whatever the equilibrium conformation of the free nickelocene molecule may be, the barrier between eclipsed and staggered conformations is very small. The conformation in the crystal would then be determined almost exclusively by packing forces and these, in the monoclinic crystal structure, clearly favour the centrosymmetric staggered conformation.

Thus, of the two extreme models for the RT crystal, one involving dynamic disorder of centrosymmetric molecules, the other involving static disorder of non-centrosymmetric molecules, the balance of the evidence seems to suggest that the former model is closer to the mark. In order to settle the question, more information about the temperature dependence of the thermal ellipsoids would be required.

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The Structures of Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) and Bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)copper(II)

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Abstract

Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) is triclinic with a = 9·576 (6), b = 9·017 (7), c = 9·129 (7) Å, α = 125·61 (8), β = 101·73 (4), γ = 94·02 (6)°, Z = 1, space group $P\bar{1}$. The structure was refined to R = 0·039 for 2019 observed reflections. The compound is monomeric, the stereochemistry at Cu being the distorted, elongated, octahedral $CuN_2O_2Cl_2$ chromophore with a Cu—Cl length of 2·92 Å. Bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)copper(II) is also triclinic, with a = 10·537 (1), b = 10·521 (1), c = 15·377 (2) Å, α = 121·031 (5), β = 110·958 (5), γ = 86·105 (3)°, Z = 2, space group $P\bar{1}$. This structure was refined to R = 0·076 for 3231 observed reflections. The stereochemistry at Cu is a distorted, elongated, octahedral CuN_2O_4 chromophore.

Introduction

In a series of papers entitled *Substituted Phenols as Ligands* (Bullock & Jones, 1970, 1971; Hobson, Ladd & Povey, 1973; Bullock, Hobson & Povey, 1974; Ladd & Povey, 1976) attempts were made to correlate the solid-state diffuse electronic reflectance spectra of some Cu^{II} complexes with the stereochemistry of the coordination polyhedra around the metal. Methods have been established (Hathaway & Tomlinson, 1970; Hathaway & Billing, 1970) whereby stereochemical deduc-

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tion can be made from the analysis of reflectance spectra within a closely related group of compounds, although it has been pointed out (McKenzie, 1970; Hathaway, 1972) that knowledge of the crystal structure of at least one member of the series is probably essential, and any deduction should be made with care.

A series of Cu^{II} complexes with nitrogen bases and substituted phenols as ligands provides a closely related group of compounds wherein such correlations between electronic spectra and stereochemistry can be investigated. The solid-state diffuse reflectance spectra of these compounds fall into three classes, and structure analysis of one member of each class led to tentative assignments of the Cu coordination polyhedra in other members of the series according to their spectral group. Subsequent structure analyses (Ladd & Povey, 1976; Greenhough & Ladd, 1978*a*) have shown that the stereochemical predictions for bis(2-methoxy-4-nitrophenolato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-copper(II) dihydrate and bis(4-formyl-2-methoxyphenolato)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)-copper(II) tetrahydrate from the solid-state diffuse reflectance spectra are essentially correct. However, the structure analysis for the anhydrous compound of the latter substance showed a result totally at variance with the prediction from the reflectance spectrum (Greenhough & Ladd, 1978*b*).

From its diffuse reflectance spectrum, bis(pyridine)-bis(2,4,6-trichlorophenolato)copper(II) was assigned a tetragonally distorted, octahedral stereochemistry, the tetragonal distortion being large (Bullock, Hobson & Povey, 1974). Spectral evidence was thought to favour a polymeric structure, with the phenolic O atoms as bridges. The steric hindrance of the pyridine ligands and poor donor properties of the 2-chloro substituent made the polymeric structure likely.

The reflectance spectrum of bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)copper(II) suggested that the tetragonal distortion in this compound would be less than that of the first-named compound, but with the distance between the Cu and O atoms of the methoxy groups somewhat greater than the average of 2·37 Å found for bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) monohydrate (Hobson, Ladd & Povey, 1973).

