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FULL PAPER

Dimethylthiophosphoryl hydrazone ligands and their copper complexes: crystal structures and analysis of their solution complexation behaviour by electrospray mass spectrometry

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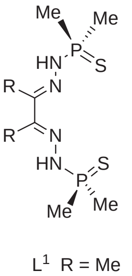
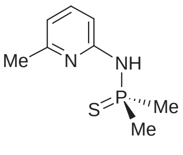
Four new thiophosphoryl ligands containing NNPS or CNPS connectivities have been prepared and three of them characterised by single-crystal X-ray diffraction. The complexation of these ligands with salts of Cu^{I}, Cu^{II}, Ni^{II} and Zn^{II} has been studied by electrospray mass spectrometry and uv-visible spectrophotometry in acetonitrile and methanol solution. Evidence for 1 : 1 and 2 : 1 complexation is presented. Two copper(I) complexes were isolated including a mixed chloride–bromide copper(I) complex in which a dimeric structure is adopted with a 22-membered metallacycle.

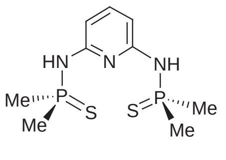
The incorporation of phosphorus-containing donors within hydrazine and hydrazide ligands has been reported in the development of new ligand systems for the co-ordination of transition metals.[1] Many of these ligands possess P–N–N–P or N–N–P–N–N connectivities and some of these systems with P=S donors have been explored[2] for the complexation of ^{99m}Tc or used as ligands in complexes with Pd^{II}, Cu^{I} and Co^{I}.[3] Thiophosphorylamide ligands themselves have been studied for well over 30 years, and sterically demanding systems with an SPNPS connectivity have attracted considerable attention,[4] in view of the tendency of nickel(II) and zinc(II) complexes to form well defined ML_2 complexes, involving tetrahedral S_4 ligation.[5] Given our recent interest in developing the co-ordination chemistry of azaphosphinate[6] and tetradentate azathiaphosphinate ligands,[7] we were attracted by the structures of the azathiaphosphoryl ligands L^1–L^4 with a view to exploring their co-ordination chemistry in ML and ML_2 complexes. An added impetus for this exploratory study was the structural resemblance of L^1 and L^2 to the 1,2-dicarbonyl-derived thiosemicarbazone ligands 'PTSM' and 'ATSM', which are being used experimentally as perfusion tracers in positron emission tomography as their readily reduced complexes of $^{62}Cu^{II}$ (^{62}Cu: β^+, $t_{\frac{1}{2}}$ 9.8 min).[8]



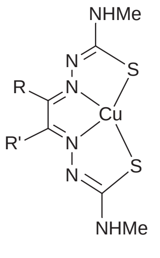
L^1 R = Me
L^2 R = Ph



L^3



L^4



R = Me, R' = H (Cu^{II}-PTSM)
R = Me = R' (Cu^{II}-ATSM)

Ligand synthesis and structure

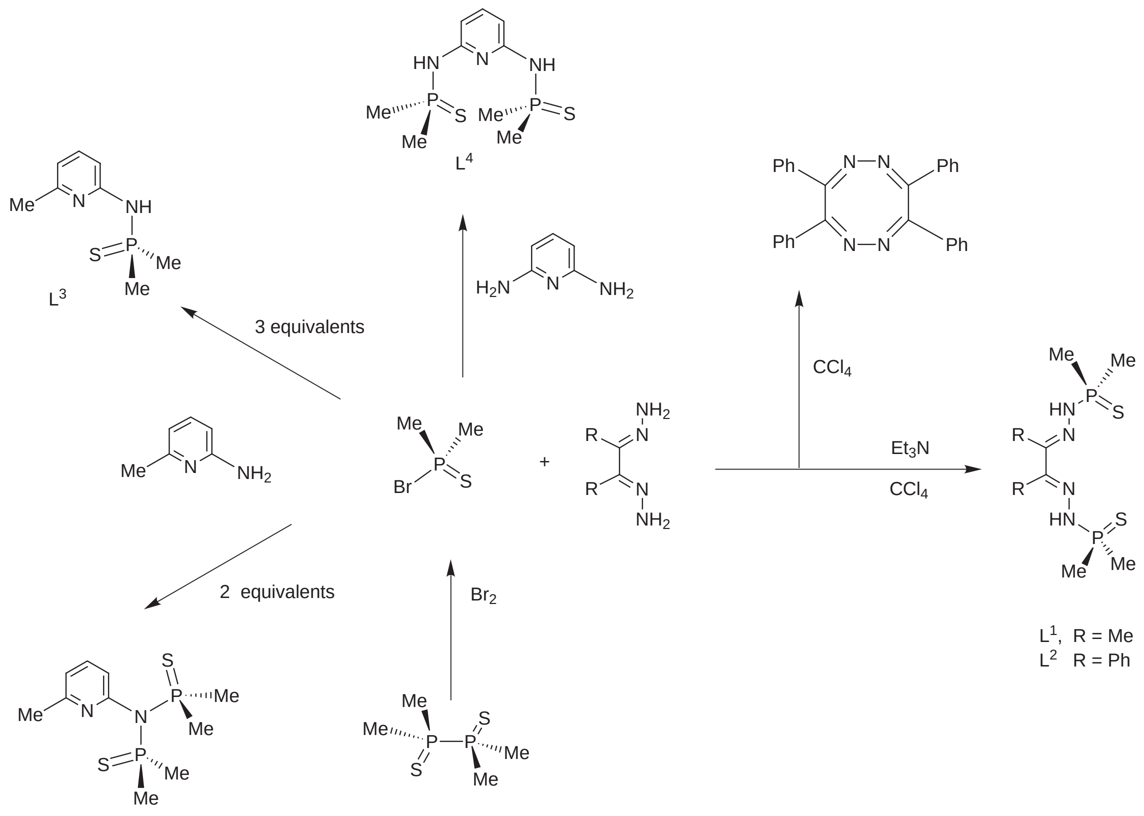
The general approach to ligands of the type L^1 to L^4 that was considered first involved an attack of a dialkylthiophosphoryl bromide on the appropriate hydrazine or primary amine. The precursor $Me_2P(S)Br$, may be prepared by cleavage of tetramethyldiphosphine disulfide with molecular bromine at −15 °C.[9,10] Reaction of $Me_2P(S)Br$ in CCl_4 with the appropriate dihydrazone, prepared following Cope's general procedure,[11] in the presence of Et_3N gave the desired ligands L^1 and L^2 in good yield (Scheme 1). In the absence of a base, the reaction with benzil dihydrazone unexpectedly led to formation of a mixture of products including an eight-membered tetrazocine ring (Scheme 1), the formation of which is well defined from the more obvious and established condensation reaction of benzil dihydrazone with benzil itself.[12]

