Reaction of anionic oxygen donors with the antitumour copper(II)–pyridine-2-carbaldehyde thiosemicarbazone (HL) system and the crystal structure of $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$†

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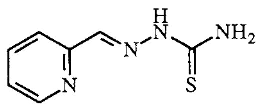
The complexes $[(CuL)_2(XO_4)]\cdot nH_2O$ (HL = pyridine-2-carbaldehyde thiosemicarbazone, X = HP, $n = 6$; X = Mo, $n = 1$), $[\{CuL(ptp)\}_2]\cdot 4H_2O$ (Hptp = *p*-tritylphenol) and $[\{CuL(tip)\}_2]$ (Htip = 2,4,6-triiodophenol) have been prepared from the reaction of aqueous solutions of $[\{CuL(CH_3CO_2)\}_2]$ with salts of the appropriate oxygen donor. Also prepared were $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot xH_3PO_4\cdot nH_2O$ ($x = 0$, $n = 3$; $x = 2$, $n = 2$) from the reaction of $[\{CuL(CH_3CO_2)\}_2]$ with 2 mol dm^{-3} H_3PO_4 and phosphate species (arising from the hydrolysis of 2 mol dm^{-3} HPF_6) respectively. The complexes have been characterized by a range of physicochemical techniques and the crystal and molecular structure of $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$ determined by single-crystal X-ray diffraction. The complex cation is a centrosymmetric dimer, the monomeric units having one-atom bridges from two $H_2PO_4^-$ anions. The copper atom has a distorted square-pyramidal geometry with three donor atoms (NNS) from the neutral, tridentate HL ligand and the fourth in-plane donor (an oxygen) from the bridging anion. The fifth position is occupied by a less strongly bound oxygen from the second bridging anion. An extensive hydrogen-bonding scheme involving the bridging $H_2PO_4^-$ anions, non-co-ordinated $H_2PO_4^-$ anions, H_3PO_4 moieties, water molecules and ligand exists with one very strong contact of 2.436 Å. These complexes may serve as simple models for the interaction of this antitumour system with oxygen donors.

Although the antitumour properties of the copper(II) pyridine-2-carbaldehyde thiosemicarbazone (HL) system have been recognized for some time,[1] its mode of action is still uncertain and it is only recently that Cu(HL) complexes have been structurally characterized.[2,3] In previous papers we have shown that in fact the Cu(HL) system is a remarkable vehicle for exploration of the co-ordination chemistry of a variety of anionic species and this may give a clue to how it exerts its biological activity.[2,4–7] The neutral ligand, HL, binds to the Cu^{2+} ion as a planar tridentate NNS entity (with the sulfur being formally a thione type) leaving a vacant equatorial site, as well as axial sites, on the metal. Hence we have characterized dinuclear sulfato[2] and trifluoroacetato[6] complexes, $[\{Cu(HL)(SO_4\}_2]$ and $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$ which contain bridging anions, as well as a mononuclear perchlorato[6] complex, $[Cu(HL)(H_2O)(ClO_4)_2]\cdot 2H_2O$. The HL ligand can also be deprotonated to give a further range of complexes, in which the sulfur may be regarded as being of the thiolato-type, *viz*. a mononuclear saccharinato[4] complex, $[CuL(C_7H_4NO_3S)(H_2O)]\cdot 0.5H_2O$, a dinuclear acetato[2] complex $[\{CuL(CH_3CO_2)\}_2]$, and a tetranuclear diphosphato[7] complex $[(CuL)_4(P_2O_7)]\cdot 12H_2O$. More recently Rojo and co-workers[8,9] have shown that the complex $[Cu(HL)Br_2]\cdot H_2O$ is monomeric and the related deprotonated ligand complexes $[\{CuL(X)\}_2]$ (X = Cl or Br) are dimers with sulfur-atom bridges.

In this paper we extend the range of anionic oxygen-donor ligands which interact with the copper(II) pyridine-2-carbaldehyde thiosemicarbazone system to include hydrogenphosphate, molybdate and phenolate ions. The crystal structure of one of the complexes, formulated as $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$ **3** is described. This is an unusual example of a ternary dihydrogenphosphato-metal complex and appears to be the first of its kind for Cu^{II}. As far as we are aware it is the first crystallographically studied example of a one-atom phosphato bridge of any type between copper. As well, it also contains three inequivalent phosphates, arising from the hydrolysis of hexafluorophosphoric acid, and an extensive hydrogen-bonding network with one very strong interaction between the $H_2PO_4^-$ and H_3PO_4 moieties of 2.436 Å.