Experimental

Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II), $C_{22}H_{14}Cl_6CuN_2O_2$, $M_r = 614{\cdot}65$, triclinic, $a = 9{\cdot}576\,(6)$, $b = 9{\cdot}017\,(7)$, $c = 9{\cdot}129\,(7)$ Å, $\alpha = 125{\cdot}61\,(8)$, $\beta = 101{\cdot}73\,(4)$, $\gamma = 94{\cdot}02\,(6)°$, $V_c = 609{\cdot}6\,(4)$ Å^3, space group $P\bar{1}$, $D_m = 1{\cdot}64\,(2)$, $D_x = 1{\cdot}673\,(7)$ Mg m^{-3}, μ(Cu $K\alpha$) = 7·54 mm^{-1}, $F(000) = 307$, $\lambda = 1{\cdot}54178$ Å.

The crystals were dark, reddish-brown plates having average dimensions of about 0·5, 0·4, 0·1 mm. Initial cell dimensions were obtained from Weissenberg photographs and refined by least squares from the θ values of 21 reflections measured on a Siemens four-circle diffractometer (AED). The reflections had θ values between 50 and 70°, and the α_1 and α_2 peaks were resolved in each case, giving 42 independent measurements. The diffractometer was operated with variable scan range and scan speed to $\theta = 70°$, the five-value measurement method (Hoppe, 1965) and Ni-filtered Cu $K\alpha$ radiation. Of the 2100 reflections collected, 2019 had $I/\sigma(I) > 2{\cdot}58$ (observational variances based on counting statistics) and were classified as observed. Lorentz and polarization corrections were made.

Bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)-copper(II), $C_{26}H_{26}CuN_4O_8$, $M_r = 586{\cdot}04$, triclinic, $a = 10{\cdot}537\,(1)$, $b = 10{\cdot}521\,(1)$, $c = 15{\cdot}377\,(2)$ Å, $\alpha = 121{\cdot}031\,(5)$, $\beta = 110{\cdot}958\,(5)$, $\gamma = 86{\cdot}105\,(3)°$, $V_c = 1349{\cdot}6\,(3)$ Å^3, space group $P\bar{1}$, $D_m = 1{\cdot}42\,(2)$, $D_x = 1{\cdot}442\,(1)$ Mg m^{-3}, μ(Cu $K\alpha$) = 1·82 mm^{-1}, $F(000) = 606$, $\lambda = 1{\cdot}54178$ Å.

The crystals, recrystallized from benzene, were dark-brown plates of average dimensions 0·5, 0·3, 0·2 mm. Experimental details were similar to those used for the first compound, 26 reflections being scanned for the cell dimensions, giving 52 independent measurements (α_1 and α_2) in all. Of the 4573 reflections collected, 3231 were classified as observed. The percentage of unobserved reflections (29·3) was much greater for this compound than for the first (3·9), possibly because of the existence of Cu atoms in special positions in the γ-picoline complex.

Derivation and refinement of structures

For both compounds, the heavy atoms were located from a Patterson synthesis. For the first compound (CUTP, T = 2,4,6-trichlorophenolato, P = pyridine), with $Z = 1$, Cu was placed at the origin; hence, the Cu—Cl vectors located the Cl atoms. An electron density synthesis computed with the phases of these atoms and an estimated isotropic temperature factor ($B = 2{\cdot}9$ Å^2) revealed all the non-hydrogen atoms in the pyridine group, and the O atom; a second such synthesis based on the phases of the known atoms revealed the remaining non-hydrogen atoms.

