1.9 Hz, H^5]; ^{13}C, δ 162.7(C^2), 140.7(C^6), 133.5(C^4), 127.2(C^5), 118.8(C^3); phosphine signals, 29.8(CH$_2$), 135.9(*i*-C), 135.0(*o*-C), 130.6(*m*-C), 131.9(*p*-C). ^{31}P, δ 15.43, $\Delta\delta = 36.7$. Complexes **2**–**4** were prepared by the same method.

$[Ag(C_5H_4NOS)\{Ph_2P(CH_2)_4PPh_2\}]$ 2. Yield 55%, mp 193–195 °C (Found: C, 57.6; H, 4.91; N, 2.34. Required for $C_{33}H_{32}AgNOP_2S$: C, 57.4; H, 4.64; N, 2.03%). IR (cm^{-1}): 1210m, 1190m, ν(C–S); 1100m, ν(P–C); 1080m, ν(N–O); 833m δ(N–O). NMR: ^{1}H, δ 8.12 [dd, $J(H^5H^6)$ 6.6, $J(H^4H^6)$ 1.4, H^6], 6.85 [td, $J(H^4H^{3,5})$ 7.7, $J(H^4H^6)$ 1.2, H^4], 7.67 [dd, $J(H^3H^4)$ 8.3, $J(H^3H^5)$ 1.9, H^3] and 6.62 [td, $J(H^5H^{4,6})$ 6.9, $J(H^3H^5)$ 1.9 Hz, H^5]; ^{13}C, δ 160.0(C^2), 137.8(C^6), 130.8(C^4), 124.8(C^5), 116.0(C^3); phosphine signals, 27.0–29.1(CH$_2$), 133.2(*i*-C), 132.0(*o*-C, J_{CP} 16.6) 129.2 (*m*-C, J_{CP} 8.5 Hz) and 128.9(*p*-C); ^{31}P, δ −1.95, $\Delta\delta = 19.0$.

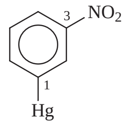
$[Ag(C_5H_4NOS)(PPh_3)]$ 3. Yield 60%, mp, 170 °C (Found: C, 54.6; H, 3.72; N, 2.17. Required for $C_{23}H_{19}AgNOPS$: C, 55.6; H, 3.83; N, 2.82%). IR (cm^{-1}): 1215s, 1190s, ν(C=S); 1105s, ν(P–C); 1080s, δ(N–O); 833m, ν(N–O); 338m, ν(Ag–O). NMR: ^{1}H, δ 8.29 [d, $J(H^5H^6)$ 6.6, H^6], 6.99 [t, $J(H^4H^{3,5})$ 7.3, H^4], 7.78 [dd, $J(H^3H^4)$ 8.3, $J(H^3H^5)$ 1.9, H^3] and 6.78 [td, $J(H^5H^{4,6})$ 6.9, $J(H^3H^5)$ 1.9 Hz, H^5]; ^{13}C, δ 164.9(C^2), 137.6(C^6), 130.7(C^4), 124.9(C^5), 116.5(C^3); phosphine signals, 130.1(*i*-C), 133.1(*o*-C, J_{CP} 16.5), 128.0(*m*-C, J_{CP} 10.4 Hz) and 129.6(*p*-C);[24] ^{31}P, δ 12.57, $\Delta\delta = 19.7$.

$[Ag(C_5H_4NOS)\{P(C_6H_4Me\text{-}m)_3\}]$ 4. Yield 55%, mp 220–225 °C (decomp.) (Found: C, 59.0; H, 4.88; N, 2.10. Required for $C_{26}H_{28}AgNOPS$: C, 58.0; H, 4.64; N, 2.60%). IR (cm^{-1}): 1209m, 1189m, ν(C=S); 1096s, ν(P–C); 1080s, ν(N–O); 831m, δ(N–O); 321m, ν(Ag–O). NMR: ^{1}H, δ 8.11 [d, $J(H^5H^6)$ 6.6, H^6], 6.81 [t, $J(H^4H^{3,5})$ 7.6, H^4], 7.60 [d, $J(H^3H^4)$ 7.2, H^3] and 6.58 [t, $J(H^5H^{4,6})$ 6.4 Hz, H^5]; ^{13}C, δ 160.9(C^2), 131.8 (C^4), 125.8(C^5), 117.1(C^3); phosphine signals, 21.5(CH$_3$), 131.8(*i*-C), 131.0(*o*-C^1, J_{CP} 14.4), 134.8(*o*-C^2, J_{CP} 20.1), 138.8(*m*-C^1), 128.8(*m*-C^2, J_{CP} 10.1 Hz) and 131.5(*p*-C); ^{31}P, δ 4.17, $\Delta\delta = 13.4$.

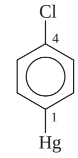
$[HgCl_2\{C_5H_4NO(SCH_2C_6H_5)\}]$ 5. This was prepared by direct reaction of mercury(II) chloride (0.100 g, 0.37 mmol) with 2-(benzylsulfanyl)pyridine 1-oxide (0.080 g, 0.37 mmol) in ethanol at room temperature under magnetic stirring (48 h) and slow evaporation gave fine crystals of the complex. Yield 50%, mp 190–192 °C (decomp) (Found: C, 29.9; H, 2.41; N, 2.89. Required for $C_{12}H_{11}Cl_2HgNOS$: C, 29.5; H, 2.25; N, 2.86%). IR (cm^{-1}): 1250m, 1220s, ν(C=S); 1090m, ν(N–O); 837s, δ(N–O); 710s, 700s, 333s, ν(Hg–O); 307m, 288m, ν(Hg–Cl). NMR: ^{1}H, δ 8.40 [d, $J(H^5H^6)$ 6.8, H^6], 7.55 (broad, H^4), 7.38 (broad, H^3) and 7.23 [td, $J(H^5H^{4,6})$ 6.8, $J(H^3H^5)$ 2.2 Hz, H^5]; ^{13}C, δ 154.5(C^2), 140.8(C^6), 129.0(C^4), 125.4(C^5) and 123.1(C^3); benzyl group, 37.1(CH$_2$), 136.9(*i*-C), 130.0–132.2(*o*-, *m*- and *p*-C).

