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Structures of Nitrato[*N*-(2-pyridylmethyl)salicylideneaminato-*N,O*]copper(II), [Cu(salimp)NO₃], and Dichloro[*N*-(2-pyridylmethyl)salicylamine-*N,N'*]copper(II)– Methanol–Water (1/1/1), [Cu(Hsalamp)Cl₂].CH₃OH.H₂O

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Abstract. (I) [Cu(C₁₃H₁₁N₂O)NO₃], $M_r = 336.80$, monoclinic, *Pn*, $a = 7.770$ (1), $b = 5.958$ (1), $c = 14.403$ (2) Å, $\beta = 101.99$ (1)°, $V = 652.2$ (3) Å³, $Z = 2$, $D_x = 1.716$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.70$ mm⁻¹, $F(000) = 342$, $T = 292$ K, $R = 0.023$ for 1099 observed data with $I \geq 2.5\sigma(I)$. (II) [Cu(C₁₃H₁₄N₂O)Cl₂].CH₄O.H₂O, $M_r = 398.77$, monoclinic, $P2_1/c$, $a = 9.959$ (1), $b = 9.924$ (1), $c = 18.197$ (2) Å, $\beta = 103.20$ (2)°, $V = 1751.1$ (6) Å³, $Z = 4$, $D_x = 1.51$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.56$ mm⁻¹, $F(000) = 820$, $T = 292$ K, $R = 0.037$ for 2377 observed data with $I \geq 3.0\sigma(I)$. In (I), the Cu atom is four-coordinate in an essentially square-planar arrangement with the ligand occupying three of the coordination positions. The fourth position is occupied by an O atom of the nitrate group, the plane of which is at an angle of 87·1 (7)° to the best plane through the remainder of the molecule. This allows a second O atom from this group to make a significant contact with the Cu atom thus increasing its coordination number to five in a pseudo-square-pyramidal arrangement. In (II), a similar situation arises with the initial square-planar coordination sphere of two N atoms from the ligand and two Cl atoms being again modified by a further Cl atom, this time from an adjacent molecule.

Introduction. Copper complexes of bi- and tetradentate ligands formed from salicylaldehyde and various mono-

or polyamines have been widely studied over the past three decades (Holm, Everett & Chakravorty, 1966; Sinn & Harris, 1969). Considerably less attention has been devoted, however, to copper complexes of tridentate Schiff bases, especially those involving a diamine in addition to the salicyl moiety. This is rather surprising since copper complexes of such ligands can be envisaged as valuable models for the so-called type II copper found in galactose oxidase (Ettinger & Kosman, 1981) or dopamine hydroxylase (Villafranca, 1981) and the mononuclear copper site of metapo-haemocyanin (Himmelwright, Eickman & Solomon, 1979).

Copper complexes of ligands formed from salicylaldehyde and *N*-substituted ethylenediamines were first reported 20 years ago (Sacconi & Bertini, 1966). A number of authors have extended these studies more recently (Chieh & Palenik, 1972; Muto & Tokii, 1978; Elias, Hims & Paulus, 1982; Mandal & Nag, 1984). On the other hand, ligands involving only imine N atoms to mimic more closely the histidine coordination have been developed only in the past few years (Nakao, Mori, Okuda & Nakahara, 1979; Wagner & Walker, 1983; Taylor & Coleman, 1982).

In order to obtain a deeper insight into the properties of biological monocopper sites, we started a systematic investigation of copper complexes of ligands resulting from the condensation of salicylaldehyde with an aminoalkylpyridine. In this contribution we describe the crystal structures of two such compounds: the copper nitrate derivative of 2-(2-pyridylmethyliminomethyl)-phenol, (I), and the dichlorocopper complex of 2-(2-pyridylmethylaminomethyl)phenol, (II).

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Experimental. Both compounds have been synthesized as described earlier (Latour, Leonard, Limosin, Povey & Tandon, 1985).