HL

Experimental

Measurements

Microanalyses (Table 1), magnetic susceptibility, conductivity, IR, electronic and X-band ESR spectral measurements were carried out as previously described.[5]

Preparations

The compound HL was synthesized following a published procedure[10] as was the complex $[\{CuL(CH_3CO_2)\}_2]$.[2]

$[(CuL)_2(HPO_4)]\cdot 6H_2O$ 1. To a hot solution of $[\{CuL(CH_3CO_2)\}_2]$ (302 mg, 0.50 mmol) in water (60 cm^3) was added $Na_2HPO_4\cdot 12H_2O$ (500 mg, 1.40 mmol). The resulting green precipitate was washed with water and dried *in vacuo*. Yield: 178 mg (52%). IR (Nujol): $\tilde{\nu}(PO)/cm^{-1}$ 1115s, 1055m and 890m. ESR (powder at 110 K): $g_{iso} = 2.069$.

$[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 3H_2O$ 2. The complex $[\{CuL(CH_3CO_2)\}_2]$ (271 mg, 0.90 mmol) was dissolved in 2 mol dm^{-3} phosphoric acid (5 cm^3) with heating. After 1 d the resulting hygroscopic crystals were carefully dried by absorbing the excess of mixture onto filter-paper. Yield: 179 mg (43%). IR

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† Di-μ-dihydrogenphosphate-κ*O*-bis[(pyridine-2-carbaldehyde-κ*N* thiosemicarbazone-κ^2*N*′,*S*)copper(II)] bis(dihydrogenphosphate)–phosphoric acid–water (1/2/2).

Table 1 Colours, analytical and magnetic data for the complexes

Complex		Colour	Analyses (%)[a]			μ_{eff}[b]/μ_B
			C	H	N	
1	$[(CuL)_2(HPO_4)]\cdot 6H_2O$	Green	24.3 (24.4)	4.3 (4.0)	15.8[c] (16.3)	1.92
2	$[\{Cu(HL)(H_2PO_4)\}_2]$-$[H_2PO_4]_2\cdot 3H_2O$	Green	18.5 (18.1)	3.8 (3.6)	12.0[d] (12.1)	1.77
3	$[\{Cu(HL)(H_2PO_4)\}_2]$-$[H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$[e]	Dark green	14.4 (14.5)	3.5 (3.6)	9.8[f] (9.7)	1.84
4	$[\{CuL(ptp)\}_2]\cdot 4H_2O$	Green	62.7 (62.6)	4.7 (5.1)	9.4 (9.1)	1.89
5	$[\{CuL(tip)\}_2]$	Green	22.3 (21.9)	1.4 (1.3)	8.3 (7.9)	2.26
6	$[(CuL)_2(MoO_4)]\cdot H_2O$	Green	25.3 (25.3)	3.0 (2.4)	16.8[g] (16.9)	1.80

[a] Calculated values are given in parentheses. [b] At 298 K per metal ion. [c] P 4.5 (4.5%). [d] P 12.8 (13.3%). [e] Molecules of hydration vary; crystal structure shows $2H_2O$ but microanalytical data indicate *ca.* $5H_2O$. [f] P 16.0 (16.0%). [g] Mo 14.7 (14.5%).

(Nujol): $\tilde{\nu}$(PO)/cm^{-1} 1020s and 982s. ESR (powder at 110 K): $g_\perp = 2.048$, $g_\parallel = 2.221$.

$[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$ 3. The complex $[\{CuL(CH_3CO_2)\}_2]$ (222 mg, 0.37 mmol) was dissolved in approximately 2 mol dm^{-3} hexafluorophosphoric acid (5 cm^3) and the filtered solution allowed to stand for 11 weeks. The resulting hygroscopic crystals were dried *in vacuo*. Yield: 254 mg (62%). IR (Nujol): $\tilde{\nu}$(PO)/cm^{-1} 1020s and 980s. ESR (powder at 110 K): $g_\perp = 2.042$, $g_\parallel = 2.217$.