Reaction of $Me_2P(S)Br$ with 3 equivalents of 2-amino-6-methylpyridine gave L^3 in 82% yield after crystallisation: reducing the amount of the aminopyridine gave rise to concomitant formation of the N,N-disubstituted ligand 6-$MeC_5H_3N\{N[PMe_2(S)]_2\text{-}2\}$, which was identified by ESMS, ^1H and ^{31}P NMR but was not isolated. The tridentate ligand L^4 was prepared in the same way.

Crystal structures of L^1, L^2 and L^3

Crystals suitable for analysis by X-ray diffraction of the ligands L^1, L^2 and L^3 were obtained from diethyl ether by slow evaporation. Compounds L^1 and L^2 contain the same $S{=}P(Me_2)$-$NHN{=}C{-}C{=}NNHP(Me_2){=}S$ backbone and differ only in the substituents at the central carbon atoms. In each case the amino N atoms have planar (sp^2) bonding geometry within experimental error. However, the molecular conformations are quite different. The molecule L^1 possesses a crystallographic inversion centre (Fig. 1). All non-H atoms (save the phosphorus-bound methyl carbons) are coplanar, with the maximum deviation from the plane being 0.07 Å and the mean one 0.03 Å. In L^2 the backbone adopts a 'curled' conformation (Fig. 2) being twisted by *ca.* 72° around the central C(1)–C(2) bond and by a smaller degree around other single bonds (see Table 1). The phenyl rings at C(1) and C(2) form dihedral angles of 11 and 19° with the planes of adjacent C=N bonds.

Comparison of the bond lengths in L^1 and L^2 (Table 1) reveals small but significant differences indicative of greater π conjugation along the chain in L^1, particularly the shortening



Scheme 1

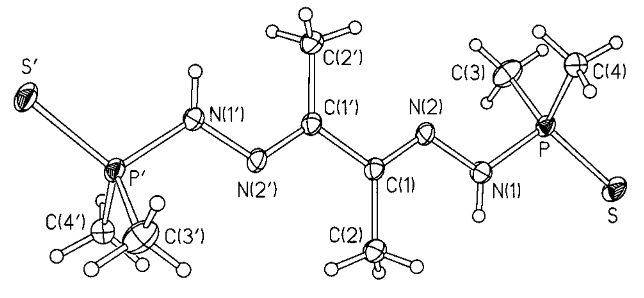


Fig. 1 Molecular structure of L^1 showing 50% probability ellipsoids. Primed atoms are symmetrically related *via* the inversion centre.

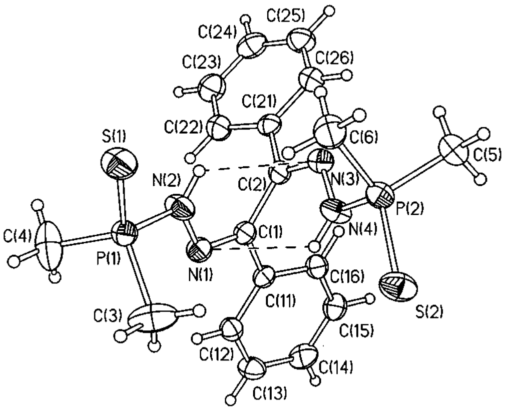


Fig. 2 Molecular structure of L^2 showing 50% probability ellipsoids and intramolecular H $\cdots$ N contacts.

of the central C–C bond by *ca.* 0.03 Å. The bulkiness of the phenyl substituents is not sufficient to explain the change of conformation, as a *trans* disposition of the phenyl groups around the C(1)–C(2) bond (as with the methyls in L^1) would not produce substantial (intramolecular) steric strain.

The absence of significant hydrogen bonding in both L^1 and L^2 is noteworthy. In L^2 the intramolecular contacts N(2)–H $\cdots$ N(3) and N(4)–H $\cdots$ N(1) exhibit H $\cdots$ N distances of 2.55(2) and 2.53(2) Å (somewhat shorter than the sum of van der Waals radii,[13] 2.74 Å) and N–H–N angles of 116(2) and 119(2)°. They cannot be regarded as hydrogen bonds, since the directions of the contacts do not correspond to the lone pair sites of N(1) and N(3). In L^1 the only intermolecular N(1)–H $\cdots$ S contact of 2.90 Å is equal to the sum of van der Waals radii (H, 1.10 + S, 1.81 Å).[13]

Molecule L^3 (Fig. 3) contains a roughly planar S=P–NH–pyridyl system. Inversion-related molecules are linked by N(2)–H $\cdots$ S′ hydrogen bonds, lying practically in the same plane. The H $\cdots$ S distance of 2.54(2) Å (for the normalised H position) is common for N–H $\cdots$ S=C bonds (2.28–2.72, mean 2.46 Å),[14] while the PS $\cdots$ H angle of 120(1)° is wider than CS $\cdots$ H (angles usually are 98–114°), although it corresponds well to the lone pair direction of the sulfur atom.