$[HgBr_2\{C_5H_4NO(SCH_2C_6H_5)]$ 6. This was prepared by the same method. Yield 60%, mp 180–185 °C (Found: C, 25.7; N, 2.40. Required for $C_{12}H_{11}Br_2HgNOS$: C, 25.4; N, 2.37%). IR (cm^{-1}): 1240m, 1220s, ν(C=S); 1090m, ν(N–O); 830s, δ(N–O); 710s, 690s, ν(C–S). NMR: ^{1}H, δ 8.19 (broad, H^6), 7.10–7.47 (broad, H^{3,4,5}); ^{13}C, δ 143.0(C^6), 125.5(C^4), 121.7(C^5), 120.5(C^3); benzyl group, 36.8(CH$_2$), 128.4(*o*-C), 127.3(*m*-C) and 128.4 (*p*-C).

[Hg(*m*-$O_2NC_6H_4$)(C_5H_4NS)] 7. To a water–acetone solution of [Hg(*m*-$O_2NC_6H_4$)(O_2CCH_3)] (25 ml) [prepared by treating Hg(*m*-$O_2NC_6H_4$)Cl (0.100 g, 0.28 mmol) with Ag(O_2CCH_3) (0.046 g, 0.28 mmol)] was added C_5H_5NS slowly (0.030 g, 0.27 mmol) in ethanol (20 ml). The contents were stirred for 5 h when a white fibrous crystalline product separated. It was filtered off washed with EtOH and then dried *in vacuo*. Yield 55% mp 140 °C (decomp.) (Found: C, 30.0; H, 1.33; N, 6.41. Required for $C_{11}H_8HgN_2O_2S$: C, 30.5; H, 1.85; N, 6.47%). IR (cm^{-1}): 1124m, ν(C=S); 478s, ν(Hg–C); 389s, ν(Hg–S). NMR: ^{1}H, δ 8.13 [d, $J(H^5H^6)$ 4.1, H^6], 7.40 [td, $J(H^4H^{3,5})$ 7.3, $J(H^4H^6)$ 1.8, H^4], 8.08 [d, $J(H^3H^4)$ 7.1, H^3] and 6.9 [td, $J(H^5H^{4,6})$ 6.2, $J(H^3H^5)$ 1.6 Hz, H^5]; ^{13}C, 168.6(C^2), 146.7(C^6), 136.1(C^4), 122.3(C^5) and 118.5(C^3); ^{1}H, (*m*-$O_2NC_6H_4$)Hg, 8.29 [d, $J(H^2H^4)$ 2.1 Hz], 7.21 [d, $J(H^5H^6)$ 8.2, H^6], 7.55 [t, $J(H^5H^{4,6})$ 7.8, H^5] and 7.71 [d, $J(H^4H^5)$ 7.3 Hz, H^4]; ^{13}C, δ 128.3(C^2,C^6), 141.7(C^3), 122.3(C^5) and 130.0(C^4). Other complexes **8**–**12** were prepared similarly (see structures **IV** and **V** for numbering scheme of RHg^+ moiety).



IV



V

[Hg(*m*-$O_2NC_6H_4$)(C_5H_4NOS)] 8. Yield 70%, mp 249–250 °C (Found: C, 29.4; H, 1.36; N, 6.12. Required for $C_{11}H_8HgN_2O_3S$: C, 29.4; H, 1.78; N, 6.23%). IR (cm^{-1}): 1209m, ν(C=S); 1089m, ν(N–O); 833m, δ(N–O); 435s, ν(Hg–C); 423s, ν(Hg–O); 336s, ν(Hg–S). NMR: ^{1}H, δ 8.48 [d, $J(H^5H^6)$ 5.7, H^6], 7.34 [td, $J(H^4H^{3,5})$ 7.8, $J(H^4H^6)$ 1.3, H^4], 8.02 [ddd, $J(H^3H^4)$ 8.5, $J(H^3H^5)$ 2.5, $J(H^3H^6)$, 1.1, H^3] and 7.15 [td, $J(H^5H^{4,6})$ 6.9, $J(H^3H^5)$ 1.6 Hz, H^5]; (*m*-$O_2NC_6H_4$)Hg, 8.41 [d, $J(H^2H^4)$ 2.4, H^2], 7.82 [dd, $J(H^5H^6)$ 8.2, $J(H^4H^6)$ 1.7, H^6], 7.65 [t, $J(H^5H^{4,6})$ 7.8, H^5] and 7.94 [d, $J(H^4H^5)$ 7.3 Hz, H^4].

[Hg(*p*-ClC_6H_4)(C_5H_4NS)] 9. Yield 60%, mp 123–126 °C (Found: C, 32.1; H, 1.69; N, 3.23. Required for $C_{11}H_8ClHgNS$: C, 31.2; H, 1.89; N, 3.31%). IR (cm^{-1}): 1124s, ν(C=S); 485s, 479s, ν(Hg–C); 389m, ν(Hg–S). NMR: ^{1}H, δ 8.09 [d, $J(H^5H^6)$ 4.6, H^6] and 6.91 [td, $J(H^5H^{4,6})$ 6.2, $J(H^3H^5)$ 1.0 Hz, H^5]; ^{13}C, δ 163.5(C^2), 146.7(C^6), 135.9(C^4), 124.1(C^5) and 118.8(C^3); ^{1}H, (*p*-ClC_6H_4)Hg, δ 7.17 [d, $J(H^{2,6}H^{3,5})$ 8.9 Hz, H^2, H^6] and 7.29–7.35(H^3,H^5); ^{13}C, δ 133.5(C^1), 127.9(C^2,C^6), 136.4(C^3,C^5) and 137.4(C^4).