$[\{CuL(ptp)\}_2]\cdot 4H_2O$ 4. *p*-Tritylphenol (Hptp) (227 mg, 0.67 mmol) was deprotonated by dissolving it in ethanol (15 cm^3) containing sodium (20 mg, 0.87 mmol) and the resulting solution was added dropwise to a filtered solution of $[\{CuL(CH_3CO_2)\}_2]$ (200 mg, 0.33 mmol) in hot water (70 cm^3). The green precipitate which formed was washed with water, ethanol and diethyl ether and dried *in vacuo*. Yield: 283 mg (70%). ESR $[(CH_3)_2SO$ at 110 K]: $g_\perp = 2.072$, $g_\parallel = 2.202$, $A_\parallel$ 185 × 10^{-4} cm^{-1}.

$[\{CuL(tip)\}_2]$ 5. This complex was prepared by the above method using 2,4,6-triiodophenol (Htip). Yield: 364 mg (77%).

$[(CuL)_2(MoO_4)]\cdot H_2O$ 6. To a filtered solution of $[\{CuL(CH_3CO_2)\}_2]$ (151 mg, 0.50 mmol) in water (75 cm^3), which had been adjusted to pH 5 by the addition of acetic acid, was added $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (103 mg, 0.083 mmol) dissolved in 0.05 mol dm^{-3} acetic acid (10 cm^3). The resulting precipitate was washed with water then dried *in vacuo*. Yield: 106 mg (32%). IR (Nujol): $\tilde{\nu}$(MoO)/cm^{-1} 894s and 817s.

Crystallography

Crystal data. $C_{14}H_{34}Cu_2N_8O_{26}P_6S_2$ **3**, $M = 1107.6$, monoclinic, space group $P2_1/c$, a 11.495(2), b 10.238(2), c 16.571(3) Å, β 107.14(2)°, $U = 1863.6(6)$ Å^3 (by least-squares refinement on the setting angles of 25 automatically centred reflections), $\lambda = 1.5418$ Å, $Z = 2$, $D_c = 1.972$ g cm^{-3}. Green crystals, dimensions 0.40 × 0.32 × 0.24 mm, mounted in a capillary; μ(Cu-Kα) = 58.73 cm^{-1}, 293 K.

Data collection and processing. CAD4 diffractometer, ω–2θ scan, with ω-scan width = 0.8 + 0.14 tan θ, ω-scan speed 7.32° min^{-1}, Cu-Kα radiation, 4071 reflections measured ($4 \leqslant \theta \leqslant 75°$, $\pm h + k + l$), 3841 unique. Data were corrected for absorption using an empirical technique.[11]

Structure analysis and refinement. The structure was solved by the heavy-atom method and refined on F^2 by a full-matrix least-squares technique. Electron and difference electron-density syntheses revealed all non-hydrogen atoms and these were refined assuming anisotropic thermal motion. Difference electron-density maps revealed all hydrogen-atom sites (except for those associated with the water molecule) and these were included at calculated positions riding on the atom to which they were attached with one overall isotropic thermal parameter. Final $R1$ and $wR2$ values were 0.0438 and 0.1240 respectively for the 255 parameters refined and with data $I > 2\sigma(I)$. The corresponding values for all data after merging were 0.493 and 0.1329 respectively; $F(000) = 1116$. Selected bond lengths and angles in Table 2. The numbering scheme employed is shown in Fig. 1. Programs used are given in ref. 12.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/402.

