Table 2. *Bond angles* (°) *at the* Mo *atoms; e.s.d.'s are* 0·01° *for* Mo—Mo—Mo, 0·03–0·04° *for* Mo—Mo—S, *and* 0·04–0·05° *for* S—Mo—S

Mo(1)	Mo(2)	Mo(3)	S(1)	S(2)	S(4)	S(11)	S(12)
Mo(3)	60·31						
S(1)	53·47	96·79					
S(2)	97·97	51·33	94·74				
S(4)	54·26	54·07	106·97	103·82			
S(11)	142·06	136·90	88·63	85·67	160·70		
S(12)	139·65	97·90	164·64	90·96	85·40	77·57	
S(41)	96·46	143·09	89·22	164·46	89·30	79·40	81·70

Mo(2)	Mo(1)	Mo(3)	S(1)	S(3)	S(4)	S(21)	S(22)
Mo(3)	60·26						
S(1)	53·64	96·87					
S(3)	99·51	51·83	96·50				
S(4)	54·19	54·04	107·07	103·81			
S(21)	141·94	136·81	88·33	85·00	160·95		
S(22)	139·24	98·16	164·47	89·74	85·06	78·03	
S(42)	97·94	145·04	89·02	161·54	91·26	77·55	80·88

Mo(3)	Mo(1)	Mo(2)	S(2)	S(3)	S(4)	S(31)
Mo(2)	59·43					
S(2)	54·46	99·63				
S(3)	100·39	53·84	100·04			
S(4)	53·79	53·82	106·58	105·53		
S(31)	145·64	138·30	91·19	84·73	157·18	
S(32)	116·18	126·57	120·34	136·15	80·15	78·50

of this plane] with the following torsion angles: Mo(1)—[1°]—Mo(2)—[−23°]—S(42)—[43°]—P(4)—[−43°]—S(41)—[21°]—Mo(1). The bridging residue reduces the maximal possible symmetry from C_{3v} to C_s [mirror plane through Mo(3), S(4), and S(1)] which is approximately fulfilled within the Mo_3S_4 core but clearly disturbed by the organic ligands. The S atoms can be grouped into four structurally different kinds with averaged bond angles of 71·95 (4) (μ_3-S), 73·81 (4) (μ-S), 87·62 (7) (bidentate ligand) and 107·71 (7)° (bridging ligand). The four dialkyldithiophosphinato ligands show the expected geometry as in

similar Mo complexes {*e.g.* $[(Et_2PS_2)_3Mo_3$-$S(S_2)_3]^+.(Et_2PS_2)^-$, Meyer & Wunderlich (1982)}; this includes the tendency to disorder within these ligands {as in $[Cd(Et_2PS_2)_2]$, Wunderlich (1986)} which cannot be excluded for the ligand involving P(1) of the present structure.

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Structure of the Antitumour Agent Di-μ-acetato-(O)-bis[(2-pyridinecarbaldehyde thiosemicarbazonato)copper(II)]

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Abstract. $[Cu_2(C_2H_3O_2)_2(C_7H_7N_4S)_2]$, $M_r = 603·62$, triclinic, $P\bar{1}$, $a = 8·834$ (1), $b = 8·989$ (1), $c = 8·801$ (1) Å, $\alpha = 117·48$ (1), $\beta = 91·77$ (1), $\gamma = 110·94$ (1)°, $V = 562·7$ (3) Å³, $Z = 1$, $D_x = 1·78$ g cm⁻³, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 21·17$ cm⁻¹, $F(000) = 306$, room temperature, final $R = 0·0291$ for 2052 observed reflections. This crystal structure reveals that the title compound is in a dimeric form with the two Cu^{2+} ions in an unusual distorted square-pyramidal coordination. There is no direct metal—metal bond. The two metallic atoms are linked by two bridging acetate groups.