View Article Online

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

[Hg(*p*-ClC$_6$H$_4$)(C$_5$H$_4$NOS)] 10. Yield 60%, mp 195–197 °C (Found: C, 31.1; H, 2.06; N, 3.06. Required for $C_{11}H_8ClHgNOS$: C, 31.1; H, 1.83; N, 3.20%). IR (cm^{-1}): 1208s, ν(C=S); 1088s, ν(N–O); 833m, δ(N–O); 480s, ν(Hg–C); 373m, ν(Hg–O); 354m, ν(Hg–S). NMR: ^{1}H, δ 8.26 [dd, $J(H^5H^6)$ 6.6, $J(H^4H^6)$ 1.0, H^6], 7.14 [td, $J(H^4H^{3,5})$ 7.8, $J(H^4H^6)$ 1.4, H^4], 7.65 [dd, $J(H^3H^4)$ 8.3, $J(H^3H^5)$ 1.8, H^3] and 6.89 [td, $J(H^5H^{4,6})$ 7.0, $J(H^3H^5)$ 1.8 Hz, H^5]; ^{13}C, δ 152.7(C^2), 139.3(C^6), 129.8(C^4), 122.4(C^5) and 118.8(C^3); ^{1}H, (*p*-ClC$_6$H$_4$)Hg, δ 7.29 [d, $J(H^{2,6}H^{3,5})$ 7.6, H^{2}H^6) and 7.35 [d, $J(H^{2,6}H^{3,5})$, 7.6 Hz, H^3,H^5]; ^{13}C, δ 133.3(C^1), 127.7(C^2,C^6), 137.1(C^3,C^5) and 139.4 (C^4).

[Hg(C$_6$H$_5$)(C$_5$H$_4$NS)] 11. Yield 70%, mp 120–122 °C (Found: C, 33.5; H, 2.06; N, 3.72. Required for $C_{11}H_9HgNS$; C, 34.0; H, 2.32; N, 3.61%). IR (cm^{-1}): 1124s, ν(C=S). NMR: ^{1}H, δ 8.18 [dd, $J(H^5H^6)$ 5.0, $J(H^4H^6)$ 0.9, H^6] and 6.98 [td, $J(H^5H^{4,6})$ 6.2, $J(H^3H^5)$ 0.9, H^5]; (C$_6$H$_5$)Hg, δ 7.41–7.46 (H^2,H^6,H^4) and 7.25–7.33 (H^3,H^5); ^{13}C, δ 164.7(C^2), 147.7(C^6), 136.5(C^4), 125.1(C^5) and 119.2(C^3).

[Hg(C$_6$H$_5$)(C$_5$H$_4$NOS)] 12. Yield 65%, mp 130–135 °C (Found: C, 32.1; H, 2.15; N, 3.37. Required for $C_{11}H_9HgNOS$: C, 32.7; H, 2.23; N, 3.46%). IR (cm^{-1}): 1214s, ν(C=S); 1088m, ν(N–O); 834m, δ(N–O); 451s, ν(Hg–C); 377m, ν(Hg–O); and 330m, ν(Hg–S). NMR: ^{1}H, δ 8.26 [dd, $J(H^5H^6)$ 6.6, $J(H^4H^6)$ 1.0, H^6], 7.11 [td, $J(H^4H^{3,5})$ 7.8, $J(H^4H^6)$ 1.0, H^4], 7.64 [dd, $J(H^3H^4)$ 8.3, $J(H^3H^5)$ 1.5, H^3] and 6.87 [td, $J(H^5H^{4,6})$ 6.9, $J(H^3H^5)$ 1.7 Hz, H^5]; ^{13}C, δ 151.9(C^2), 139.3(C^6), 127.6(C^4), 126.0(C^5) and 118.7(C^3); ^{1}H, (C$_6$H$_5$)Hg, δ 7.37 [dd, $J(H^3H^{2,6})$ 8.0, $J(H^4H^{2,6})$ 1.4, H^2, H^6], 7.30[t, $J(H^2H^4)$, $J(H^6H^{2,4})$ 7.0, H^2(or H^6), H^4] and 7.19 [t, $J(H^4H^{3,5})$ 7.3 Hz, H^4]; ^{13}C, 129.8(C^1), 136.2(C^{2,6}) and 127.8(C$^{3–5}$).

NMR of ligands

C$_6$H$_5$NS: ^{1}H, δ 7.56 [ddd, $J(H^5H^6)$ 6.3, $J(H^4H^6)$ 1.6, $J(H^3H^6)$ 0.8, H^6], 7.34 [ddd, $J(H^3H^4)$ 8.7, $J(H^4H^5)$ 7.0, $J(H^4H^6)$ 1.8, H^4], 7.49 [dt, $J(H^3H^4)$ 8.7, $J(H^3H^{5,6})$ 0.8, H^3] and 6.73 [td, $JH^5H^{4,6})$ 6.7, $J(H^3H^5)$ 1.2 Hz, H^5]; ^{13}C, δ 175.6(C^2), 137.0(C^6), 135.9(C^4), 132.8(C^5) and 113.1(C^3). C$_5$H$_5$NOS: ^{1}H, δ 8.02 [dd, $J(H^5H^6)$ 6.7, $J(H^4H^6)$ 1.2, H^6], 7.21 [td, $J(H^4H^{3,5})$ 7.9, $J(H^4H^6)$ 1.4, H^4], 7.60 [dd, $J(H^3H^4)$ 8.6, $J(H^3H^5)$ 1.5, H^3] and 6.72 [td, $J(H^5H^{4,6})$ 7.0, $J(H^3H^5)$ 1.6 Hz, H^5]; ^{13}C, 166.0(C^2), 131.6(C^6), 130.3(C^4), 131.2(C^5) and 113.1(C^3). C$_5$H$_4$NO(SCH$_2$C$_6$H$_5$): ^{1}H, δ 8.18 [d, $J(H^5H^6)$ 6.4, H^6], 7.09 (broad), 7.37 (broad) and 6.98 [td, $J(H^4H^5)$ 6.5, $J(H^3H^5)$ 2.6 Hz, H^5]; ^{13}C, δ 137.8(C^2), 133.8(C^6), 124.6(C^4), 121.0(C^5) and 119.6(C^3).