The P–S bond lengths in $R_3P{=}S$ molecules average 1.954(5) Å, but are contracted to an average of 1.922(14) Å if one of the carbon substituents (R) at the phosphorus atom is replaced by a more electronegative O or N group.[15] Particularly, in the $Me_2(RNH)P{=}S$ moieties, the P–S distance is 1.940 Å in the absence of hydrogen bonds, but can increase to 1.949–1.962 Å when the sulfur atom is engaged in such bonds.[16] Our results are in good agreement with the earlier data: P–S distances average 1.941 Å in L^1 where sulfur atoms accept no hydrogen bonds compared to 1.966 Å in L^3 with a strong hydrogen bond.

Preliminary assessment of solution complexation by electrospray mass spectrometry

The use of electrospray mass spectroscopy in the qualitative investigation of the solution speciation of metal complexes has attracted considerable recent attention.[17–20] Samples were prepared in dry acetonitrile using equimolar mixtures of $[Cu^I(MeCN)_4]BF_4$ or $Cu(ClO_4)_2$, and were examined in positive ion mode in the presence of dry methanol. With L^1 and copper(II) perchlorate a single species was observed at *m*/*z* 359.94 corresponding very closely to the theoretical isotope model for

Table 1 Selected bond distances (Å), bond and torsion angles (°) for L^1, L^2, L^3 and complex **1**

L^1			
P–S	1.955(1)	P–N(1)	1.676(1)
N(1)–N(2)	1.382(1)	C(1)–N(2)	1.296(2)
C(1)–C(1′)	1.478(2)	P–C mean	1.801(2)
L^2			
P(1)–S(1)	1.935(1)	P(2)–S(2)	1.947(1)
P(1)–N(2)	1.680(2)	P(2)–N(4)	1.689(2)
N(1)–N(2)	1.376(2)	N(3)–N(4)	1.380(2)
C(1)–N(1)	1.292(2)	C(2)–N(3)	1.291(2)
C(1)–C(2)	1.506(2)	P–C mean	1.786(5)
N(4)···N(1)	3.156(2)	N(2)···N(3)	3.139(2)
N(1)–C(1)–C(2)–N(3)	71.9(2)		
S(1)–P(1)–N(2)–N(1)	167.4(1)	N(3)–N(4)–P(2)–S(2)	−177.1(1)
P(1)–N(2)–N(1)–C(1)	−168.7(1)	C(2)–N(3)–N(4)–P(2)	−165.6(1)
L^3			
P–S	1.966(1)	P–N(2)	1.677(1)
C(2)–N(2)	1.400(2)	P–C mean	1.798(2)
N(2)···S′	3.544(2)		
N(2)–H(2)···S′	166(1)		
S–P–N(2)–C(2)	176.2(1)	P–N(2)–C(2)–N(1)	7.2(2)
1			
Cu–S(1)	2.270(1)	Cu–S(2′)	2.265(1)
Cu–Cl/Br	2.293(2)	C(1)–C(2)	1.485(4)
P(1)–S(1)	1.988(1)	P(2)–S(2)	1.997(1)
P(1)–N(1)	1.678(2)	P(2)–N(4)	1.685(2)
N(1)–N(2)	1.386(3)	N(3)–N(4)	1.398(3)
C(1)–N(2)	1.296(3)	C(2)–N(3)	1.296(3)
S(1)–Cu–S(2′)	117.45(3)		
S(1)–Cu–Cl/Br	117.75(3)	S(2′)–Cu–Cl/Br	124.33(3)
S(1)–P(1)–N(1)–N(2)	−151.5(1)	N(3)–N(4)–P(2)–S(2)	−70.1(1)
P(1)–N(1)–N(2)–C(1)	−168.1(1)	P(2)–N(4)–N(3)–C(2)	153.9(1)

$[Cu(L^1 - H)]^+$ ($C_8H_{19}CuN_4P_2S_2$ requires *m*/*z* 359.98). Using the copper(I) salt, as the source of copper, the only species observed (100 V core voltage) was at *m*/*z* 360.78, corresponding well to $C_8H_{20}CuN_4P_2$, *i.e.* $[CuL^1]^+$ (Calc. *m*/*z* 360.99). With $Ni(ClO_4)_2$ a strong signal was observed for $[NiL^1 - H]^+$, but with $Zn(ClO_4)_2$ several species were identified including $[ZnL^1(L^1 - H)]^+$.

Under the experimental conditions, copper may form monopositive 1:1 complexes with L^1 in both the monovalent and divalent state, in the latter case by loss of one of the ligand NH protons. With the C-phenyl analogue, L^2, addition of $Cu(ClO_4)_2$ gave rise to species at *m*/*z* 484.74 and 906.27, corresponding to $[ML]^+$ and $[ML_2]^+$ formation. The isotope pattern at lower mass showed peaks separated by one mass unit and corresponded to formation of a 1:1 copper(I) complex ($C_{18}H_{24}CuN_4P_2S_2{}^+$ requires *m*/*z* 485.02). The higher mass pattern corresponds to the loss of one ligand proton, suggesting that it may be due to a copper(II) complex. Complexation with zinc produced a similar result and $[Zn(L^2 - H)]^+$ and $[ZnL^2(L^2 - H)]^+$ species were observed, but in addition a $[ZnL^2(ClO)_4]^+$ species was found and a doubly charged $[ZnL^2]^{2+}$ species at half-mass (*i.e.* with non-integral isotope separations). Complexes of nickel produced similar spectra to those of zinc, with $[NiL^2]^+$, $[NiL^2(L^2 - H)]^+$ and $[NiL^2]^{2+}$ species dominant.