Results and Discussion

Two general methods were employed for complex synthesis. Compounds **1** and **4**–**6**, where L is anionic, were prepared *via* metathetical displacement of acetate from $[\{CuL(CH_3CO_2)\}_2]$ under basic or weakly acidic conditions. This system has displayed an ability to co-ordinate to a large range of anions, often in unusual modes. An attempt was therefore made to prepare an adduct of the polymolybdate anion $[Mo_7O_{24}]^{6-}$. At pH 5.0 this anion is favoured and the thiosemicarbazone ligand is not protonated.[5] The complex isolated however is that of molybdate, $[(CuL)_2(MoO_4)]\cdot H_2O$ **6**, showing that rearrangement has occurred even at this pH. The IR absorbances at 894 and 817 cm^{-1} are consistent with the presence of this anion.[13] Reaction with HPO_4^{2-} yields **1** with IR absorbances at 1115, 1055 and 890 cm^{-1}, consistent with a bidentate phosphato moiety.[14]

In the presence of a strong acid the ligand is protonated to give neutral HL complexes **2** and **3**. Remarkably, when 2 mol dm^{-3} phosphoric acid is added the copper remains co-ordinated and crystalline $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 3H_2O$ **2** is isolated. No precipitation of highly insoluble $Cu_3(PO_4)_2\cdot 3H_2O$ is observed. Changing the acid concentration changes the hydration level and the crystal morphology. Reaction of $[\{CuL(CH_3CO_2)\}_2]$ with HPF_6 did not yield the PF_6^- complex but resulted in the isolation of $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2\cdot 2H_3PO_4\cdot 2H_2O$ **3**. Hydrolysis of HPF_6 yielded phosphoric acid which preferentially reacted to give **3**. The IR absorbances at *ca.* 1020 and 980 cm^{-1} are consistent with monodentate dihydrogenphosphato species.[14]

Analytical data indicated that all complexes, except **5**, should

Table 2 Selected bond lengths (Å) and angles (°) for $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$ **3**

Cu–O(11)	1.924(2)	P(1)–O(13)	1.509(2)	P(3)–O(31)	1.490(3)	N(3)–C(7)	1.353(4)
Cu–O(11$^{\text{I}}$)	2.444(2)	P(1)–O(11)	1.519(2)	P(3)–O(32)	1.537(2)	N(4)–C(7)	1.309(4)
Cu–N(1)	2.015(3)	P(1)–O(12)	1.559(2)	P(3)–O(34)	1.544(3)	C(1)–C(2)	1.387(5)
Cu–N(2)	1.955(3)	P(1)–O(14)	1.564(2)	P(3)–O(33)	1.554(3)	C(2)–C(3)	1.373(6)
Cu–S	2.2802(10)	P(2)–O(23)	1.503(2)	N(1)–C(1)	1.334(3)	C(3)–C(4)	1.400(5)
Cu–O(14)	3.155(2)	P(2)–O(21)	1.521(2)	N(1)–C(5)	1.363(4)	C(4)–C(5)	1.378(5)
Cu···Cu$^{\text{I}}$	3.2951(11)	P(2)–O(24)	1.553(2)	N(2)–C(6)	1.274(4)	C(5)–C(6)	1.463(4)
S–C(7)	1.708(3)	P(2)–O(22)	1.555(2)	N(2)–N(3)	1.363(4)		
O(11)–Cu–N(2)	175.44(11)	O(13)–P(1)–O(12)	110.86(13)	O(31)–P(3)–O(34)	111.3(2)	C(7)–N(3)–N(2)	116.9(3)
O(11)–Cu–N(1)	95.21(11)	O(11)–P(1)–O(12)	108.50(13)	O(32)–P(3)–O(34)	106.9(2)	N(1)–C(1)–C(2)	122.1(3)
N(2)–Cu–N(1)	80.62(11)	O(13)–P(1)–O(14)	110.75(13)	O(31)–P(3)–O(33)	112.8(2)	C(3)–C(2)–C(1)	119.5(3)
O(11)–Cu–S	99.78(8)	O(11)–P(1)–O(14)	106.10(12)	O(32)–P(3)–O(33)	102.66(14)	C(2)–C(3)–C(4)	119.3(4)
N(2)–Cu–S	84.67(8)	O(12)–P(1)–O(14)	106.76(14)	O(34)–P(3)–O(33)	107.6(2)	C(5)–C(4)–C(3)	118.0(3)
N(1)–Cu–S	161.24(8)	O(23)–P(2)–O(21)	113.20(14)	Cu–O(11)–Cu$^{\text{I}}$	97.23(9)	N(1)–C(5)–C(4)	122.7(3)
O(11)–Cu–O(11$^{\text{I}}$)	82.77(9)	O(23)–P(2)–O(24)	108.37(13)	C(1)–N(1)–C(5)	118.3(3)	N(1)–C(5)–C(6)	113.7(3)
N(2)–Cu–O(11$^{\text{I}}$)	95.40(9)	O(21)–P(2)–O(24)	108.54(14)	C(1)–N(1)–Cu	128.7(2)	C(4)–C(5)–C(6)	123.5(3)
N(1)–Cu–O(11$^{\text{I}}$)	91.00(10)	O(23)–P(2)–O(22)	112.30(14)	C(5)–N(1)–Cu	112.5(2)	N(2)–C(6)–C(5)	115.7(3)
S–Cu–O(11$^{\text{I}}$)	101.98(7)	O(21)–P(2)–O(22)	105.91(14)	C(6)–N(2)–N(3)	122.9(3)	N(4)–C(7)–N(3)	117.3(3)
C(7)–S–Cu	96.48(12)	O(24)–P(2)–O(22)	108.38(13)	C(6)–N(2)–Cu	117.1(2)	S–C(7)–N(2)	89.4(2)
O(13)–P(1)–O(11)	113.54(14)	O(31)–P(3)–O(32)	114.9(2)	N(3)–N(2)–Cu	120.0(2)		