Physical measurements

The elemental analyses for C,H and N were obtained with a Carlo-Erba 1108 microanalyser (Santiago, Spain) or from RSIC Chandigarh. The melting points were determined with a Gallenkamp electrically heated apparatus. The infrared spectra were recorded in KBr pellets (4000–400 cm^{-1}) or Nujol mulls in polyethene sheets (500–100 cm^{-1}) on a Bruker 1FS 66V spectrometer. The NMR spectra were recorded in CDCl$_3$ using (i) a Bruker AMX 300.13 spectrometer and 75.48 MHz probe frequencies (^{1}H and ^{13}C respectively) with TMS as the internal reference and (ii) a Bruker AMX 500 spectrometer at 202.45 MHz probe frequency (^{13}P-{^{1}H} with 85% H$_3$PO$_4$ as the external reference (δ 27.5).

X-Ray data collection and reduction

Suitable colourless prismatic crystals of complexes **1**, **5** and **11** were mounted on glass fibers and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least squares refinement of the diffraction data from 25 reflections in the ranges (a) $11.491 < \theta < 42.234°$ for **1**, (b) $9.372 < \theta < 18.159°$ for **5** and $9.319 < \theta < 20.811°$ in an Enraf-Nonius MACH3 automatic diffractometer.[28] Data were collected at 293 K using Mo-Kα radiation ($\lambda = 0.71073$ Å) and the ω scan technique and corrected for Lorentz-polarisation effects.[29] A semiempirical absorption correction (ψ scan) was made.[30] A summary of the crystal data, experimental details and refinement results is given in Table 1.

Structure solution and refinement. The structures were solved by direct methods[31] which revealed the positions of all non-hydrogen atoms and refined on F^2 by a full matrix least squares procedure using anisotropic displacement parameters.[32] The hydrogen atoms were located from difference maps and refined isotropically. Atomic scattering factors were taken from ref. 33, while molecular graphics were drawn with ZORTEP.[34]

CCDC reference number 186/1422.

See http://www.rsc.org/suppdata/dt/1999/1819/ for crystallographic files in .cif format.

Results and discussion

General comments

Stoichiometric reactions of Ag(O$_2$CCH$_3$) with C$_5$H$_5$NOS in the presence of tertiary phosphines formed Ag(C$_5$H$_4$NOS)L products [L = Ph$_2$P(CH$_2$)$_m$PPh$_2$, *m* = 1 or 4, PPh$_3$ or P(C$_6$H$_4$Me-*m*)$_3$]. The complexes were generally soluble in organic solvents, though organomercury derivatives have relatively low solubility in C$_6$H$_6$, EtOH and MeOH. Direct reactions of HgX$_2$ (X = Cl or Br) with C$_5$H$_4$NO(SCH$_2$C$_6$H$_5$) in EtOH formed products of stoichiometry [HgX$_2${C$_5$H$_4$NO(SCH$_2$C$_6$H$_5$}] (X = Cl or Br). However, there was no reaction with HgI$_2$ and products with CuX (X = Cl, Br or I) were air sensitive and adducts could not be isolated. Reaction of HgRCl with NaC$_5$H$_4$NS (or NaC$_5$H$_4$NOS) in EtOH {or of Hg(R)(O$_2$CCH$_3$) with neutral ligands} formed Hg(R)L products [R = *m*-O$_2$NC$_6$H$_4$, *p*-ClC$_6$H$_4$ or C$_6$H$_5$; L = C$_5$H$_4$NS$^-$ or C$_5$H$_4$NOS$^-$]. Reactions of Hg(R)L with tertiary phosphines were complex and no product could be established. This is in line with the chemistry of the RHg$^+$ moiety which prefers two- or three-co-ordinated complexes and extension of the co-ordination number to 4 or higher is not common.[35]

Crystal and molecular structures

The atomic numbering schemes of [Ag(C$_5$H$_4$NOS)(dppm)], **1**, [HgCl$_2${C$_5$H$_4$NO(SCH$_2$C$_6$H$_5$)}] **5** and [Hg(C$_6$H$_5$)(C$_5$H$_4$NS)] **11** are shown in Figs. 1–3 respectively; bond lengths/angles are listed in Table 2. Complex **1** exists as a centrosymmetric dimer with no interaction between the dimers. The two dppm molecules bridge two Ag(C$_5$H$_4$NOS) moieties forming a eight membered Ag$_2$P$_4$C$_2$ metallacyclic ring with C$_5$H$_4$NOS chelated to each Ag. Each Ag atom acquires distorted tetrahedral geometry by co-ordinating to one O, one S and two P atoms. The angles about each Ag atom vary from 72.85(7) to 137.92(4)° with the bite angle of C$_5$H$_4$NOS$^-$, O(1)–Ag–S(1) being the shortest and P(1)–Ag–P(2) the largest (Table 2). Two Ag–P distances are different [2.4254(10), 2.4914(11) Å], while two Ag–S and two Ag–O distances are equal [Ag–S 2.5844(12), Ag–O 2.440(3) Å].[20] This is unlike those in **3** where the Ag–P and Ag–O distances are equal [Ag–P 2.3824(10), Ag–O 2.343(3) Å] while the Ag–S distances are significantly different [Ag–S 2.5072(10), 2.8218(11) Å] obviously due to sulfur bridging the two Ag atoms, **VI**. There is no Ag · · · Ag interaction [3.8457(7) Å][37] unlike that observed in **3** [Ag · · · Ag 3.2472(11) Å].[24] This weak interaction is similar to the Cu^I · · · Cu^I interaction in the sulfur bridged dinuclear complex [{CuI(C$_5$H$_5$NS)[P(C$_6$H$_4$Me-*p*)$_3$]}$_2$].[15] The S(1)–C(1)$_{py}$, N(1)–O(1) and N(1)–C(1) distances suggest double bond character and thus charge density is delocalised in the S–C–N–O moiety.[4–6,24,37]