With the bidentate ligand L^3 separate sets of experiments were carried out with 1:1 and 2:1 ligand to metal ion ratios. With $Cu(ClO_4)_2$, at both 2:1 and 1:1 stoichiometry, an $[ML_2]$ species dominated the spectrum, in addition to some [ML] and the protonated ligand. The $[CuL^3]^+$ and $[Cu(L^3)_2]^+$ species at *m*/*z* 262.98 and 462.95 were consistent with the loss of ligand protons in neither species, suggesting that copper(I) complexes had formed. With both nickel and zinc the major species observed at 2:1 stoichiometry was the protonated ligand, and at a 1:1 ratio this species was also dominant. A much less intense (≤20%) peak of an $[ML^3(L^3 - H)]^+$ species was conspicuous in each case, with the nickel complex twice as intense as the corresponding zinc one.

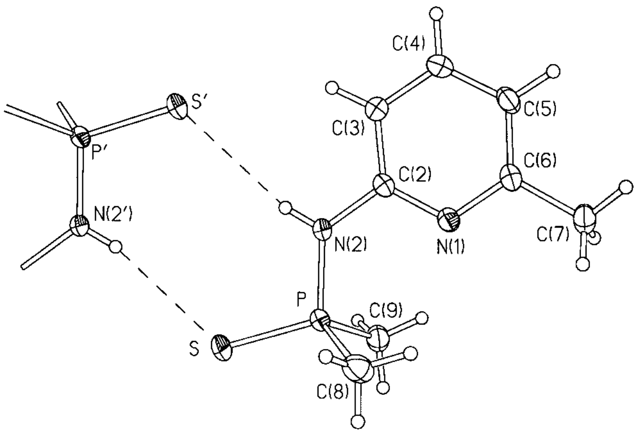


Fig. 3 Molecular structure of L^3 showing 50% probability ellipsoids and hydrogen bonds with an inversion related molecule (primed atoms).

Using the tridentate NS_2 ligand L^4, addition of copper(II) perchlorate gave a simple mass spectrum (*m*/*z* 355.8 and 357.75 in 2:1 ratio) showing only formation of a 1:1 complex of copper(I). Analysis of the spectra of the corresponding nickel and zinc perchlorate complexes revealed that several species were present including $[M(L^4 - H)]^+$, $[M(L^4 - H)(ClO)_4]^+$, $[ML^4(L^4 - H)]^+$ and $[M(L^4)_2(ClO)_4]^+$. In this case, as with copper complexes of L^1–L^3, it is unclear if reduction to a copper(I) species occurred prior to mass spectral study or during the ionisation process. Accordingly, the copper complexes were examined further by uv-visible spectral analysis.

Spectrophotometric studies of copper complexes

Ultraviolet and visible spectra of ligands L^1 to L^4 were recorded in acetonitrile in the absence and presence of $[Cu(MeCN)_4]BF_4$ and anhydrous $Cu(CF_3SO_3)_2$. Comparison of the results in the presence of added copper-(II) and -(I) salt (Table 2) reveals that only L^1 forms a well defined copper(II) complex (λ_{max}^{d-d} = 636 nm; ε = 210 dm³ mol⁻¹ cm⁻¹) while in the presence of L^2, L^3 and L^4 the metal ion is reduced and a copper(I) complex is formed. Direct addition of the copper(I) tetraacetonitrile complex to L^2, L^3 and L^4 gives rise to a species with identical spectral characteristics. In contrast, addition of Cu^I and Cu^{II} to L^1 yields the corresponding ligated complexes of Cu^I and Cu^{II}. In the latter case there is a strong LMCT band at 392 nm, and in the former a relatively intense MLCT band at 430 nm responsible for the observed yellow colour in solution. The copper(I) complex was isolated as an analytically pure orange solid and characterised as a neutral complex, $[Cu(L^1 - H)]$, formed by monodeprotonation of the ligand. It gave identical ESMS and spectrophotometric data to those of the same complex prepared *in situ* and discussed above.

The complexes formed in solution between L^1–L^4 and copper(II) triflate were also examined in MeOH. With L^1 a dark green solution was observed again (λ_{max} 638, ε 150 dm³ mol⁻¹ cm⁻¹) while with L^2, L^3 and L^4 there was no sign of this d–d band, consistent with reduction to a copper(I) complex. The only significant difference was with L^2, for which an extra charge transfer band at 404 nm (ε = 180 dm³ mol⁻¹ cm⁻¹) was identified which may be related to the enhanced stabilisation of the charge-transfer state by the protic solvent.