(I). Compound crystallizes as brown triangular plates, accurate unit-cell parameters from a least-squares analysis using 25 accurately centred reflections $(21 \leq \theta \leq 23°)$ measured on a CAD-4 diffractometer from a crystal of dimensions $0.3 \times 0.25 \times 0.1$ mm. 1319 reflections with $(\sin\theta)/\lambda \leq 0.6$ Å^{-1}; range of hkl: $h -9 \rightarrow 9$, $k 0 \rightarrow 7$, $l 0 \rightarrow 17$; standard reflection 020 measured every one hour of exposed X-ray time; reduced to 1144 unique reflections. D_m not determined. Enraf–Nonius CAD-4 diffractometer with graphite monochromator on incident beam, ω–2θ scanning mode with variable scan speed; Lorentz–polarization but no absorption corrections. Space group determined from systematic absences and $N(z)$ test. Structure solved by heavy-atom method with some difficulty due to pseudo-symmetry introduced by positioning of the heavy atom. Full-matrix least-squares refinement with H-atom positions determined from a difference-Fourier synthesis during the final stages; 232 parameters, atomic coordinates, anisotropic temperature factors for all non-H atoms, isotropic thermal parameters for H atoms refined each cycle with the heavy-atom x and z coordinates fixed to determine the origin in space group Pn. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(I) + (0.052F^2)^2]^{-1/2}$, $S = 1.064$, $R = 0.023$, $wR = 0.029$ for 1099 observed reflections $[I \geq 2.5\sigma(I)]$. Final difference-Fourier excursions of 0.30 and -0.26 e Å^{-3}. Max. shift/e.s.d. = 0.1 in last cycle.

(II) Compound crystallizes as green needles; accurate unit-cell parameters from a least-squares analysis using 25 accurately centred reflections $(19 \leq \theta \leq 22°)$ measured on a CAD-4 diffractometer from a crystal of dimensions $0.5 \times 0.1 \times 0.2$ mm. 3477 reflections (including systematic absences) with $(\sin\theta)/\lambda \leq 0.58$ Å^{-1}; range of hkl: $h 0 \rightarrow 11$, $k 0 \rightarrow 11$, $l -21 \rightarrow 21$; standard reflection 006 remeasured every one hour of X-ray exposure time, reduced to 3075 unique reflections. D_m not determined. Enraf–Nonius CAD-4 diffractometer with graphite monochromator on incident beam, ω–2θ scanning mode with variable scan speed; ψ scans on five suitable reflections. Lorentz–polarization and empirical absorption corrections (max. and min. transmission 0.99, 0.91). Space group from systematic absences. Structure solved by heavy-atom method. Full-matrix least-squares refinement, H atoms from difference Fourier synthesis (except phenolic and those of methanol and water). 250 parameters, atomic coordinates, anisotropic temperature factors for all non-H atoms, isotropic thermal parameters for H atoms refined each cycle. Solvent identified from difference synthesis; based on methanol and water rather than ethanol by geometry, diffuse electron density and high temperature factors indicating disorder. $\sum w(|F_o| - |F_c|)^2$ minimized with $w^{-1} =$