In compound **5** Hg forms normal bonds to two Cl and one O atom; however, an S atom binds to a second HgCl$_2${C$_5$H$_4$NO(SCH$_2$C$_6$H$_5$)} unit leading to the formation of the dimer

View Article Online

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

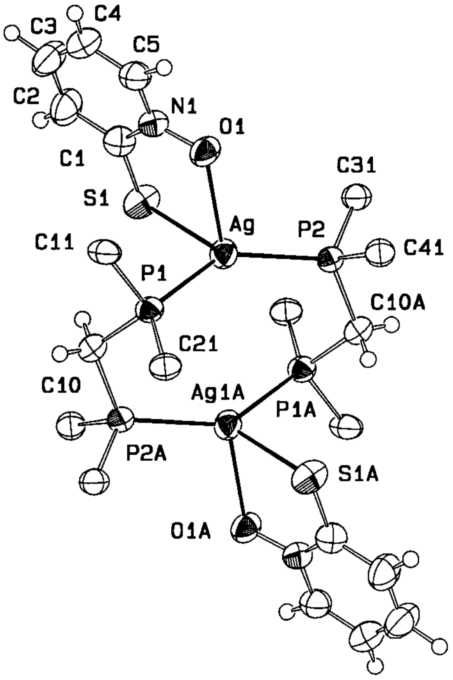


Fig. 1 Perspective view of [{Ag(C_5H_4NOS)(dppm)}$_2$] **1** with the numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

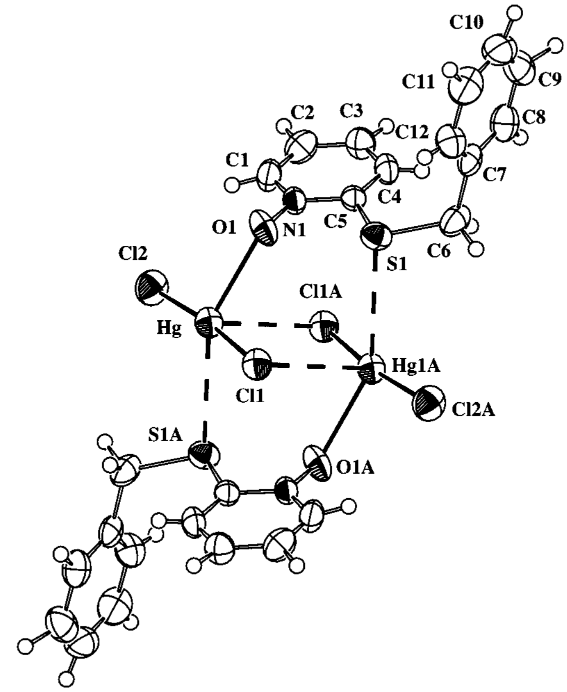
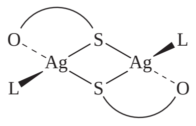


Fig. 2 Perspective view of [$HgCl_2${$C_5H_4NO(SCH_2C_6H_5)$}] **5**. Details as in Fig. 1.



VI

[{$HgCl_2[C_5H_4NO(SCH_2C_6H_5)]$}$_2$] (Fig. 2). This Hg···S(1*) interaction is weak [3.3116(14) Å] and close to the sum of the van der Waals radii.[37] Similarly, the Hg···Cl(1*) distance 3.2317(14) Å is slightly longer than sum of the van der Waals radii [3.30 Å]. In the dimer the geometry about each Hg can be described as distorted trigonal bipyramidal with Cl(1)–Hg–Cl(2) (equatorial) and O(1)–Hg–S(1*) (axial) bond angles of 172.84(5) and 151.70(9)° respectively. There is a weak O(1)···S(1) interaction [2.679(4) Å] less than the sum of the van der Waals radii [3.30 Å], but more than a normal single bond [O–S 1.75 Å].[36,37] The S(1)–C(6) distance [1.831(7) Å] is somewhat longer than a single bond [1.81 Å] and lengthening of this bond as well as some other bonds of the $CH_2C_6H_5$ moiety could be due to the combined effect of Hg–O co-ordination and O···S interaction (Table 2). The phenyl group makes an angle of 79.24° with the plane of the pyridyl group. Similarly the pyridyl group makes an angle of 50.01° with the plane defined by Cl(1)HgCl(2)O(1).

In compound **11** the mercury atom is bonded strongly to one C{Hg(1)–C(11) 2.062(9) Å} and one S atom {Hg(1)–S(1) 2.376(3) Å] (Fig. 3, Table 2). The N(1) atom of one pyridyl moiety is at a distance of 2.795(10) Å from the Hg atom and it shows weak interaction {sum of van der Waals radii, 3.05 Å}. However, this Hg···N(1) interaction is stronger than that in $HgCH_3(C_5H_4NS)$ {Hg···N 2.980(5) Å}.[23] Further, the Hg(1)–S(2) distance of 3.365(3) Å is close to the van der Waals distance (3.30 Å) and thus **11** forms a weak centrosymmetric dimer, [{$Hg(C_6H_5)(C_5H_4NS)$}$_2$]. The angle (C11)–Hg(1)–S(1) [175.2(3)°] deviates from linearity and the S(1)–Hg(1)–N(1) angle is 60.57(18)°. This shows that the geometry about each Hg can be treated as distorted T-shaped. The plane defined by atoms Hg, C(11)–C(16) makes an angle of 89.65 with that defined by S(1), C(17)–C(19), C(40), C(111), N(1), Hg(1).