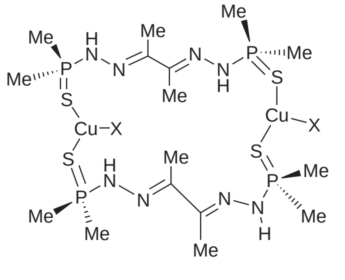
Isolation of $[Cu_2(L^1)_2Cl_{2-x}Br_x]$ 1 and X-ray analysis

Repeated attempts to isolate crystals of the copper complexes of L^1, L^2 and L^3 with triflate and tetrafluoroborate counter ions

Table 2 Spectral details of ligands L^1 to L^4 in MeCN and in the presence of 1 equivalent of $[Cu(MeCN)_4]BF_4$ or $Cu(CF_3SO_3)_2$

Ligand or complex	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
L^1	274	3.1×10^4
L^2	276	3.1×10^4
L^3	232	1.1×10^4
	286	6.3×10^3
L^4	244	7.5×10^3
	300	6.0×10^3
$L^1 + Cu^{II}$	206	1.96×10^4
	302	1.25×10^4
	392	4.7×10^3
	636	2.1×10^2
$L^2 + Cu^{II}$	208	shoulder
	280	7.8×10^4
$L^3 + Cu^{II}$	232	4.9×10^4
	286	1.5×10^4
$L^4 + Cu^{II}$	240	shoulder
	302	8.8×10^3
$L^1 + Cu^{I}$	204	4×10^4
	274	3.5×10^4
	430	2.0×10^3
$L^2 + Cu^{I}$	280	7.8×10^4
$L^3 + Cu^{I}$	232	1.85×10^4
	286	6.25×10^4
$L^4 + Cu^{I}$	240	1.84×10^4
	302	1.2×10^4

were unsuccessful. However when an acetonitrile solution of $[Cu(L^1 - H)]$ was inadvertently exposed to HCl/HBr vapour it slowly lost its very pale yellow colour and deposited colourless crystals [λ_{abs} (MeCN) = 274 nm with no 430 nm band; δ_P 66.0 (CD_3CN); δ_H 1.91 (24 H, d, J = 10.7 Hz, PMe), 1.97 (6 H, s, CMe overlapping with solvent), 2.05 (6 H, s, CMe)]. A solution of this solid complex in MeCN was stable for at least 2 months in dry acetonitrile, but decomposed fairly rapidly in the presence of water or methanol. Analysis of an aged (24 h) solution containing MeOH or water by ^{31}P NMR revealed a loss of the original peak (P=S) and appearance of 2 peaks at δ 59.0 and 32.1 consistent with hydrolysis of one of the phosphorus–sulfur bonds. Such a reaction may be mediated by the metal acting as a charge sink, facilitating attack at phosphorus by a water molecule, leading to the formation of a P=O bond. At the same time the band at 274 nm disappeared to be replaced by a new band at 230 nm. An electrospray mass spectrum of a fresh sample in CD_3CN revealed a relatively intense peak of a singly charged species clustered around *m*/*z* 862 {corresponding to $[Cu_2Cl_4(L^1 - H)]^+$} with a daughter peak at *m*/*z* 800. The peaks both disappeared slowly following addition of water or MeOH.



1 X = Cl, Br

Complex **1** was characterised by a single-crystal structure analysis. The 2:2 dimer molecule (Fig. 4, Tables 1 and 3) possesses crystallographic C_i symmetry. Each copper(I) centre is co-ordinated in a trigonal-planar fashion by two sulfur atoms from different L^1 ligands and a chloride ligand, which is in part isomorphously substituted by bromide. Thus the molecule contains an unusual 22-membered ring, stabilised by two transannular N(1)–H···Cl(Br) hydrogen bonds. The central N(1)N(2)=C(1)C(2)=N(3)N(4) system of the L^1 ligand adopts an essentially planar, all-*trans*, conformation, as in unco-ordinated L^1 (see above). However, the P=S bonds are no longer coplanar with this moiety, but are tilted out of its plane to the same side. The methyl substituents at C(1) and C(2) are no longer equivalent, the former pointing into the molecular cavity and the latter outwards. Co-ordination with Cu^I results in a lengthening of the P=S bonds by *ca.* 0.04 Å, but other bond distances change insignificantly. There is only one other structurally characterised metal complex of a ligand that incorporates the NNPS sub-unit,[21] which involves a sulfur bridged copper dimer. There are, however, several examples of heterocyclic compounds with such a constitution.[22]

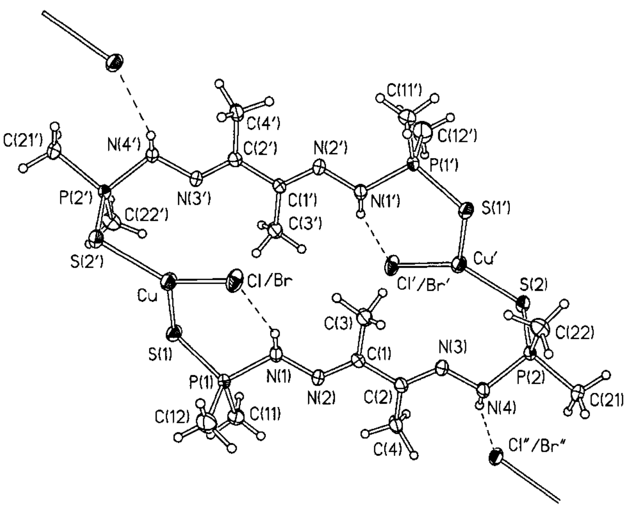


Fig. 4 Molecular structure of complex **1**, showing 50% probability ellipsoids and hydrogen bonds. Primed atoms are related *via* an inversion centre, double primed *via* a 2_1 axis.

The N(4)–H groups, pointing outward, form hydrogen bonds with the halogenide ligands of adjacent molecules, symmetrically related *via* a 2_1 axis, giving rise to a layered molecular packing. The H···Cl(Br) distances (2.37 Å for the intramolecular and 2.48 Å for the intermolecular bonds) are comparable with the average H···Cl (2.22 Å) and H···Br (2.39 Å) hydrogen bond lengths.[23]

In solution, this isolated halogenocopper(I) dimer behaved quite differently to the complexes prepared in the presence of the non-co-ordinating triflate or perchlorate anions: such differences are often encountered in the co-ordination chemistry of relatively weakly binding ligands, such as those described herein.