Symmetry transformation used to generate equivalent atoms: I $-x$, $-y$, $-z$.

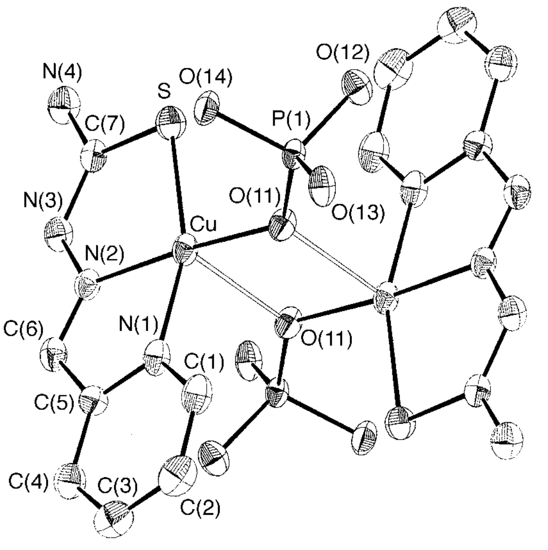

Fig. 1 Structure of the $[\{Cu(HL)(H_2PO_4)\}_2]^{2+}$ cation showing the numbering scheme. Ellipsoids are drawn at the 50% probability level

be formulated as hydrates and this was confirmed by IR data. Formulation of the complexes as dimers was based on the crystal structure of **3** (see below) and previously reported one-atom, oxygen-bridged structures of Cu$^{\text{II}}$ with this ligand.[2,3,6]

Crystal structure of $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$ 3

A thermal ellipsoid diagram for the cation is depicted in Fig. 1. Selected bond length and angle data are given in Table 2. The complex cation $[\{Cu(HL)(H_2PO_4)\}_2]^{2+}$ is a centrosymmetric dimer bridged by two dihydrogenphosphate ($H_2PO_4^-$) ligands. The co-ordinated oxygen, O(11), from this anion is asymmetrically bound to the two Cu atoms at distances of 1.924(2) and 2.444(2) Å. The copper adopts a distorted square-pyramidal geometry comprised of the neutral, tridentate NNS constellation from HL and a dihydrogenphosphato oxygen in the basal plane. The co-ordination sphere is completed by a more weakly co-ordinated bridging $H_2PO_4^-$ oxygen in the apical position. The structure of the cationic dimer is similar to those found in $[\{Cu(HL)(CF_3CO_2)\}_2][CF_3CO_2]_2$,[6] $[\{Cu(HL)(SO_4)\}_2]$ and $[\{CuL(CH_3CO_2)\}_2]$.[2] A sixth contact exists between the copper atom and the bridging dihydrogenphosphato group, Cu and O(14), 3.155(2) Å, which effectively blocks approach of a potential axial ligand. Such an interaction exists in the three other acetato and sulfato centrosymmetric, anion-bridged complexes of copper(II) with this ligand (see above). However, a comparison with the complex most structurally similar to **3**, $[\{Cu(HL)(SO_4)\}_2]$, shows this contact is 0.149 Å longer for **3**. The O(11)–Cu–O(11′) angle for **3** is 82.77(9)° compared with 77.3(1)° for $[\{Cu(HL)(SO_4)\}_2]$. This widening of the angle between the in-plane and axial $H_2PO_4^-$ oxygens brings the two copper atoms in the dimer significantly closer together, as seen in the Cu ··· Cu′ separations of 3.295(1) Å for **3** and 3.376(2) Å for $[\{Cu(HL)(SO_4)\}_2]$.[2]