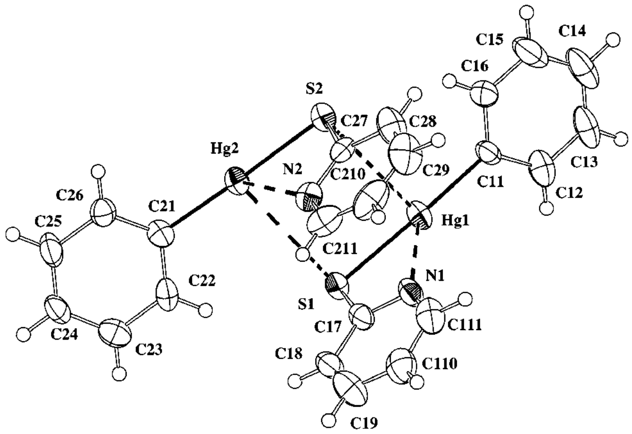


Fig. 3 Perspective view of [$Hg(C_6H_5)(C_5H_4NS)$] **11**. Details as in Fig. 1.

Spectroscopy

The infrared and NMR spectral data are listed in the Experimental section. The IR spectrum of complex **1** showed diagnostic ν(C=S) peaks at 1215m, 1190m, ν(N–O) at 1080m and δ(N–O) at 830m cm^{-1} [*cf.* C_5H_5NOS, 1225s, ν(C=S); 1082, ν(N–O); 832m, δ(N–O)] supporting the O,S binding of the C_5H_4NOS moiety in its characteristic modes.[7] A similar situation pertains for the complexes **2**–**4**, **8**, **10** and **12**. The ν(M–S), ν(M–O) or ν(Hg–Cl) bands could be located for **3**, **5**, **6**, **8**, **10** and **12**. For the $C_5H_4NS^-$ complexes **7**, **9** and **11** the ν(C=S) peak shows a low energy shift of 15 cm^{-1} [*cf.* C_5H_5NS, ν(C=S) 1139s cm^{-1}][7–16] supporting Hg–S interaction. The weak Hg···N interaction revealed from the crystal data could not be identified from IR data. The spectra of **5** and **6** show mainly intensity changes in the characteristic regions for C–S single (710–690 cm^{-1}) and C=S double or partially double bonds (1250–1180 cm^{-1}).[7–16]

^{1}H and ^{13}C NMR spectra (see structure Ia for numbering scheme). From the proton NMR of complexes **7**, **9** and **11**, the absence of a NH signal shows that anionic $C_5H_4NS^-$ is bonded to Hg. The diagnostic H(6) and H(5) signals of the pyridyl moiety provide information about the co-ordination of the

View Article Online

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

Table 1 Summary of crystal data for compounds **1**, **5** and **11**

	1	**5**	**11**
Chemical formula	$C_{30}H_{26}AgNOP_2S$	$C_{12}H_{11}Cl_2HgNOS$	$C_{11}H_9HgNS$
M	618.39	488.77	387.84
K	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a/Å	11.2139(4)	6.4265(5)	30.135(3)
b/Å	12.2698(9)	11.1825(11)	6.7304(11)
c/Å	12.6138(11)	11.7128(9)	23.061(3)
U/Å^3	1355.86(16)	713.70(10)	4355.7(10)
α/°	60.275(6)	112.297(6)	
β/°	67.096(4)	99.680(6)	111.371(9)
γ/°	88.802(5)	105.797(6)	
Z	2	2	16
μ(Mo-Kα)/mm^{-1}	7.983	11.289	14.283
No. reflections collected	5823	3149	5367
No. unique reflections	5526	2880	5234
R_{int}	0.0251	0.0179	0.0733
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0396, 0.1008	0.0259, 0.0596	0.0427, 0.0728
(all data)	0.0657, 0.1116	0.0469, 0.0650	0.1953, 0.0971

Table 2 Selected bond lengths (Å) and angles (°)

[{Ag(C_5H_4NOS)(dppm)}$_2$] **1**			
Ag–P(2)	2.4254(10)	N(1)–C(5)	1.369(6)
Ag–P(1)	2.4914(11)	N(1)–C(1)	1.370(5)
Ag–O(1)	2.440(3)	Ag···Ag*	3.8457(7)
Ag–S(1)	2.5844(12)	S(1)–C(1)	1.721(5)
P(2)–Ag–P(1)	137.92(4)	Ag–O(1)–N(1)	117.6(2)
P(2)–Ag–O(1)	107.22(8)	Ag–S(1)–C(1)	101.52(15)
P(2)–Ag–S(1)	124.55(4)	S(1)–C(1)–N(1)	121.1(3)
P(1)–Ag–O(1)	96.58(8)	O(1)–Ag–S(1)	72.85(7)
P(1)–Ag–S(1)	95.16(4)		
[$HgCl_2(C_{12}H_{11}NOS)$] **5**			
Hg–Cl(2)	2.289(2)	S(1)–C(5)	1.750(5)
Hg–Cl(1)	2.316(1)	S(1)···C(6)	1.831(7)
Hg–O(1)	2.568(4)	S(1)–O(1)	2.679(4)
Cl(1)···Cl(1*)	4.081(3)	Hg···Hg*	3.869(5)
Hg···S(1*)	3.312(1)	Hg···Cl(1*)	3.232(1)
Cl(2)–Hg–Cl(1)	172.84(5)	Hg–O(1)–S(1)	117.6(2)
Cl(2)–Hg–O(1)	98.43(11)	C(6)–S(1)–O(1)	159.3(2)
Cl(1)–Hg–O(1)	87.12(1)	N(1)–O(1)–Hg	120.3(3)
C(5)–S(1)–C(6)	101.6(3)	N(1)–O(1)–S(1)	71.8(3)
C(5)–S(1)–O(1)	58.3(2)		
[$Hg(C_6H_5)(C_5H_4NS)$] **11**			
Hg(1)–C(11)	2.062(9)	Hg(1)···S(2)	3.365(3)
Hg(1)–S(1)	2.376(3)	S(1)···Hg(2)	3.312(3)
Hg(1)···N(1)	2.795(10)	Hg(2)–C(21)	2.054(9)
Hg(2)···N(2)	2.879(9)	Hg(2)–S(2)	2.380(3)
C(11)–Hg(1)–S(2)	95.3(3)	C(11)–Hg(1)–S(1)	175.2(3)
S(1)–Hg(1)–S(2)	85.23(9)	C(11)–Hg(1)–N(1)	124.2(3)
N(1)–Hg(1)–S(2)	89.4(2)	S(1)–Hg(1)–N(1)	60.57(18)
C(21)–Hg(2)–S(1)	96.1(3)	S(2)–Hg(2)–N(2)	59.97(19)
Hg(1)–S(1)–Hg(2)	93.6(2)	S(2)–Hg(2)–S(1)	86.38(9)
C(21)–Hg(2)–S(2)	177.3(3)	N(2)–Hg(2)–S(1)	78.38(17)
C(21)–Hg(2)–N(2)	119.6(3)	Hg(2)–S(2)–Hg(1)	92.34(9)