Experimental

General procedures and instrumentation have been reported recently.[6,20] Dimethylthiophosphinic bromide was prepared according to the literature method,[9,10] mp 33–34 °C (lit.,[10] 34 °C), and the hydrazones of butane-2,3-dione[24] and benzil[11] were prepared following Cope's original procedure[11] as analytically pure samples.

Electrospray mass spectrometry

Electrospray mass spectra were obtained using a VG-Platform II (Fisons Instruments), with a capillary voltage of 4 kV and a source temperature of 60 °C. Cone voltages and analyte concentrations were varied according to the nature of the experiment, but were typically 40 to 60 V and 10^{-5} to 10^{-6} M respectively. The solvent flow was maintained using a Hewlett Packard HPLC instrument that was directly linked to the mass spectrometer. The sample was inserted into the flow using an injection valve with a 10 µL steel loop and transported to the electrospray capillary through a silica tube.

Major ions are quoted as a percentage of the base peak intensity and isotope patterns were modelled using Mass lynx software. Typically, a stock solution of the ligand was prepared (*ca.* 0.3 mM) in freshly distilled dry methanol (Aristar grade, BDH) and stock solutions of the dried metal trifluoromethanesulfonate or perchlorate (**CAUTION**: hazard) salts (*ca.* 1.0 mM) also prepared in dry methanol. Samples were prepared in polypropylene Eppendorf vials and transferred using Gilson Pipetman micropipettes. To a sample of the ligand solution (1 ml) and methanol (1 ml) was added the appropriate volume of the metal triflate/perchlorate salt, to make a 1:1 or 1:2 metal:ligand ratio. A 10 µL sample of this solution was injected and mass spectra recorded in positive or negative ion mode, as stated.

Preparations

Butane-2,3-dione bis[(dimethylthiophosphoryl)hydrazone] L^1. To a solution of $Me_2P(S)Br$ (27.6 mmol) in carbon tetrachloride (10 ml), butane-2,3-dione dihydrazone (1.5 g, 13.2 mmol) and triethylamine (3 g, 30 mmol) were added. The reaction mixture was stirred under an inert atmosphere for 15 h. A yellow precipitate formed which was isolated by filtration and washed thoroughly with water to remove the triethylamine salts. The pale yellow solid was dried *in vacuo* (3.5 g, 89%); mp > 250 °C; δ_P ($CDCl_3$) 65.43; δ_H ($CDCl_3$) 1.92 [12 H, d, ^2J_P = 13.5 Hz, $P(CH_3)_2$], 1.98 (6 H, s, CH_3C) and 5.99 (2 H, d, ^2J = 21 Hz, PNHN); δ_C ($CDCl_3$) 9.93 (C–CH$_3$), 22.64 [d, ^1J = 68 Hz, $P(S)(CH_3)_2$] and 148.30 (s, CH_3–*C*=NNP); *m*/*z* (EI$^+$) 298 (20, M$^+$) and 205 [100%, M − $P(S)(CH_3)_2$]; ν_{max} 3270 br (NH), 1580, 1410–1400, 1375, 1350, 1290, 1280, 1060s, 940, 900, 850, 730, 630 and 580 cm^{-1} (Found: C, 31.8; H, 6.67; N, 18.3%. $C_4H_{10}N_2PS$ requires C, 32.2; H, 6.76; N, 18.8%); λ_{max}(MeCN) 274 nm ($\varepsilon = 3.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

1,2-Diphenylethane-1,2-dione bis[(dimethylthiophosphoryl)-hydrazone] L^2. To a solution of dimethylthiophosphinic bromide, (2.9 mmol) in carbon tetrachloride (10 ml), benzil dihydrazone (328 mg, 1.4 mmol) and triethylamine (0.42 ml, 3.03 mmol) were added. The reaction mixture was stirred under an inert atmosphere for 15 h and yielded a white precipitate. The solid was removed by filtration and the solvent evaporated from the mother-liquor under reduced pressure to leave an orange oil. This was triturated with diethyl ether and dark yellow crystals formed (4.0 g, 70%). If crystals did not form easily, the ether solution was, instead, washed with water (3 × 30 ml), dried (Na_2SO_4) and the solvent removed under reduced pressure to give the pale orange solid product, mp 164–167 °C; δ_P ($CDCl_3$) 66.71; δ_H ($CDCl_3$) 2.05 [12 H, d+d, ^2J_P = 12, $P(S)(CH_3)_2$], 6.15 (2 H, d, ^2J_P = 21.5 Hz, PNHN), 7.26–7.37 (6 H, m, *m*-, *p*-H of Ph) and 7.51–7.55 (4 H, m, *o*-H of Ph); δ_C ($CDCl_3$) 22.71 [d, ^1J_P = 68, $P(S)(CH_3)_2$], 23.20 [d, ^1J_P = 68, $P(S)(CH_3)_2$], 126.52 (*m*-C of Ph), 129.74 (*o*-C of Ph), 130.88 (*p*-C of Ph), 133.53 (PPh) and 143.00 (d, ^3J = 14.5 Hz, Ph-*C*=NNH); *m*/*z* (ESMS$^+$, MeOH) 423.07 (100%, M + H$^+$); ν_{max} (KBr) 3290, 1440, 1380, 1290, 1125, 1060, 1035, 1010, 990, 950, 910, 860, 740s, 670s and 600s cm^{-1} (Found: C, 51.3; H, 5.78; N, 13.0. $C_9H_{12}N_2PS$ requires C, 51.2; H, 5.73; N, 13.3%); λ_{max} (MeCN) 276 nm ($\varepsilon = 3.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}).