The in-plane bond distances for complex **3** agree well with those for related complexes with the copper to phosphato bond distance agreeing well with literature values for phosphato-co-ordinated nucleotides to Cu$^{\text{II}}$.[15–17] The pyridine-2-carbaldehyde thiosemicarbazone ligand, HL, displays normal bonding parameters.[2–9]

The complex appears to be unique in that it is the only reported ternary complex of copper containing dihydrogenphosphate anions for which a crystal structure has been determined and it also appears to be the only complex presently to have co-ordinated and non-co-ordinated dihydrogenphosphate anions within the one structure.

The co-ordinated dihydrogenphosphato group in this complex links the two copper atoms in the dimer by a one-atom bridge. A number of nucleotide phosphates form dimeric complexes with Cu$^{\text{II}}$ but invariably have three-atom bridges (*e.g.* Cu–O–P–O–Cu′).[16–18] The formation of a single-atom bridge, again, appears to be a first. This follows the trend for the dimeric copper(II) complexes with this ligand where the unusual one-oxygen-atom bridging modes for both acetato and sulfato species have been observed.[2,3,6]

Within the phosphate ions the P–O distances range from 1.490(3) to 1.564(2) Å with a mean value of 1.534 Å. This value agrees well with that found for $KH_5(PO_4)_2$ in which there is strong hydrogen bonding.[19] The P–O bond-length data presented in Table 2 can be grouped into three categories. In the first of these, containing six of the twelve bonds, the P–O distance is significantly longer than the others. The oxygen atoms involved [O(12), O(14), O(22), O(24), O(33) and O(34)] have a mean P–O bond length of 1.555 Å and can be considered to belong to hydroxyl groups. The mean value for P–OH bonds in $KH_5(PO_4)_2$ of 1.555 Å is in agreement with this result.[19] In the second group, containing the three oxygens O(13), O(23) and O(31), the mean P–O bond distance is 1.501 Å and these corre-

Table 3 Hydrogen-bonding contacts (< 3.05 Å) for $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$ **3**

O(1)···O(31^{II})	2.890(4)	O(21)···O(32^{III})	2.436(4)
O(1)···O(14^{III})	2.976(4)	O(21)···O(34^{V})	2.638(4)
O(1)···N(4)	2.882(4)	O(22)···O(32^{VI})	2.618(3)
O(12)···O(31)	2.578(3)	O(23)···N(3^{VI})	2.730(3)
O(13)···O(24)	2.532(3)	O(24)···N(4^{VI})	2.942(3)
O(13)···O(33^{I})	2.640(3)	O(34)···N(4^{VII})	3.032(4)
O(14)···O(23^{IV})	2.522(3)		

Symmetry transformations used to generate equivalent atoms: I $-x, -y, -z$; II $x, y + 1, z$; III $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; IV $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; V $x + 1, -y - \frac{1}{2}, z + \frac{1}{2}$; VI $x + 1, y, z$; VII $-x - 1, -y, -z$.

spond to 'keto' (P=O) oxygens. The analogous $KH_5(PO_4)_2$ bonds are 1.502 Å, again in agreement.[19] The average bonding distance of 1.526 Å for the remaining three oxygens, O(11), O(21) and O(32), is intermediate between the 'hydroxyl' and 'keto' lengths found in the two previous groups. For O(11) this undoubtedly is due to its being involved in bonding to the copper centres. For the other two oxygens one possibility is that the hydrogen, H(32), formally assigned as bonded to O(32) and involved in a very short hydrogen bond to O(21) [2.436(4) Å], participates in a symmetrical hydrogen bond; it may be shared equally between O(21) and O(32). Its existence is supported by the P(2)–O(21) and P(3)–O(32) bond distances which are both significantly shorter than the 'pure' P–OH bonds and longer than the P=O bonds. Also, the hydrogen bond between O(32) and O(21) of 2.436(4) Å is significantly shorter than the average for the other interphosphate contacts of 2.588 Å and ranks amongst the shortest ever found.[19,20] A very similar situation exists[19] in the compound $KH_5(PO_4)_2$ where the possibility of a symmetrical hydrogen bond has been postulated between two phosphate oxygens with a separation of 2.405 Å.