As this compound has a relatively large linear-absorption coefficient, a correction for absorption was included (de Meulenaer & Tompa, 1965); it depends strongly on the accuracy of the crystal-dimension measurements, which are not easy to obtain accurately for a triclinic crystal. The values obtained for perpendicular distances between pairs of parallel planes in the crystal used for data collection were: (100)–($\bar{1}$00)

0·141, (010)–(0$\bar{1}$0) 0·261, (001)–(00$\bar{1}$) 0·291, (0$\bar{1}$1)–(01$\bar{1}$) 0·437 mm. Inclusion of absorption-corrected intensities resulted in a marked improvement in R (0·053 to 0·044). Scattering factors were those of Freeman & Watson (1961) for Cu, Dawson (1960) for Cl, Hoerni & Ibers (1954) for the other non-hydrogen atoms and Stewart, Davidson & Simpson (1965) for H.

For the second compound (CUNPIC, N = 2-methoxy-4-nitrophenolato, PIC = γ-picoline) also, the Cu atoms were located from a Patterson synthesis; the Cu–Cu vector in the unit cell had the coordinates 0,0,$\frac{1}{2}$. Thus, the Cu atoms were either at centres of symmetry separated by $c/2$ with two centrosymmetric unique molecules in the unit cell, or in general positions with the two molecules related by a centre of symmetry, and with the two Cu atoms along **c**.

As the heavy atom made a comparatively small contribution [less than 10% of $F(000)$], an electron density synthesis computed with the phases of this atom and an estimated isotropic temperature factor (B = 4·3 Å^2) gave a comparatively poor agreement (R = 0·57). Scattering factors used were those of Cromer & Waber (1974) for non-hydrogen atoms, and Stewart, Davidson & Simpson (1965) for H.

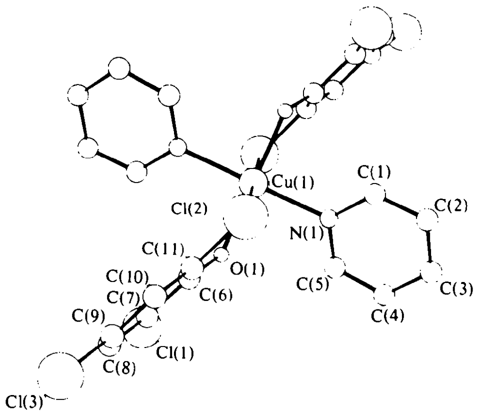

Fig. 1. Perspective view of the CUTP molecule, showing the atom labelling.

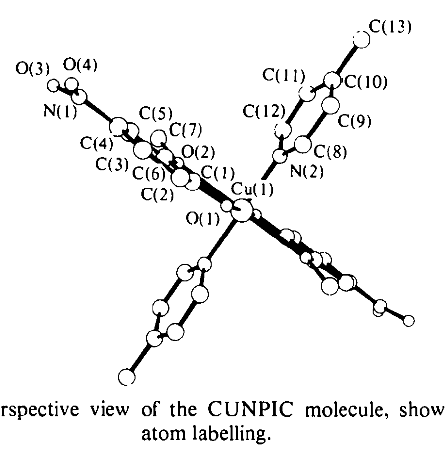

Fig. 2. Perspective view of the CUNPIC molecule, showing the atom labelling.