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and B_{eq} thermal parameters* (Å²)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}
Compound (I)				
Cu	0.000	0.02488 (7)	0.000	3.116 (7)
O(1)	−0.1547 (4)	0.2514 (5)	−0.0564 (2)	4.08 (7)
O(2)	0.1847 (5)	−0.0782 (7)	−0.2277 (2)	6.06 (8)
O(3)	0.0123 (4)	−0.0939 (5)	−0.1292 (2)	3.57 (6)
O(4)	0.2361 (5)	0.1298 (7)	−0.1040 (3)	5.83 (8)
N(1)	0.1531 (4)	−0.2188 (6)	0.0652 (2)	3.15 (7)
N(2)	0.0106 (4)	0.1319 (6)	0.1280 (2)	3.17 (6)
N(3)	0.1471 (5)	−0.0107 (6)	−0.1548 (3)	3.62 (7)
C(1)	0.2166 (5)	−0.3951 (8)	0.0254 (3)	3.49 (8)
C(2)	0.3291 (6)	−0.5483 (7)	0.0763 (3)	3.87 (9)
C(3)	0.3795 (6)	−0.5195 (7)	0.1743 (4)	4.2 (1)
C(4)	0.3135 (6)	−0.3416 (8)	0.2157 (3)	3.89 (9)
C(5)	0.2006 (5)	−0.1947 (7)	0.1612 (3)	3.27 (8)
C(6)	0.1189 (6)	−0.0013 (7)	0.2024 (3)	3.9 (1)
C(7)	−0.0727 (5)	0.3043 (8)	0.1496 (3)	3.41 (8)
C(8)	−0.1792 (5)	0.4529 (7)	0.0852 (3)	3.38 (8)
C(9)	−0.2475 (5)	0.6469 (9)	0.1229 (3)	4.08 (9)
C(10)	−0.3417 (6)	0.8030 (8)	0.0667 (4)	4.7 (1)
C(11)	−0.3752 (6)	0.7714 (9)	−0.0310 (4)	4.9 (1)
C(12)	−0.3150 (7)	0.5844 (9)	−0.0705 (3)	4.6 (1)
C(13)	−0.2134 (6)	0.4193 (8)	−0.0145 (3)	3.74 (9)
Compound (II)				
Cu	0.05137 (4)	0.65003 (4)	0.04341 (2)	3.063 (9)
Cl(1)	0.10040 (9)	0.5656 (1)	−0.06446 (5)	3.59 (2)
Cl(2)	0.2489 (1)	0.5696 (1)	0.11722 (5)	4.32 (2)
O(1)	−0.2472 (3)	1.0744 (3)	−0.0326 (2)	5.42 (7)
O(2)	0.5855 (4)	0.2234 (4)	0.4918 (2)	7.27 (9)
O(3)	0.5649 (6)	0.1573 (8)	0.5812 (5)	19.9 (3)
N(1)	0.0027 (3)	0.7706 (3)	0.1218 (2)	3.66 (7)
N(2)	−0.1265 (3)	0.7280 (3)	−0.0198 (2)	3.30 (6)
C(1)	0.0881 (5)	0.8111 (5)	0.1867 (2)	4.8 (1)
C(2)	0.0442 (6)	0.8953 (5)	0.2359 (2)	6.2 (1)
C(3)	−0.0882 (6)	0.9402 (6)	0.2184 (3)	7.4 (1)
C(4)	−0.1768 (5)	0.9023 (5)	0.1522 (3)	6.0 (1)
C(5)	−0.1271 (4)	0.8154 (4)	0.1046 (2)	4.05 (9)
C(6)	−0.2145 (4)	0.7612 (4)	0.0323 (2)	4.07 (9)
C(7)	−0.1005 (4)	0.8461 (4)	−0.0663 (2)	3.94 (8)
C(8)	−0.2269 (4)	0.8996 (4)	−0.1184 (2)	4.04 (9)
C(9)	−0.2797 (6)	0.8388 (5)	−0.1876 (3)	5.7 (1)
C(10)	−0.3949 (6)	0.8900 (6)	−0.2378 (3)	7.4 (1)
C(11)	−0.4595 (6)	1.0016 (5)	−0.2182 (3)	7.1 (1)
C(12)	−0.4124 (5)	1.0634 (5)	−0.1508 (3)	5.4 (1)
C(13)	−0.2963 (4)	1.0120 (4)	−0.1007 (2)	4.36 (9)
C(15)	0.620 (1)	0.2690 (8)	0.6046 (7)	15.2 (3)

$[\sigma^2(F_o) + 0.05F_o^2]$. $S = 1.247$, $R = 0.037$, $wR = 0.053$ for 2377 observed reflections $[I \geq 3.0\sigma(I)]$. Final difference-Fourier excursions of 0.35 and -0.25 e Å^{-3}. Max. shift/e.s.d. = 0.14 in last cycle.

All calculations were carried out using a DEC PDP 11/73 computer using the *SDP Plus* system (Frenz, 1983). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and bond distances and angles for both compounds are listed in Tables 1 and 2, respectively.*

The structure of (I) is shown in Fig. 1. For (I) the coordination of the Cu atom can be described as

Table 2. *Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Compound (I)