Introduction. The tridentate ligand 2-(2-pyridine-methylene)hydrazinecarbothioamide (more commonly called 2-pyridinecarbaldehyde thiosemicarbazone

or 2-formylpyridine thiosemicarbazone, Hpats) has aroused great interest because of its proven anti-tumour activity (Agrawal & Sartorelli, 1975). Recent work has shown that iron and copper complexes, especially the latter, are even more potent inhibitors of cell proliferation than the ligand itself. In the case of the copper(II) complex, it appears that it initially binds to glutathione by way of Cu—S bonds, this adduct then initiating redox reactions with thiols leading to the generation of copper(I) (Antholine & Taketa, 1984). The chemical properties of copper complexes of Hpats are well documented (Antholine, Knight & Petering, 1977) but no crystallographic data have hitherto been reported. We now describe the structure of the title compound, which should help in the interpretation of spectroscopic investigations and in the elucidation of the mode of drug action.

Experimental. Black rod-like crystals of Cu(pats)-(OCOCH$_3$) were prepared by allowing copper acetate solution (0·17 mol dm^{-3}) and a saturated solution of Hpats in aqueous acetic acid (0·5 mol dm^{-3}) to diffuse into each other in a silica gel prepared by adding molar acetic acid in slight excess to a solution of sodium silicate in water (Bridle & Lomer, 1965). Elemental analyses (C, H, N and S) for the complex were in good agreement with the proposed formula. Full intensity data were obtained from a crystal 0·30 × 0·30 × 0·25 mm, on an Enraf–Nonius CAD-4 four-circle diffractometer using an ω–2θ scanning routine. The

Table 2. *Bond lengths* (Å) *and angles* (°) *for* [Cu(pats)(OAc)]$_2$

S(1)—Cu(1)	2·268 (1)	O(1)—Cu(1)	2·422 (2)
N(1)—Cu(1)	2·052 (2)	O(1')—Cu(1)	1·946 (2)
C(7)—S(1)	1·717 (3)	C(8)—O(1)	1·279 (3)
C(8)—O(2)	1·224 (3)	C(1)—N(1)	1·333 (3)
C(5)—N(1)	1·350 (3)	N(2)—Cu(1)	1·969 (2)
N(3)—N(2)	1·360 (3)	C(6)—N(2)	1·287 (3)
C(7)—N(3)	1·336 (3)	C(7)—N(4)	1·336 (4)
C(2)—C(1)	1·380 (4)	C(3)—C(2)	1·365 (4)
C(4)—C(3)	1·380 (4)	C(5)—C(4)	1·382 (4)
C(6)—C(5)	1·452 (4)	C(9)—C(8)	1·507 (4)
O(1)—Cu(1)—S(1)	99·4 (1)	N(1)—Cu(1)—S(1)	162·5 (1)
N(1)—Cu(1)—O(1)	91·8 (1)	N(2)—Cu(1)—S(1)	83·2 (1)
N(2)—Cu(1)—N(1)	80·5 (1)	C(8)—O(1)—Cu(1)	137·9 (2)
C(7)—S(1)—Cu(1)	95·9 (1)	C(1)—N(1)—Cu(1)	111·5 (2)
C(5)—N(1)—C(1)	118·2 (2)	N(3)—N(2)—Cu(1)	124·4 (2)
C(6)—N(2)—Cu(1)	116·3 (2)	C(6)—N(2)—N(3)	119·2 (2)
C(7)—N(3)—N(2)	111·2 (2)	C(2)—C(1)—N(1)	122·0 (3)
C(3)—C(2)—C(1)	119·5 (3)	C(4)—C(3)—C(2)	119·5 (3)
C(5)—C(4)—C(3)	118·1 (3)	C(4)—C(5)—N(1)	122·6 (3)
C(6)—C(5)—N(1)	115·3 (2)	C(6)—C(5)—C(4)	122·1 (2)
C(5)—C(6)—N(2)	116·3 (2)	N(3)—C(7)—S(1)	125·2 (2)
N(4)—C(7)—S(1)	118·8 (2)	N(4)—C(7)—N(3)	116·0 (2)
C(9)—C(8)—O(1)	115·9 (3)	C(9)—C(8)—O(2)	120·4 (3)
O(2)—C(8)—O(1)	124·4 (2)	O(1')—Cu(1)—N(1)	96·7 (1)
O(1')—Cu(1)—O(1)	76·5 (1)	O(1')—Cu(1)—N(2)	174·5 (1)
O(1')—Cu(1)—S(1)	98·9 (1)		