An extensive network of hydrogen bonds is involved in the stabilization and packing of the dimeric $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$ units and the non-co-ordinated water and phosphate molecules. The hydrogen-bonding contacts are listed in Table 3. The co-ordinated dihydrogenphosphato moiety containing P(1) is involved in a total of five contacts, four to the remaining two unco-ordinated phosphate oxygens and one to the water molecule, O(1). Around the di- or tri-hydrogenphosphates, two of the oxygens of P(2) form hydrogen bonds to protons H(31) and H(42) of the protonated thioamide, N(3), and amine, N(4), nitrogens respectively of the organic ligand. These are a part of the seven contacts for the P(2) phosphate. The number of contacts for the P(3) anion is six and three for the water molecule. Dimers related by the two-fold screw axis along the *c* direction are separated by a column of hydrogen-bonded di- or tri-hydrogenphosphates. The dimers between these rows are all connected *via* a hydrogen-bonding network forming a stable and well defined structure for this novel complex.

Physicochemical studies

Solid-state electronic spectral and conductivity data for the complexes are presented in Table 4. The intense band for all the complexes in the range 394–440 nm is assigned to a $S{\rightarrow}Cu^{II}$ ligand-to-metal charge-transfer transition (l.m.c.t.). The l.m.c.t. maxima for the phenolato complexes **5** and **6** show broadening, with a tail running into the visible part of the spectrum which tends to obscure any d–d transitions. This may result from a phenolato→Cu^{II} l.m.c.t. band[21] being superimposed on the low-energy side of the $S{\rightarrow}Cu^{II}$ l.m.c.t. The d–d bands, which fall in the range 600–713 nm, are consistent with square-pyramidal or tetragonal geometries as found in **3** and previously for related structures.[2–7] The ESR spectral parameters at 110 K are consistent with an axial stereochemistry about the copper(II) centre and with an oxygen-donor atom in the plane giving an N_2OS donor set.

Table 4 Electronic spectral and molar conductivity data for the complexes

Complex		Absorption maxima[a]/nm		
		S→Cu	d–d	Λ^{b}/S cm^2 mol^{-1}
1	$[(CuL)_2(HPO_4)]{\cdot}6H_2O$	440	605	*c*
2	$[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}3H_2O$	404	713	3[d]
3	$[\{Cu(HL)(H_2PO_4\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$	394	670	22[e]
4	$[\{CuL(ptp)\}_2]{\cdot}4H_2O$	427	654	0
5	$[\{CuL(tip)\}_2]$	415	*f*	9
6	$[(CuL)_2(MoO_4)]{\cdot}H_2O$	430	600	4

[a] Nujol mull transmittance spectra. [b] In $(CH_3)_2SO$, values given per monomeric unit. [c] Low solubility in $(CH_3)_2SO$. [d] In H_2O, $\Lambda = 329$ S cm^2 mol^{-1}. [e] In H_2O, $\Lambda = 579$ S cm^2 mol^{-1}. [f] Obscured by phenolato→Cu c.t. absorption.

The molar conductance values in $(CH_3)_2SO$, Table 4, indicate at most only partial ionization and are consistent with other CuL(X) and $Cu(HL)X_2$ (X = *e.g.* halide, NO_3, ClO_4) species where anion co-ordination occurs in this solvent. However, in water both **3** and **4** are strong acids and have conductance values indicating extensive ionization. The higher value for **3** is consistent with its formulation containing 'H_3PO_4' as seen in the crystal structure.