Cu–O(1)	1·876 (3)	C(1)–C(2)	1·367 (9)
Cu–O(3)	2·012 (3)	C(2)–C(3)	1·395 (8)
Cu–O(4)	2·672 (3)	C(3)–C(4)	1·367 (8)
Cu–N(1)	1·985 (4)	C(4)–C(5)	1·366 (7)
Cu–N(2)	1·936 (4)	C(5)–C(6)	1·497 (7)
O(1)–C(13)	1·299 (6)	C(7)–C(8)	1·418 (7)
O(2)–N(3)	1·215 (6)	C(8)–C(9)	1·425 (7)
O(3)–N(3)	1·280 (6)	C(8)–C(13)	1·420 (7)
O(4)–N(3)	1·226 (5)	C(9)–C(10)	1·345 (8)
N(1)–C(1)	1·339 (7)	C(10)–C(11)	1·390 (8)
N(1)–C(5)	1·363 (5)	C(11)–C(12)	1·376 (9)
N(2)–C(6)	1·453 (7)	C(12)–C(13)	1·406 (9)
N(2)–C(7)	1·287 (6)		
O(1)–Cu–O(3)	90·1 (1)	C(1)–C(2)–C(3)	118·3 (6)
O(1)–Cu–N(1)	176·3 (2)	C(2)–C(3)–C(4)	119·0 (6)
O(1)–Cu–N(2)	94·1 (2)	C(3)–C(4)–C(5)	120·0 (4)
O(3)–Cu–N(1)	92·4 (2)	N(1)–C(5)–C(4)	121·5 (4)
O(3)–Cu–N(2)	174·8 (2)	N(1)–C(5)–C(6)	115·9 (4)
N(1)–Cu–N(2)	83·6 (2)	C(4)–C(5)–C(6)	122·7 (4)
Cu–O(1)–C(13)	127·5 (3)	N(2)–C(6)–C(5)	110·8 (4)
Cu–O(3)–N(3)	109·2 (3)	N(2)–C(7)–C(8)	126·5 (4)
Cu–N(1)–C(1)	127·6 (3)	C(7)–C(8)–C(9)	118·0 (4)
Cu–N(1)–C(5)	114·3 (3)	C(7)–C(8)–C(13)	122·3 (4)
C(1)–N(1)–C(5)	118·1 (4)	C(9)–C(8)–C(13)	119·6 (5)
Cu–N(2)–C(6)	115·2 (3)	C(8)–C(9)–C(10)	122·0 (5)
Cu–N(2)–C(7)	124·7 (3)	C(9)–C(10)–C(11)	118·7 (6)
C(6)–N(2)–C(7)	120·1 (4)	C(10)–C(11)–C(12)	121·3 (6)
O(2)–N(3)–O(3)	118·6 (4)	C(11)–C(12)–C(13)	121·9 (6)
O(2)–N(3)–O(4)	122·3 (5)	O(1)–C(13)–C(8)	124·6 (5)
O(3)–N(3)–O(4)	119·1 (4)	O(1)–C(13)–C(12)	118·9 (5)
N(1)–C(1)–C(2)	123·1 (5)	C(8)–C(13)–C(12)	116·5 (5)

Compound (II)