* $-x + 1, -y + 1, -z + 1$.

N-donor atom. These proton signals generally move downfield relative to those of the "free" ligand when it is N,S bonded and upfield when S bonded, as for example, for $M(C_5H_4NS)_2$ and $M(C_5H_4NS)_2(PPh_3)_2$ complexes (M = Pd or Pt) respectively.[38] Thus in **7**, **9** and **11**, C_5H_4NS is N, S bonded which is supported by the X-ray study of **11**, though weak Hg···N interaction occurs. The weak NH···X (halogen) interaction in copper(I) complexes, *viz.* [{Cu(C_5H_5NS)(X)(R_3P)}$_2$] (X = Cl, Br or I) having S-bonded C_5H_5NS, also leads to a similar effect on the H(5) and H(6) protons of the pyridyl group.[15] The position of the ^{13}C NMR signals of **7**, **9** and **11** support neither essentially S-bonded nor N,S-chelating or bridging $C_5H_4NS^-$ when compared with literature trends because the C(6) carbon remains significantly low field. This points to an intermediate situation where weak Hg···N interaction is suggested in addition to normal Hg–S bonding.[8,15,16,23,38,39] The spectral trends of $C_5H_4NOS^-$ compounds of mercury (**8**, **10**, **12**) and silver (**1**–**4**) are suggestive of O,S chelation as these show characteristic upfield shifts for C(2) and C(4) carbons,[40] while other carbons show trends similar to that of $C_5H_4NS^-$. In the case of the silver compounds, tertiary phosphines do shift the C(2) signals to low field as compared to those of the mercury compounds. For compounds **5** and **6** all the pyridyl protons except H(3) and carbons undergo low-field shifts.

The ^{31}P NMR spectra of the silver(I) complexes show single peaks at positions different from the ligand peaks. The lack of coupling from ^{107}Ag/^{109}Ag {^{107}Ag, abundance 51.35%, $I = 1/2$; ^{109}Ag, abundance, 48.65%, $I = 1/2$} suggests fast equilibrium between co-ordinated and dissociated phosphines. The co-ordination shifts ($\Delta\delta P = \delta_{complex} - \delta_{ligand}$) for **1**, **2**, **3** and **4** are 36.7, 19.0, 19.7 and 13.4 ppm respectively which shows that the binding of phosphine ligands to the Ag(C_5H_4NOS) moiety varies in the sequence: dppm > PPh_3 ≈ dppb > P(C_6H_4Me-*p*)$_3$. The binding of tertiary phosphines to Cu^I in analogous dimeric [{CuX(C_5H_5NS)L}$_2$] complexes [L = P(C_6H_4Me-*m*)$_3$ or P(C_6H_4Me-*p*)$_3$; X = Cl, Br or I] was also labile.[15]

Acknowledgements

One of us (S. P.) is grateful to the Guru Nanak Dev University for a research fellowship. We thank Professor J. S. Casas, University of Santiago, Spain for instrumental facilities, and to the referees for useful comments.

References

1 M. N. Hughes, *The Inorganic Chemistry of Biological Processes*, 2nd edn. Wiley, New York, 1972, p. 125; M. J. Stillman, A. Y. C. Law and J. A. Szymanska, in *Chemical Toxicology and Clinical Chemistry of Metals*, eds. S. S. Brown and J. Savoy, Academic Press, London, 1985, p. 275; H. C. Freeman, in *Coordination Chemistry-21*, ed. J. P. Laurent, Pergamon, New York, 1980, p. 29; L. Casella, M. Gullotti and R. Vigano, *Inorg. Chim. Acta*, 1988, **124**, 121; M. Gullotti, P. Casello, A. Pinter, E. Suardi, P. Zanello and S. Mangani, *J. Chem. Soc., Dalton Trans.*, 1989, 1979; H. Thomann, T. V. Morgan, H. Jin, S. J. N. Burmeister, R. Ebani and E. I. Steifel, *J. Am. Chem. Soc.*, 1983, **109**, 7913; E. Block, H. Y. Kang, G. Ofori-Okai and J. Zubieta, *Inorg. Chim. Acta*, 1989, **166**, 155; D. R. Haynes and M. N. Whitehouse, in *New Developments in Anti-Rheumatic Therapy*, eds. K. D. Rainsforth and G. P. Velo, Kluwer, Dordrecht, 1989, p. 207.

Published on 01 January 1999. Downloaded on 28/10/2014 23:55:58.