Table 1. *Atomic coordinates and e.s.d.'s for all atoms of CUTP*

	x	y	z
Cu	0	0	0
Cl(1)	0·46186 (9)	−0·11185 (11)	0·12600 (12)
Cl(2)	0·11526 (8)	0·38041 (12)	0·35215 (12)
Cl(3)	0·61591 (9)	0·51246 (12)	0·84591 (11)
O	0·20774 (20)	0·03257 (28)	0·07522 (28)
N	0·02514 (25)	0·10199 (33)	−0·14451 (34)
C(1)	−0·06685 (31)	0·20525 (42)	−0·15714 (44)
C(2)	−0·04631 (36)	0·29212 (48)	−0·23653 (50)
C(3)	0·07263 (38)	0·27153 (50)	−0·30997 (51)
C(4)	0·16481 (35)	0·16912 (50)	−0·29545 (47)
C(5)	0·13860 (31)	0·08634 (44)	−0·21294 (43)
C(6)	0·29545 (27)	0·14136 (38)	0·24812 (39)
C(7)	0·42455 (29)	0·09513 (39)	0·29872 (42)
C(8)	0·52221 (30)	0·20557 (42)	0·48003 (44)
C(9)	0·49364 (31)	0·37106 (42)	0·61846 (42)
C(10)	0·36963 (32)	0·42620 (40)	0·57996 (43)
C(11)	0·27367 (29)	0·31139 (40)	0·39828 (42)
H(1)	0·009 (4)	0·162 (6)	−0·109 (6)
H(2)	0·033 (5)	0·335 (6)	−0·269 (6)
H(3)	−0·021 (5)	0·314 (7)	−0·317 (7)
H(4)	0·250 (5)	0·153 (6)	−0·344 (6)
H(5)	0·206 (5)	0·012 (6)	−0·205 (6)
H(6)	0·611 (5)	0·166 (6)	0·508 (6)
H(7)	0·350 (4)	0·545 (6)	0·680 (6)

It was necessary to compute a series of electron density syntheses, and they were backed up by use of direct methods with *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977; an update of *MULTAN* 72). This work showed that the Cu atoms were at centres of symmetry, and the positions of all the non-hydrogen atoms in the structure were deduced.

Both structures were refined by full-matrix least-squares methods, with anisotropic temperature factors. Positions of H atoms were obtained from both known molecular geometry and difference syntheses. Corrections for anomalous dispersion for the heavy atoms (Cromer & Liberman, 1970), and the extinction parameter, r^* (Larson, 1970), were included in the refinement of CUTP. The final values for R were 0·039 for CUTP and 0·076 for CUNPIC ($R = \sum||\Delta F||\sum|F_o|$).†

Fig. 1 shows the structure of the CUTP molecule with the atom labelling. Table 1 lists the atomic coordinates. Fig. 2 shows the structure of the CUNPIC molecule with the atom labelling. Table 2 lists the coordinates of the non-hydrogen atoms and Table 3 those of the H atoms of CUNPIC.

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† Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35434 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic coordinates and e.s.d.'s for non-hydrogen atoms of CUNPIC*