2-(Dimethylthiophosphorylamino)-6-methylpyridine L^3. To a solution of $Me_2P(S)Br$ (5.46 mmol) in carbon tetrachloride (50 ml) was added 2-amino-6-methylpyridine (1.78 g, 16.4 mmol) and the resultant solution stirred for 5 h at room temperature under an inert atmosphere. A white precipitate formed, was isolated by filtration and then washed thoroughly with cold diethyl ether. White crystals formed in the ether layer which were isolated by filtration and dried *in vacuo* (0.9 g, 82%); mp 138–140 °C; δ_P ($CDCl_3$) 59.96; δ_H ($CDCl_3$) 2.17 [6 H, d, ^2J_P = 14, $PS(CH_3)_2$], 2.41 (3 H, s, CH_3 of py), 5.14 (1 H, br s, NH), 6.41 [1 H, d, ^3J = 8, H(3) of py], 6.68 [1 H, d, ^3J = 7.5, H(4) of py] and 7.41 (1 H, t, ^3J = 8 Hz); δ_C ($CDCl_3$) 23.53 (d, ^1J_P = 68 Hz, PCH_3), 24.74 (s, CH_3), 130.81, 131.31, 131.82, 162.17 and 169.65. ν_{max} 3280 (aryl H), 1600 (aryl H), 1570, 1450–1370, 1280s, 950s, 910–860, 780, 740s, 700, 580 and 530 cm^{-1}; *m*/*z* (DCI) 201 (100, M + H$^+$) and 185 (5%, M − CH_3) (Found: C, 47.6; H, 6.50; N, 13.80. $C_8H_{13}N_2PS$ requires C, 48.0; H, 6.54; N, 14.0%). λ_{max} (MeCN) 232 ($\varepsilon = 1.6 \times 10^4$) and 286 nm ($\varepsilon = 6.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}).

2,6-Bis(dimethylthiophosphorylamino)pyridine L^4. To a stirred solution of $Me_2P(S)Br$ (4.28 mmol) in carbon tetrachloride (15 ml) 2,6-diaminopyridine (110 mg, 1.02 mmol) and triethylamine (0.31 ml, 2.24 mmol) were added and the reaction mixture was stirred for 16 h at room temperature under an inert atmosphere. A white precipitate formed which was isolated by filtration, washed with water and dried *in vacuo* (0.75 g, 60%); mp 201–203 °C (decomp.); δ_P ($CDCl_3$) 56.99; δ_H ($CDCl_3$) 2.14 [12 H, d, ^2J = 13.7, $P(CH_3)_2$], 5.19 (2 H, d, ^2J_P = 5.5, NH), 6.31 [2 H, d, ^3J = 8, H(3), H(5) of py], 7.43 [1 H, t, ^3J = 8 Hz, H(4) of py]; δ_C ($CDCl_3$) 24.06 [d, ^1J_P = 68, $P(CH_3)_2$], 104.42 [d, ^2J_P = 4.5 Hz, C(3) and C(5) of py], 140.92 [C(4) of py] and 153.9 [C(2) and C(6) of py]; ν_{max} 3150 (aryl H), 1600s, 1580s, 1450s, 1400, 1290, 1210, 1160, 1040, 950–930, 890, 790s, 720s, 650 and 580 cm^{-1}; *m*/*z* (DCI) 294 (100, M + H$^+$) and 202 [20%, M − P(S)Me$_2$ + 2H$^+$] (Found: C, 36.1; H, 5.81; N, 14.17. $C_9H_{17}N_3P_2S_2\cdot$ 0.5H_2O requires C, 35.8; H, 6.00; N, 13.90%); λ_{max} (MeCN) 244 (ε 7.5 × 10^3) and 300 nm (ε 6 × 10^3 dm^3 mol^{-1} cm^{-1}).

{Butane-2,3-dione bis[(dimethylthiophosphoryl)hydrazonato]}copper(I) [Cu(L^1 − H)]. To a solution of tetrakis(acetonitrile)copper(I) tetrafluoroborate (295 mg, 0.94 mmol) in acetonitrile (35 ml) a solution of L^1 (280 mg, 0.94 mmol) in dichloromethane (30 ml) was added. After stirring the deep orange solution a precipitate formed which was isolated by centrifugation, washed with acetonitrile (2 × 10 ml) and dried *in vacuo* to give an orange solid (350 g, 85%); δ_P (CD_3CN) 66.74; *m*/*z* (ESMS$^+$, MeOH) 360.82 (CuL$^+$) (Found: C, 26.5, H, 5.47; N, 15.1. $C_8H_{19}CuN_4P_2S_2$ requires C, 26.6; H, 5.30; N, 15.5%); λ_{max} (MeCN) 274 (ε 3.5 × 10^4) and 430 mn (2.0 × 10^3 dm^3 mol^{-1} cm^{-1}).

A solution of this complex in acetonitrile slowly lost its colour on exposure to an atmosphere of HCl/HBr vapour, and colourless crystals of the dimer **1** were deposited over 18 h: λ (MeCN) 274 nm (no band at 430 nm); δ_P (CD_3CN) +66.0; δ_H (CD_3CN, 300 MHz, 293 K) 1.91 (24 H, d, *J* = 10.5 Hz, PMe), 1.97 (6 H, s, CMe) and 2.05 (6 H, s, CMe) (Found: C, 46.0; H, 9.31; N, 26.7. $C_{16}H_{40}Br_{0.5}Cl_{1.5}Cu_2N_8P_4S_4$ requires C, 46.2; H, 9.65; N, 27.0%).