2 S. Fujieda, E. Tabata, A. Hatano and T. Osa, *Heterocycles*, 1981, **15**, 743; J. Dehand, J. Jordanov and J. P. Beck, *Chem. Biol. Interact.*, 1975, **11**, 605.
3 T. S. Lobana and P. K. Bhatia, *J. Sci. Ind. Res.*, 1989, **48**, 394 and refs. therein.
4 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
5 E. S. Raper, *Coord. Chem. Rev.*, 1994, **129**, 91.
6 E. S. Raper, *Coord. Chem. Rev.*, 1996, **153**, 199.
7 T. S. Lobana and S. Paul, *Transition Met. Chem.*, 1996, **21**, 300 and refs. therein.
8 T. S. Lobana and R. Singh, *Polyhedron*, 1995, **14**, 907.
9 T. S. Lobana and P. K. Bhatia, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 1407.
10 T. S. Lobana and P. K. Bhatia, *Indian J. Chem.*, *Sect. A*, 1990, **29**, 1225.
11 T. S. Lobana, P. K. Bhatia and E. R. T. Tiekink, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 749.
12 T. S. Lobana and P. K. Bhatia, *Indian J. Chem.*, *Sect A*, 1991, **30**, 877.
13 E. R. T. Tiekink, T. S. Lobana and R. Singh, *J. Cryst. Spectrosc. Res.*, 1991, **21**, 205.
14 E. Horn, T. S. Lobana, E. R. T. Tiekink and R. Singh, *Z. Kristallogr.*, 1993, **205**, 29.
15 T. S. Lobana, S. Paul and A. Castineiras, *Polyhedron*, 1997, **16**, 4023.
16 T. S. Lobana, R. Verma, R. Singh and A. Castineiras, *Transition Met. Chem.*, 1998, **23**, 25.
17 E. Block, D. Macherone, S. N. Shaikh and J. Zubieta, *Polyhedron*, 1990, **9**, 1429; J. Vicente, M. T. Chicote and C. Rubio, *Chem. Ber.*, 1996, **129**, 327; P. A. Perez-Lourido, J. A. Garcia-Vazquez, J. Romero, M. S. Louro, A. Sousa, Q. Chen, Y. Chang and J. Zubieta, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2047.
18 S. K. Hadjikakou, P. Aslanidis, P. Karagiannidis, A. Aubry and S. Skoulika, *Inorg. Chim. Acta*, 1992, **193**, 129; I. P. Evans and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 946; P. Karagiannidis, P. Aslanidis, S. Kokkou and C. J. Cheer, *Inorg. Chim. Acta*, 1990, **172**, 247.
19 G. Giusti, G. Geier, A. Currao and R. Nesper, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 1914; S. K. Hadjikakou, P. Aslanidis, P. D. Akrivos, P. Karagiannids, B. K. Prodic and M. Luic, *Inorg. Chim. Acta*, 1992, **197**, 31; P. D. Akrivos, S. K. Hadjikakou, P. Karagiannidis, M. Grdanic and S. Kosturkiewicz, *Polyhedron*, 1994, **13**, 753.
20 P. Aslanidis, P. Karagiannidis, P. D. Akrivos, B. Krebs and M. Lage, *Inorg. Chim. Acta*, 1997, **254**, 277.
21 G. F. de Sousa and C. A. L. Filgueiras, *Transition Met. Chem.*, 1990, **15**, 290; 286.
22 E. Block, M. Britto, M. Gernen, D. McGouety, H. Kang and J. Zubieta, *Inorg. Chem.*, 1990, **29**, 3172 and refs. therein.
23 A. Castineiras, W. Hiller and J. Strahle, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 1945.
24 (*a*) Part 9. T. S. Lobana, S. Paul, G. Hundal and S. Obrai, *Transition Met. Chem.*, 1999, **24**, 202; (*b*) R. A. Jones and A. R. Katritzky, *J. Chem. Soc.*, 1960, 2937.
25 R. E. Lessy and J. Y. Kim, *J. Am. Chem. Soc.*, 1960, **82**, 696.
26 G. B. Deacon and B. S. F. Taylor, *Aust. J. Chem.*, 1981, **34**, 301.
27 J. L. Wardell, in *Dictionary of Organometallic Compounds*, eds. S. A. Cotton, K. Smith and D. J. Cardin, Chapman and Hall, London, 1984, vol. 1, p. 1016.
28 B. V. Nonius, ENRAF-NONIUS, CAD4-Express Software, Version 5.1, Enraf-Nonius, Delft, 1995.
29 A. L. Spek, HELENA, A Program for data reduction of CAD4 data, University of Utrecht, 1997; M. Kretschmer, GENHKL, Program for the reduction of CAD4 Diffractometer data, University of Tuebingen, 1997.
30 A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, University of Utrecht, 1997; A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.
31 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.
32 G. M. Sheldrick, SHELXL 97, Program for the Refinement of Crystal Structures, University of Göttingen, 1997.
33 *International Tables for X-Ray Crystallography*, Kluwer, Dordrecht, 1995, vol. C.
34 L. Zsolnai, ZORTEP, A Program for the Presentation of Thermal Ellipsoids, University of Heidelberg, 1997.
35 T. S. Lobana, *Coord. Chem. Rev.*, 1985, **63**, 161.
36 B. L. Barnett, H. C. Kretschnar and F. A. Hartmen, *Inorg. Chem.*, 1977, **16**, 1834.
37 J. E. Huheey, E. A. Keiter and R. L. Keiter (Editors), *Inorganic Chemistry-Principles of Structure and Reactivity*, 4th edn., Harper Collins College Publishers, London, 1993.
38 T. S. Lobana, R. Verma and A. Castineiras, *Polyhedron*, 1998, **17**, 3753.
39 P. D. Cookson and E. R. T. Tiekink, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 259.
40 J. C. Shi, T. B. Wen, Y. Zheng, S. J. Zhong, D. X. Wu, Q. T. Liu, B. S. Kang, B. M. Wu and T. C. W. Mak, *Polyhedron*, 1997, **16**, 369.

Paper 9/00405J