Note: O(1') is related to O(1) by a centre of symmetry.

structure was solved by direct methods, and refined using full-matrix least-squares techniques based on F. Non-H atoms were refined anisotropically. H atoms were located from ΔF maps and refined. Lattice-constants determination: 25 reflections, with $22 < \theta < 24°$. Total data collected = 2359, total unique data = 2149, with $1 < \theta < 26°$, $0 < h < 10$, $-11 < k < 11$, $-10 < l < 10$, $R_{int} = 0·01$. Unobserved reflections = 162, significance test $F_o > 3\sigma(F_o)$. Refined parameters 194, final $R = 0·0291$, $wR = 0·0301$, weighting scheme $w = (\sigma^2 F + 0·0001 F^2)^{-1}$. Final cycle: max. Δ/σ 0·15, max. ΔF peak 0·5 e Å^{-3}. No absorption correction, scanning rate 4° min^{-1}, four standard reflections (328, 3,4,10, 746, 756), intensity variation < 1%. Scattering factors have been obtained from *International Tables for X-ray Crystallography* (1974). All calculations were carried out using *SHELX*76 (Sheldrick, 1976), *PLUTO*78 (Motherwell & Clegg, 1978), and private programs, on a CRAY-1S and a Honeywell Multics computer.

Discussion. The space group was confirmed by successful structure solution. The final atomic parameters are presented in Table 1, and bond lengths and angles in Table 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43314 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates* (×10^4) *and thermal parameters* (×10^3 Å^2) *for* [Cu(pats)(OAc)]$_2$

$U_{eq} = 0·33$ trace U.

	x	y	z	U_{eq}/U_{iso}
Cu(1)	9578 (1)	380 (1)	3321 (1)	29 (1)
S(1)	8189 (1)	2186 (1)	4466 (1)	44 (1)
O(1)	8628 (2)	−1555 (2)	4613 (2)	33 (1)
O(2)	7082 (3)	−3337 (3)	5563 (3)	65 (1)
N(1)	10508 (3)	−1345 (3)	1589 (3)	30 (1)
N(2)	7927 (3)	−719 (3)	1124 (3)	29 (1)
N(3)	6665 (3)	−221 (3)	998 (3)	34 (1)
N(4)	5595 (4)	1824 (4)	2542 (4)	46 (1)
C(1)	11841 (4)	−1635 (4)	1871 (4)	38 (2)
C(2)	12243 (4)	−2917 (4)	536 (4)	46 (1)
C(3)	11258 (4)	−3924 (4)	−1131 (4)	47 (1)
C(4)	9884 (4)	−3630 (4)	−1462 (4)	40 (1)
C(5)	9543 (3)	−2336 (3)	−64 (3)	30 (2)
C(6)	8133 (3)	−1923 (3)	−283 (3)	32 (2)
C(7)	6741 (3)	1176 (4)	2540 (3)	34 (2)
C(8)	7257 (3)	−2766 (4)	4529 (3)	34 (2)
C(9)	5811 (5)	−3480 (7)	3054 (6)	59 (3)
H(1)	12489 (39)	−891 (42)	3082 (42)	52 (9)
H(2)	13136 (39)	−3090 (40)	807 (39)	48 (9)
H(3)	11469 (39)	−4777 (41)	−2028 (39)	52 (9)
H(4)	9175 (37)	−4296 (40)	−2603 (38)	44 (8)
H(51)	4953 (43)	1408 (44)	1656 (47)	52 (10)
H(52)	5648 (43)	2826 (48)	3551 (46)	62 (10)
H(6)	7398 (35)	−2465 (36)	−1424 (36)	37 (7)
H(91)	4919 (64)	−4326 (65)	2966 (58)	113 (18)
H(92)	6098 (50)	−3783 (55)	2120 (57)	78 (15)
H(93)	5502 (70)	−2573 (78)	3371 (70)	141 (25)