	x	*y*	*z*
Cu(1)	0	0	0
Cu(1)′	0	0	0·5
N(1)	0·4875 (5)	0·2830 (7)	0·5109 (4)
N(2)	0·1534 (5)	−0·0209 (5)	−0·0561 (4)
N(1)′	−0·3564 (8)	−0·5897 (7)	−0·0061 (6)
N(2)′	0·0637 (5)	−0·1483 (5)	0·5489 (4)
O(1)	0·1034 (4)	−0·0756 (4)	0·0909 (3)
O(2)	0·1438 (4)	0·2213 (4)	0·1744 (3)
O(3)	0·4898 (6)	0·4202 (6)	0·5574 (4)
O(4)	0·5675 (4)	0·2233 (6)	0·5547 (4)
O(1)′	0·0361 (4)	−0·1283 (4)	0·3683 (3)
O(2)′	−0·2110 (4)	−0·1672 (5)	0·3691 (3)
O(3)′	−0·3436 (7)	−0·6377 (8)	−0·0937 (6)
O(4)′	−0·4526 (7)	−0·6351 (6)	0·0022 (5)
C(1)	0·1912 (5)	0·0105 (6)	0·1897 (4)
C(2)	0·2656 (6)	−0·0485 (7)	0·2538 (5)
C(3)	0·3616 (6)	0·0385 (7)	0·3578 (5)
C(4)	0·3851 (6)	0·1911 (7)	0·4018 (5)
C(5)	0·3128 (6)	0·2577 (7)	0·3437 (5)
C(6)	0·2195 (6)	0·1698 (6)	0·2402 (5)
C(7)	0·1761 (10)	0·3727 (8)	0·2099 (7)
C(8)	0·2316 (6)	−0·1291 (7)	−0·0671 (5)
C(9)	0·3370 (6)	−0·1454 (8)	−0·1041 (5)
C(10)	0·3633 (7)	−0·0457 (9)	−0·1318 (5)
C(11)	0·2843 (7)	0·0678 (8)	−0·1174 (6)
C(12)	0·1806 (6)	0·0777 (7)	−0·0813 (6)
C(13)	0·4776 (8)	−0·0645 (11)	−0·1744 (6)
C(1)′	−0·0553 (6)	−0·2360 (6)	0·2810 (4)
C(2)′	−0·0271 (7)	−0·3318 (7)	0·1854 (5)
C(3)′	−0·1249 (8)	−0·4442 (8)	0·0921 (6)
C(4)′	−0·2533 (7)	−0·4700 (7)	0·0911 (5)
C(5)′	−0·2858 (6)	−0·3806 (6)	0·1827 (5)
C(6)′	−0·1887 (6)	−0·2666 (6)	0·2742 (4)
C(7)′	−0·3495 (7)	−0·1654 (10)	0·3608 (6)
C(8)′	0·1588 (6)	−0·2358 (7)	0·5178 (5)
C(9)′	0·2017 (7)	−0·3392 (7)	0·5465 (6)
C(10)′	0·1438 (7)	−0·3610 (7)	0·6100 (5)
C(11)′	0·0485 (7)	−0·2718 (7)	0·6393 (5)
C(12)′	0·0105 (6)	−0·1686 (6)	0·6087 (5)
C(13)′	0·1872 (9)	−0·4735 (8)	0·6430 (7)

Table 3. *Fractional coordinates for* H *atoms in CUNPIC*

	x	*y*	*z*
H(1)	0·253	−0·167	0·217
H(2)	0·423	−0·017	0·400
H(3)	0·331	0·370	0·378
H(4)	0·213	−0·201	−0·047
H(5)	0·395	−0·232	−0·113
H(6)	0·300	0·143	−0·140
H(7)	0·120	0·180	−0·062
H(8)	0·150	0·447	0·277
H(9)	0·117	0·390	0·143
H(10)	0·277	0·400	0·230
H(11)	0·433	−0·133	−0·243
H(12)	0·540	−0·150	−0·160
H(13)	0·483	−0·007	−0·007
H(1)′	0·067	−0·317	0·187
H(2)′	−0·130	−0·523	0·016
H(3)′	−0·384	−0·429	0·143
H(4)′	0·198	−0·225	0·471
H(5)′	0·274	−0·402	0·523
H(6)′	0·006	−0·281	0·686
H(7)′	−0·050	−0·090	0·609
H(8)′	−0·347	−0·187	0·377
H(9)′	−0·317	−0·050	0·443
H(10)′	−0·413	−0·150	0·300
H(11)′	0·150	−0·423	0·583
H(12)′	0·257	−0·483	0·617
H(13)′	0·200	−0·567	0·713

Table 4. *Bond lengths* (Å) *and their e.s.d.'s for non-hydrogen atoms in CUTP*

Cu–O	1·911 (2)	Cu–N	2·036 (4)
Cl(1)–C(7)	1·732 (3)	Cl(2)–C(11)	1·745 (3)
Cl(3)–C(9)	1·742 (3)	O–C(6)	1·306 (3)
N–C(1)	1·362 (5)	N–C(5)	1·337 (5)
C(1)–C(2)	1·367 (7)	C(2)–C(3)	1·407 (6)
C(3)–C(4)	1·363 (6)	C(4)–C(5)	1·374 (7)
C(6)–C(7)	1·408 (5)	C(7)–C(8)	1·389 (4)
C(8)–C(9)	1·380 (4)	C(9)–C(10)	1·378 (5)
C(10)–C(11)	1·385 (4)	C(11)–C(6)	1·411 (4)
Cl(2)–Cu	2·916 (4)		