Cu–Cl(1)	2·287 (1)	C(3)–C(4)	1·373 (6)
Cu–Cl(2)	2·259 (1)	C(4)–C(5)	1·392 (5)
Cu–N(1)	2·004 (3)	C(5)–C(6)	1·501 (5)
Cu–N(2)	2·033 (4)	C(7)–C(8)	1·490 (6)
O(1)–C(13)	1·373 (10)	C(8)–C(9)	1·387 (6)
N(1)–C(1)	1·351 (5)	C(8)–C(13)	1·388 (9)
N(1)–C(5)	1·334 (4)	C(9)–C(10)	1·389 (7)
N(2)–C(6)	1·468 (6)	C(10)–C(11)	1·369 (7)
N(2)–C(7)	1·503 (5)	C(11)–C(12)	1·356 (6)
C(1)–C(2)	1·367 (6)	C(12)–C(13)	1·395 (8)
C(2)–C(3)	1·359 (8)		
O(3)–C(15)	1·266 (10)		
Cl(1)–Cu–Cl(2)	93·05 (4)	N(1)–C(5)–C(4)	121·6 (3)
Cl(1)–Cu–N(1)	164·42 (8)	N(1)–C(5)–C(6)	115·0 (3)
Cl(1)–Cu–N(2)	89·0 (1)	C(4)–C(5)–C(6)	123·4 (3)
Cl(2)–Cu–N(1)	96·16 (1)	N(2)–C(6)–C(5)	109·5 (2)
Cl(2)–Cu–N(2)	177·7 (1)	N(2)–C(7)–C(8)	114·0 (4)
N(1)–Cu–N(2)	81·6 (1)	C(7)–C(8)–C(9)	120·9 (4)
Cu–N(1)–C(1)	126·4 (3)	C(7)–C(8)–C(13)	122·1 (5)
Cu–N(1)–C(5)	114·2 (2)	C(9)–C(8)–C(13)	117·0 (5)
C(1)–N(1)–C(5)	119·3 (4)	C(8)–C(9)–C(10)	121·5 (5)
Cu–N(2)–C(6)	106·9 (2)	C(9)–C(10)–C(11)	119·4 (5)
Cu–N(2)–C(7)	112·0 (3)	C(10)–C(11)–C(12)	121·0 (4)
C(6)–N(2)–C(7)	113·3 (4)	C(11)–C(12)–C(13)	119·3 (5)
N(1)–C(1)–C(2)	121·5 (5)	O(1)–C(13)–C(8)	118·6 (5)
C(1)–C(2)–C(3)	119·1 (5)	O(1)–C(13)–C(12)	119·8 (6)
C(2)–C(3)–C(4)	120·7 (4)	C(8)–C(13)–C(12)	121·6 (8)
C(3)–C(4)–C(5)	117·9 (4)		

The present results can be compared with the structure of the chlorocopper complex of 2-[2-(dimethylamino)ethyliminomethyl]phenol (Elias *et al.,* 1982). The latter compound exhibits an important distortion of the copper coordination sphere which is apparent from the value (15°) of the torsion angle of the O—Cu—Cl and N—Cu—N planes. Such a distortion is not present in (I). Interestingly also, the lengths of the Cu—O(phenol) and Cu—N(pyridine) bonds are significantly shorter than their counterparts (1·876 *vs* 1·90 Å and 1·985 *vs* 2·08 Å, respectively). Owing to the long axial Cu—O(nitrate) distance it is unlikely that the presence of this fifth ligand is responsible for this effect. Thus it reflects the complementarity of the two ligands involved: a phenolate (strong donor) and a pyridine (good acceptor).

This combination of ligands has already been observed to bind copper with an exceptional strength (Sigel, 1980). The structure, shown in Fig. 2, exists as discrete units, the closest approach between atoms of adjacent molecules being 3·29 Å.

In contrast with (I), compound (II) is not an isolated molecule, but forms an infinite one-dimensional chain. Fig. 3 illustrates the basic structural unit of the chain. It comprises a Cu atom surrounded by two N atoms from
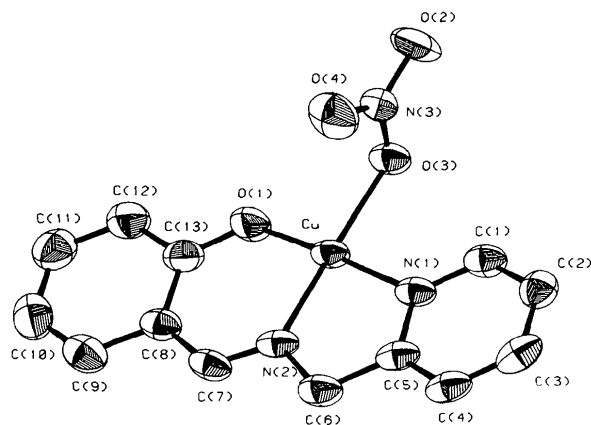

Fig. 1. Structure of (I) showing the numbering scheme used. Thermal ellipsoids are shown at 50% probability.