The asymmetric unit was found to be one Cu(pats)-(OAc) unit, (I), with the molecule as a whole containing two such units. The centrosymmetrically related Cu^{II} ions are linked by bridging acetate groups (Fig. 1). Bond lengths and angles within the organic moieties are comparable to those found in similar complexes (Mathew & Palenik, 1969). Fig. 2 contains the structure viewed along the c axis.
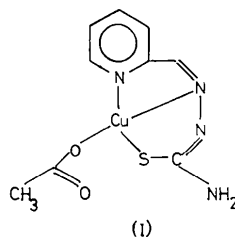

(I)

Table 3 compares the metal—ligand bonds found in this structure with those found for similar ones in the literature (Gabe, Taylor, Glusker, Minkin & Patterson, 1969; Brown & Chidamabaram, 1973; Frasson, Bardi & Bezzi, 1959; Pignedoli & Peyronel, 1962; Takii, Emori & Muto, 1979). The acetate group acts as a monoatomic bridging group (Hämäläinen, Ahlgren & Turpeinen, 1982), with two distinct Cu—O bond lengths. The shortest Cu—carbonyl O distance is 2·922 (2) Å, significantly longer than the average Cu—O bond length quoted in the literature. The coordination number of each Cu^{II} ion is, therefore, five, with this Cu—carbonyl non-bonded contact contributing to the distortion of the geometry round the Cu^{2+} ion. This was found to be distorted square pyramidal. The *base* of the pyramid is made up of the acetate oxygen O(1'), S(1), N(1) and N(2). The Cu^{2+} ion is displaced from the mean plane of the base. The apex of the pyramid is made up of the second acetate oxygen O(1). The pats moiety acts as a tridentate ligand, forming two planar five-membered chelate rings with the metal ion. Within the asymmetric unit the mean planes of the two chelate rings are approximately coplanar with each other and with the pyridyl group, the maximum dihedral angle subtended between pairs of these rings being only 5 (1)°. The Cu···Cu distance of 3·442 (1) Å is longer than in cases where some metal—metal interactions occur, such as copper(II) acetate monohydrate. The absence of a Cu···Cu interaction is indicated by the magnetic moment of 1·83 BM at 293 K (Bell, Lott & Hearn, 1986) (1 BM ≃ 9·274 × 10⁻²⁴ JT⁻¹).

Coordination numbers of five are remarkably common for Cu^{II} chelates, and the slightly distorted square-based pyramidal coordination round Cu^{II} is widely found in both chemical and biochemical situations. Furthermore, five-coordinate copper complexes in the solid state may show the structural feature of an

atom of a neighbouring chelate being located in a site further away from the other donors, giving 'quasi-octahedral' structures (Hoskins & Whillans, 1973). No evidence for this has been found in the structure of the title compound; the shortest Cu···ligand contacts between nearest neighbours are well in excess of 3 Å. The unusual coordination present in this complex may well be due to the fact that the ligand is too bulky as a whole to allow the close approach of a sixth donor atom in the solid state.

ESR studies (Bell *et al.*, 1986) of the complex in Me$_2$SO at 77 K are consistent with distorted six-coordination around Cu. It is likely that a solvent molecule coordinates to the metal ion at a distance, thus converting the distorted square pyramid into a quasi-octahedral structure.

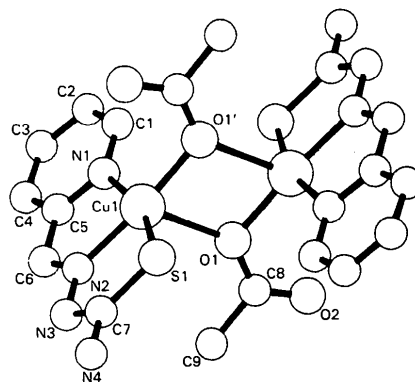Further studies on the structure of the complex in solution are in progress.