Results and discussion

Tables 4 and 5 list the bond lengths and angles in CUTP. The Cu atom shows the expected square-planar coordination and, in addition, there are two Cl atoms from the *ortho* position in the phenolato ring at a coordinating distance of about 2·92 Å. These values are in accordance with predictions from the reflectance spectrum, the octahedral symmetry showing large tetragonal distortion. (*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)bis(2,4,6-trichlorophenolato)copper(II), in a different spectral class, has a distorted, square-planar configuration (Vogt, La Placa & Bednowitz, 1968) with the shortest Cu–Cl distance of 3·05 Å. The upper limit for the Cu–Cl bond following the spectral change is not known, but its difference between these two compounds is only 0·15 Å.

CUTP is monomeric, not bridged by way of the phenolato O atoms, and the polymeric structure (Bullock, Hobson & Povey, 1974) mentioned in the *Introduction* is incorrect.

Another 2,4,6-trichlorophenolatocopper(II) complex (CUTI), the structure of which has been reported (Wong, Palmer & Tomimcetsu, 1976), is that with imidazole groups replacing the pyridine groups in CUTP. Table 6 lists corresponding bond lengths in the two compounds.

Cu–N lengths are normally in the range 1·95–2·01 Å (Iverson, Lindberg & Tigri, 1972), although slightly longer bonds have been found, particularly in bis(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II) (Hobson, Ladd & Povey, 1973) where the lengths

Table 5. *Bond angles (°) and their e.s.d.'s involving non-hydrogen atoms in CUTP and bond lengths* (Å) *and angles* (°) *and their e.s.d.'s for* H *atoms*

O–Cu–N	89·0 (1)	O–C(6)–C(11)	125·1 (3)
Cl(2)–Cu–N	89·0 (2)	C(7)–C(6)–C(11)	114·0 (2)
Cl(2)–Cu–O	74·0 (1)	C(6)–C(7)–C(8)	123·4 (3)
Cu–O–C(6)	126·2 (2)	C(7)–C(8)–C(9)	118·9 (3)
Cu–N–C(1)	119·9 (3)	C(8)–C(9)–C(10)	121·1 (3)
Cu–N–C(5)	121·8 (3)	C(9)–C(10)–C(11)	118·4 (3)
C(1)–N–C(5)	118·1 (4)	C(10)–C(11)–C(6)	124·1 (3)
N–C(1)–C(2)	122·3 (3)	C(6)–C(7)–Cl(1)	118·0 (2)
C(1)–C(2)–C(3)	118·8 (4)	C(8)–C(7)–Cl(1)	118·5 (3)
C(2)–C(3)–C(4)	118·7 (5)	C(6)–C(11)–Cl(2)	117·8 (2)
C(3)–C(4)–C(5)	119·7 (4)	C(10)–C(11)–Cl(2)	118·0 (2)
C(4)–C(5)–N	122·6 (4)	C(8)–C(9)–Cl(3)	119·5 (3)
O–C(6)–C(7)	120·9 (2)	C(10)–C(9)–Cl(3)	119·4 (2)

C(1)–H(1)	0·96 (6)	C(5)–H(5)	0·85 (4)
C(2)–H(2)	1·00 (10)	C(8)–H(6)	0·97 (4)
C(3)–H(3)	1·02 (13)	C(10)–H(7)	0·99 (6)
C(4)–H(4)	0·97 (9)		

N–C(1)–H(1)	115 (4)	C(3)–C(4)–H(4)	118 (3)
C(2)–C(1)–H(1)	123 (4)	C(4)–C(5)–H(5)	118 (3)
C(1)–C(2)–H(2)	126 (8)	N–C(5)–H(5)	119 (3)
C(3)–C(2)–H(2)	112 (8)	C(7)–C(8)–H(6)	118 (1)
C(2)–C(3)–H(3)	102 (9)	C(9)–C(8)–H(6)	123 (1)
C(4)–C(3)–H(3)	132 (8)	C(9)–C(10)–H(7)	121 (2)
C(5)–C(4)–H(4)	123 (3)	C(11)–C(10)–H(7)	120 (2)