belonging to the 4+1 type with an approximate square-pyramidal arrangement of the ligands. Three equatorial positions are occupied by the tridentate ligand, and the last one by a nitrato O atom. The axial position is filled by a second O atom, O(4), of the nitrate which is at a far longer distance than the equatorial one: 2·67 *vs* 2·01 Å. The plane of the nitrate is almost perpendicular to the mean plane of the remainder of the molecule. The axial interaction with the nitrato O atom induces a displacement of the Cu atom from the mean plane of 0·25 (1) Å.
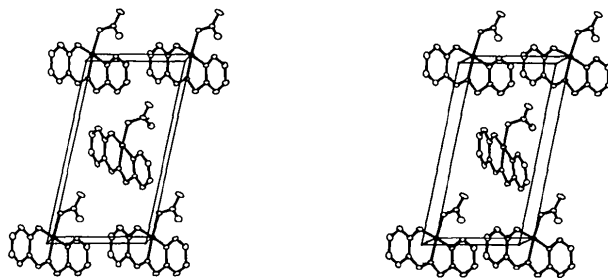

Fig. 2. Stereo packing diagram of (I). Origin is at bottom right looking down *b* with *a* horizontal and *c* vertical.

the ligand and two Cl atoms. An axial Cl atom from a neighbouring unit completes the coordination sphere of the metal, giving a 4+1 square-pyramidal environment. The chain is thus formed through an infinite Cl—Cu—Cl*—Cu* arrangement with alternating short equatorial (ca 2·27 Å) and long axial (2·70 Å) Cu—Cl bonds. The polymeric nature of the structure is depicted in Fig. 4. This sort of equatorial–axial bridging is very common for chlorocopper complexes where it has been shown to produce either dimers or infinite polymeric networks (Hodgson, 1975).

It is worth noting that the phenolic O atom is not bound to the Cu atom. This feature is rather surprising since one might have expected that the chelate effect would stabilize the salicylic bonding mode. In fact, the electron-donating effect of the aminomethyl substituent lowers the acidity of the phenol compared with salicyl derivatives. This effect probably compensates for the chelate stabilization, and the balance is dictated by the counter anion; with strong donors like Cl, the phenol is not ionized or bound to the metal. In contrast, with weak donors like nitrate, coordination of the phenolate occurs (Latour *et al.*, 1985).

It follows that (II) more closely resembles amino-methylpyridine (amp) complexes than salicyl derivatives. Chloro complexes of aminomethylpyridine derivatives have been recently described and shown to

Table 3. *A comparison of pertinent bond lengths (Å) in compounds related to* [Cu(Hsalamp)Cl$_2$]

	Cu(amp)Cl$_2$	CuLCl$_2$	(II)
Cu—Cl	2·240 (2)	2·283 (2)	2·287 (1)
	2·270 (2)	2·253 (3)	2·259 (1)
Cu—N	1·998 (5)	2·036 (4)	2·004 (3)
	1·988 (5)	1·991 (5)	2·033 (4)
Cu—Cl'	3·206 (3)	2·862 (3)	2·697 (1)
Cu—Cu	3·615 (2)	3·683 (3)	3·417 (1)

adopt dimeric or polymeric arrangements (O'Connor, Edouk, Fronczek & Kahn, 1985; O'Connor, Eduok, Owens, Stevens & Klein, 1986). Table 3 summarizes pertinent bond lengths of Cu(amp)Cl$_2$ and CuLCl$_2$ with L:

L
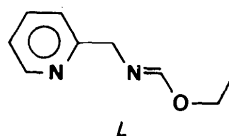
Comparison of these values with the corresponding parameters of (II) shows that, although the basic unit of (II) is structurally very similar to CuLCl$_2$, it adopts the linear chain structure exhibited by Cu(amp)Cl$_2$. This suggests that packing forces are more important for the overall structural arrangement than the detailed structural parameters of the monomeric unit.
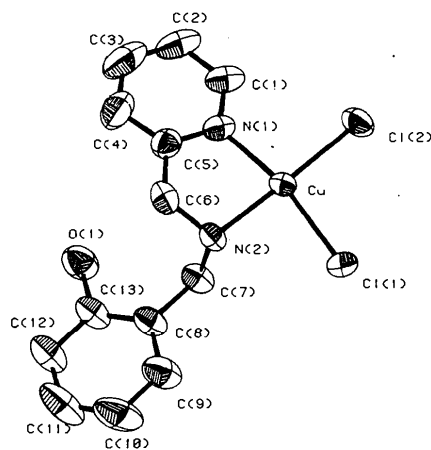

Fig. 3. Structure of (II) showing the numbering scheme used. Thermal ellipsoids are shown at 50% probability.
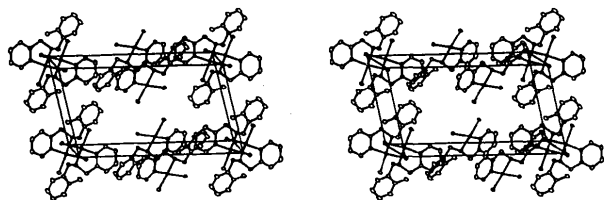

Fig. 4. Stereo packing diagram of (II). Origin is at bottom left looking down **b** with **a** vertical and **c** horizontal.