Fig. 1. The molecular structure of the Cu(pats)(OAc) dimer. The H atoms have been omitted for clarity. The asymmetric unit bears the numbering scheme.
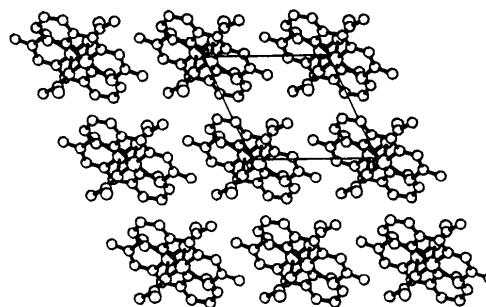

Fig. 2. The title crystal structure viewed along the c axis.

Table 3. *Interatomic distances (Å) in* [Cu(*pats*)(O*Ac*)]₂ *and related compounds*

Compound[a]	[Cu(pats)-(OAc)]₂	Cu(dtc)₂	Cu(OAc)₂	Cu(dmg)₂	[Cu(mspd)-(OAc)]₂
Reference	This work	(1)	(2)	(3)	(4,5)
Cu···Cu	3·442 (3)	3·38	2·62		3·38
Cu···O	2·422 (2)		1·969	2·45	2·51
	1·946 (2)				2·83
Cu···N	2·052 (2)[b]			1·94[c]	
	1·969 (2)				
Cu···S	2·268 (1)	2·32		2·30	
		2·71		2·31	

(*a*) dtc = dialkyldithiocarbamato; dmg = dimethylglyoximato; mspd = *N*-methyl-*N'*-salicylidene-1,3-propanediaminato. (*b*) Cu–N(pyridyl) bond. (*c*) Mean bond length.

References: (1) Pignedoli & Peyronel (1962); (2) Brown & Chidamabaram (1973); (3) Frasson *et al.* (1959); (4) Hämäläinen *et al.* (1982); (5) Takii *et al.* (1979).

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Structure of a Dinuclear Gold(II) Ylide Complex Containing a Gold–Selenium Bond

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Abstract. [{Au(CH₂)₂P(C₆H₅)₂}₂(Cl)(C₆H₅Se)], $M_r = 1011·9$, triclinic, $P\bar{1}$, $a = 11·966$ (5), $b = 14·970$ (4), $c = 9·466$ (3) Å, $\alpha = 98·37$ (2), $\beta = 97·50$ (3), $\gamma = 100·41$ (3)°, $V = 1628·4$ (9) Å³, $D_x = 2·064$ Mg m⁻³, $Z = 2$, $\mu = 10·29$ mm⁻¹, $\lambda(\text{Mo } K\alpha) = 0·71073$ Å, $F(000) = 952$, $T = 298$ K. The X-ray crystal structure of the first gold(III) complex possessing bonds to selenium, benzeneselenolato[bis-μ-(dimethylene)-diphenylphosphoranyl-*C,C'*]chlorodigold(II), is described. The asymmetric unit consists of one complete dinuclear gold(II) ylide bridged symmetrically by ylide anion ligands. The gold centers have square-planar coordination geometries and are linked by a 2·655 (1) Å metal–metal bond. Each Au atom forms bonds to two methylene carbons of the ylide ligands, with one bonded to a chloride ligand, the other to the Se atom of a phenyl selenide group. Convergence to

conventional R values of $R = 0·0342$ and $wR = 0·0366$ was obtained using 361 variable parameters and 3037 reflections with $F > 3\sigma(F)$.

Introduction. We recently reported the structures of two novel organometallic complexes containing pairs of dinuclear Auᴵᴵ ylide dimers linked together by four- and five-atom polysulfide bridges (Fackler & Porter, 1986). The unusual structures of these large twelve- and thirteen-atom polysulfide rings containing Auᴵᴵ centers piqued our interest in preparing and characterizing other dinuclear Auᴵᴵ ylide complexes containing chalcogenide ligands. As part of this investigation, we examined the reaction of diphenyl diselenide, (C₆H₅)₂Se₂, with the dinuclear Auᴵ ylide, [Au(CH₂)P(C₆H₅)₂]₂. Previous work has shown that this complex readily undergoes two-center two-electron oxidative-addition reactions in the presence of a number of halide and alkyl halide substrates leading to the formation of

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