Table 6. *Bond lengths* (Å) *and angles* (°) *for comparable atoms in CUTP and CUTI*

	CUTP	CUTI
Cu–O	1·91	1·97
Cu–N	2·04	1·98
O–C(6)	1·31	1·32
C(6)–C(7)	1·41	1·41
C(6)–C(11)	1·41	1·41
C(7)–C(8)	1·39	1·39
C(11)–C(10)	1·39	1·39
C(8)–C(9)	1·38	1·36
C(9)–C(10)	1·38	1·36
C(7)–Cl(1)	1·73	1·74
C(11)–Cl(2)	1·75	1·74
C(9)–Cl(3)	1·74	1·75
Cu–Cl(2)	2·92	2·85
O–Cu–N	89·0	89·7
Cu–O–C(6)	126·2	129·5
C(7)–C(6)–C(11)	114·0	113·9
C(6)–C(7)–C(8)	123·4	123·8
C(6)–C(11)–C(10)	124·1	123·8
C(7)–C(8)–C(9)	118·9	118·0
C(9)–C(10)–C(11)	118·4	118·0
C(8)–C(9)–C(10)	121·1	122·5

are 2·05 and 2·08 Å; so the length of 2·04 Å in CUTP is in close agreement with that result. The Cu–O length is slightly shorter than the value normally quoted, but agrees with the 1·91 Å in (*N,N,N',N'*-tetramethylethylenediamine)bis(2,4,6-trichlorophenolato)copper(II) (Vogt, La Placa & Bednowitz, 1968).

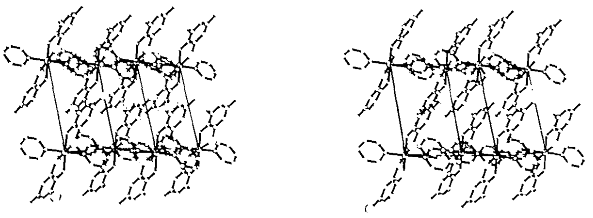

Fig. 3. Stereoview of the molecular packing in CUTP, as seen along *y*.

Table 7. *Bond lengths* (Å) *and their e.s.d.'s for non-hydrogen atoms in CUNPIC*

	Molecule (1)	Molecule (2)
Cu(1)–N(2)	2·040 (6)	2·038 (6)
Cu(1)–O(1)	1·927 (5)	1·933 (4)
Cu(1)–O(2)	2·458 (3)	2·402 (3)
O(1)–C(1)	1·294 (5)	1·291 (5)
C(1)–C(2)	1·409 (11)	1·418 (10)
C(2)–C(3)	1·371 (7)	1·370 (8)
C(3)–C(4)	1·382 (10)	1·391 (12)
C(4)–C(5)	1·398 (11)	1·386 (10)
C(5)–C(6)	1·357 (7)	1·365 (6)
C(6)–C(1)	1·436 (9)	1·419 (9)
C(6)–O(2)	1·372 (9)	1·384 (7)
O(2)–C(7)	1·413 (10)	1·419 (9)
C(4)–N(1)	1·446 (6)	1·444 (7)
N(1)–O(3)	1·234 (8)	1·228 (13)
N(1)–O(4)	1·232 (9)	1·222 (13)
N(2)–C(8)	1·332 (9)	1·358 (8)
C(8)–C(9)	1·381 (11)	1·367 (13)
C(9)–C(10)	1·394 (15)	1·433 (14)
C(10)–C(11)	1·375 (11)	1·361 (10)
C(11)–C(12)	1·368 (13)	1·376 (10)
C(12)–N(2)	1·358 (12)	1·339 (11)
C(10)–C(13)	1·523 (13)	1·499 (13)