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Tetraphenylarsonium Tetracyanoaurate(III) Dichloromethane Solvate

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Abstract. $[As(C_6H_5)_4][Au(CN)_4].CH_2Cl_2$, $M_r = 769.3$, orthorhombic, *Pbcm*, $a = 9.205$ (2), $b = 13.776$ (2), $c = 23.213$ (3) Å, $V = 2943.6$ Å^3, $Z = 4$, $D_x = 1.74$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 6.3$ mm^{-1}, $F(000) = 1480$, $T = 293$ K, $R = 0.042$ for 2043 unique observed reflections. The Au atom occupies the special position $\frac{1}{2},\frac{1}{2},0$ with crystallographic symmetry $\bar{1}$, but the actual symmetry of the anion is close to the ideal $4/mmm$. The As atom lies in the mirror plane $x,y,\frac{1}{4}$. The solvent molecule is ordered, its central C atom lying on the twofold axis $x,\frac{3}{4},\frac{1}{2}$. The extended structure consists of two kinds of layers, one composed of cations and the other of anions and solvent. The Au—C bond lengths, 1.999 (7) and 2.014 (7) Å, are appreciably longer than in Au(CN)$_2^-$ complexes with large cations.

Introduction. We have recently reported the synthesis and structure of Ph$_4$As$^+$.Au(SeCN)$_4^-$ (Jones & Thöne, 1987); the compound had already been reported by Schmidtke & Garthoff (1967). The reaction between this compound and Ph$_3$As gave a colourless solution, from which the title compound could be isolated as a white powder. Presumably the reaction also leads to the formation of Ph$_3$AsSe, but we have not proved this. One of us (Jones, 1976) has already reported the synthesis of the title compound by other methods.

Experimental. The title compound was recrystallized by liquid diffusion of diisopropyl ether into a dichloromethane solution. Colourless prisms were obtained, which gradually became opaque on exposure to air. This loss of solvent is, however, slow enough to permit the crystals to be mounted in glass capillaries without special precautions.

A crystal 0.6 × 0.15 × 0.15 mm was used to collect 6752 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer; $\omega/2\theta$ scans; monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 50°$, octants $+h$ $+k$ $+l$ and $-h$ $-k$ $-l$ and some additional equivalents. Merging equivalents gave 2643 unique reflections ($R_{int} = 0.025$, index ranges h 0 to 10, k 0 to 16, l 0 to 27), of which 2043 with $F > 4\sigma(F)$ were used for all calculations. The program system was *SHELX*76 (Sheldrick, 1976), locally modified by its author. An absorption correction based on ψ scans was applied; transmission factors 0.78–0.92. Three check reflections decreased in intensity by 14%, and an appropriate scaling was applied. Cell constants were refined from 2θ values of 44 reflections in the range 20–24°.

The structure was solved by the heavy-atom method and subjected to full-matrix anisotropic least-squares refinement on F. H atoms were included using a riding model. The solvent molecule was well-behaved. The final R was 0.042, $wR = 0.037$; 177 parameters, $S = 1.7$, weighting scheme $w^{-1} = \sigma^2(F) + 0.00015F^2$, max. $\Delta/\sigma = 0.014$, max. $|\Delta\rho| = 0.8$ e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Final atomic coordinates are presented in Table 1,† with derived bond lengths and angles in Table 2.

Discussion. The three separate species present in the structure all exhibit crystallographic symmetry. The Au(CN)$_4^-$ anions are associated with symmetry centres $\frac{1}{2},\frac{1}{2},0$, but their actual symmetry is close to the ideal

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51307 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.