The magnetic moments for the complexes, Table 1, are within the range expected for spin-only Cu^{II} at room temperature. Poor overlap of the magnetic orbitals for dimeric complexes such as **3** results in weak antiferromagnetic interactions, as the determined 2*J* values for the dimeric $[\{CuL(CH_3CO_2)\}_2]$ and tetrameric $[(CuL)_4(P_2O_7)]{\cdot}xH_2O$ of −6.4 and −6.0 cm^{-1}, respectively, show.[7]

Conclusion

The isolation and characterization of a range of oxygen donors, including phosphate and phenolate, to the antitumour-active copper(II) complex of pyridine-2-carbaldehyde thiosemicarbazone adds credence to the possibility of such adduct formation *in vivo* and may serve as simple models for these. The remarkable stability of this system and its versatility and use as an unusual anion-binding moiety are demonstrated by the isolation of the highly acidic complex $[\{Cu(HL)(H_2PO_4)\}_2][H_2PO_4]_2{\cdot}2H_3PO_4{\cdot}2H_2O$ from the hydrolysis of 2 mol dm^{-3} HPF_6. The one-atom ternary dihydrogenphosphato bridge between copper(II) centres, the presence of both co-ordinated and non-co-ordinated dihydrogenphosphates and three inequivalent phosphates within one structure all appear to be unique. This system warrants further study as a vehicle for anion binding.

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References

1 W. E. Antholine, B. Kalyanaraman and D. H. Petering, *Environ. Health Persp.*, 1985, **64**, 19 and refs. therein.
2 A. G. Bingham, H. Bögge, A. Müller, E. W. Ainscough and A. M. Brodie, *J. Chem. Soc., Dalton Trans.*, 1987, 493.
3 C. F. Bell and C. R. Theocharis, *Acta Crystallogr., Sect. C*, 1987, **43**, 26.

4 E. W. Ainscough, E. N. Baker, A. M. Brodie, R. J. Cresswell, J. D. Ranford and J. M. Waters, *Inorg. Chim. Acta*, 1990, **172**, 185.

5 E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 1991, 1737.

6 E. W. Ainscough, A. M. Brodie, J. D. Ranford and J. M. Waters, *J. Chem. Soc., Dalton Trans.*, 1991, 2125.

7 E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters and K. S. Murray, *Inorg. Chim. Acta*, 1992, **197**, 107.

8 J. García-Tojal, J. García-Jaca, R. Cortés, T. Rojo, M. K. Urtiaga and M. I. Arriortua, *Inorg. Chim. Acta*, 1996, **249**, 25.

9 J. García-Tojol, M. K. Urtiaga, R. Cortés, L. Lezama, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1994, 2233.

10 F. E. Anderson, C. J. Duca and J. V. Scudi, *J. Am. Chem. Soc.*, 1951, **73**, 4967.

11 A. C. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

12 B. A. Frenz, CAD4, Structure Determination Package, Enraf-Nonius, Delft, 1983; G. M. Sheldrick, SHELX 76, University of Cambridge, 1976; SHELXL 93, University of Göttingen, 1993.

13 K. Nakamoto, *Infrared and Raman Spectra*, Wiley-Interscience, New York, 1986.

14 S. F. Lincoln and D. R. Stranks, *Aust. J. Chem.*, 1968, **21**, 37.

15 K. Aoki and H. Yamazaki, *J. Am. Chem. Soc.*, 1980, **102**, 6878.

16 B. E. Fischer and R. Bau, *Inorg. Chem.*, 1978, **17**, 27.

17 K. Aoki, *J. Am. Chem. Soc.*, 1978, **100**, 7106.

18 W. S. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 460; G. R. Clark, J. D. Orbell and J. M. Waters, *Biochim. Biophys. Acta*, 1979, **562**, 361; K. Aoki, *J. Chem. Soc., Chem. Commun.*, 1977, 600.

19 E. Philipoot and O. Lindquist, *Acta Chem. Scand.*, 1971, **25**, 512.

20 J. Emsley, N. M. Reza, H. M. Dawes, M. B. Hursthouse and R. Kuroda, *Phosphorus Sulphur, Relat. Elem.*, 1988, **35**, 141; A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 1984.

21 E. W. Ainscough, A. G. Bingham, A. M. Brodie, J. M. Husbands and J. E. Plowman, *J. Chem. Soc., Dalton Trans.*, 1981, 1701.

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