{Butane-2,3-dione bis[(dimethylthiophosphoryl)hydrazone]-copper(II) bis(trifluoromethanesulfonate), [CuL^1][CF$_3$SO$_3$]$_2$. To a stirred solution of copper(II) triflate (120 mg, 0.34 mmol) in dry acetonitrile (7 ml) was added solid L^1 (100 mg, 0.34 mmol). The reaction mixture immediately turned deep green and was heated at 80 °C for 4 h then left to cool. Diethyl ether (15 ml) was added and the solution left to stand at −5 °C, however crystallisation did not occur over 48 h. The solvents were removed under reduced pressure to give a green oil. Crystallisation was attempted using tetrahydrofuran but no solid was formed although visible spectroscopy and mass spectral analysis confirmed the formation of the complex; *m*/*z* (ESMS$^+$, MeOH) 359.98 (100, M$^+$) and 362.02 (50%) corresponding to calculated copper isotope pattern; λ_{max} (MeCN) 206 (ε 1.96 × 10^4), 302 (1.25 × 10^4), (392 4.7 × 10^3) and 636 nm (210 dm^3 mol^{-1} cm^{-1}).

{1,2-Diphenylethane-1,2-dione bis[(dimethylthiophosphoryl)-hydrazone]}copper(I) tetrafluoroborate, [CuL^2]BF$_4$. To a solution of tetrakis(acetonitrile)copper(I) tetrafluoroborate (37 mg, 0.12 mmol) in acetonitrile (5 ml) was added a solution of L^2

Table 3 Crystal data for compounds L^1–L^3 and complex **1**

	L^2	L^1	L^3	**1**
Formula	$C_{18}H_{24}N_4P_2S$	$C_8H_{20}N_4P_2S_2$	$C_8H_{13}N_2PS$	$C_{16}H_{40}Br_{0.54}Cl_{1.46}Cu_2N_8P_4S_4$
Formula weight	422.5	298.3	200.2	415.1
Colour	Yellow	Orange	Colourless	Colourless
Crystal size/mm	0.3 × 0.5 × 0.5	0.15 × 0.2 × 0.4	0.2 × 0.3 × 0.4	0.1 × 0.35 × 0.35
T/K	150	120	150	150
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	9.588(1)	6.220(1)	11.415(1)	11.649(1)
b/Å	11.402(1)	12.146(1)	8.348(1)	15.064(1)
c/Å	11.620(1)	10.141(1)	11.983(1)	9.682(1)
α/°	69.43(1)			
β/°	87.11(1)	97.94(1)	114.54(1)	94.11(1)
γ/°	69.74(1)			
V/Å^3	1112.1(2)	758.8(2)	1038.7(2)	1694.7(2)
Z	2	4	4	4
D_c/g cm^{-3}	1.26	1.31	1.28	1.63
μ/cm^{-1}	3.9	5.5	4.2	27.5
Maximum 2θ/°	51	55	61	60
Data total, unique	4911, 3567	5381, 1718	8012, 2806	13814, 4588
R(int)	0.027	0.024	0.028	0.041
Transmission, minimum, maximum	0.828, 0.906	0.726, 0.843	0.857, 0.952	0.442, 0.787
Data observed, $I > 2\sigma(I)$	3319	1595	2425	4087
Number of variables	332	114	161	241
R(F, observed data)	0.032	0.025	0.033	0.039
wR(F^2, all data)	0.094	0.073	0.082	0.086
Goodness of fit	1.05	1.06	1.16	1.31
Maximum, minimum $\Delta\rho$/e Å^{-3}	0.26, −0.30	0.38, −0.27	0.35, −0.26	0.46, −0.44

(50 mg, 0.12 mmol) in acetonitrile (5 ml). After mixing, the yellow solution was cooled to −5 °C but crystallisation attempts were unsuccessful, even following the slow addition of diethyl ether. Visible spectroscopy and mass spectral analysis confirmed the formation of a copper(I) complex; m/z (ESMS$^+$, MeOH) 485.02 (Calc. for $[C_{18}H_{24}CuN_4P_2S_2]^+$ m/z 485.02 corresponding to the calculated isotope pattern); λ_{max} (MeCN) 280 nm (ε 7.8 × 10^4 dm^3 mol^{-1} cm^{-1}).

Crystal structure analyses

X-Ray diffraction experiments were carried out on a Siemens SMART 3-circle diffractometer with a CCD area detector, using graphite-monochromated Mo-Kα radiation ($\bar{\lambda}$ = 0.71073 Å) and a Cryostream open-flow cryostat. Crystal data and experimental parameters are listed in Table 3. Data were collected by scanning over a full hemisphere of reciprocal space in frames of 0.3° ω. Structures were solved by direct methods and refined by full matrix least squares against F^2 of all data, using SHELXTL software.[25] Absorption corrections were performed for L^1, L^2 and L^3 by a semiempirical method based on Laue equivalents and multiple measurements of strong reflections, using the SADABS program.[26] For complex **1**, crystal faces were indexed and the absorption correction was made by numerical integration. All non-H atoms were refined with anisotropic displacement parameters; all H atoms were located from the Fourier difference map and refined in isotropic approximation. Statistically disordered Cl and Br atoms were refined as a single atom with a mixed scattering factor; the contributions were refined to 27.2(3)% Br and 72.8(3)% Cl.

CCDC reference number 186/1271.

See http://www.rsc.org/suppdata/dt/1999/323 for crystallographic files in .cif format.

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