There is also close agreement between other bond lengths and angles in CUTP and CUTI, and the angular distortion from octahedral symmetry is similar in both compounds. The Cu–O–C angles are larger (126·2 in CUTP, 129·5° in CUTI) than those in 2-methoxyphenolato complexes (118°, Bullock, Hobson & Povey, 1974), presumably due to the greater size of the Cl atom compared with that of the O atom. Both compounds show similar distortion in the benzene ring, particularly the small angle (114 in CUTP, 113·9° in CUTI) at the C linked to the O atom. Wong, Palmer & Tomimcetsu (1976) comment that this is probably attributable to the non-uniform thermal motion of the atoms in the ring. Fig. 3 shows the molecular packing, indicating the monomeric nature of the complex.

Tables 7 and 8 give the bond lengths and angles other than those involving H in CUNPIC. Table 9 lists bond lengths and angles involving H; e.s.d.'s are not included as the H atoms were held invariant during refinement. Corresponding values for the two molecules show good agreement with each other. Some of the

Table 8. *Bond angles* (°) *and their e.s.d.'s for non-hydrogen atoms in CUNPIC*

	Molecule (1)	Molecule (2)
O(1)–Cu(1)–N(2)	90·6 (2)	90·2 (2)
O(2)–Cu(1)–N(2)	88·7 (2)	89·5 (2)
O(2)–Cu(1)–O(1)	74·6 (2)	75·1 (2)
Cu(1)–O(1)–C(1)	122·6 (4)	121·6 (4)
O(1)–C(1)–C(2)	121·1 (5)	121·4 (6)
O(1)–C(1)–C(6)	122·7 (6)	122·8 (5)
C(2)–C(1)–C(6)	116·1 (4)	115·8 (4)
C(1)–C(2)–C(3)	122·9 (6)	121·4 (7)
C(2)–C(3)–C(4)	118·3 (7)	120·0 (7)
C(3)–C(4)–C(5)	121·8 (5)	121·0 (5)
C(4)–C(5)–C(6)	119·2 (6)	118·5 (7)
C(5)–C(6)–C(1)	121·6 (7)	123·3 (6)
C(3)–C(4)–N(1)	118·5 (7)	120·6 (7)
C(5)–C(4)–N(1)	119·7 (6)	118·5 (7)
C(4)–N(1)–O(3)	117·9 (6)	117·4 (9)
C(4)–N(1)–O(4)	119·7 (6)	119·0 (8)
O(3)–N(1)–O(4)	122·4 (5)	123·6 (6)
C(1)–C(6)–O(2)	113·7 (4)	113·1 (4)
C(5)–C(6)–O(2)	124·7 (6)	123·6 (6)
C(6)–O(2)–C(7)	118·4 (5)	116·5 (4)
C(6)–O(2)–Cu(1)	106·4 (3)	107·3 (3)
C(7)–O(2)–Cu(1)	134·3 (5)	134·6 (3)
Cu(1)–N(2)–C(8)	121·5 (6)	120·9 (6)
Cu(1)–N(2)–C(12)	120·6 (4)	122·1 (4)
C(8)–N(2)–C(12)	117·9 (7)	117·0 (7)
N(2)–C(8)–C(9)	122·8 (9)	122·7 (9)
C(8)–C(9)–C(10)	119·1 (7)	120·0 (7)
C(9)–C(10)–C(11)	117·5 (8)	115·7 (8)
C(10)–C(11)–C(12)	120·7 (10)	121·6 (9)
C(11)–C(12)–N(2)	121·9 (7)	123·1 (6)
C(9)–C(10)–C(13)	119·5 (8)	121·9 (7)
C(11)–C(10)–C(13)	123·0 (10)	122·4 (9)

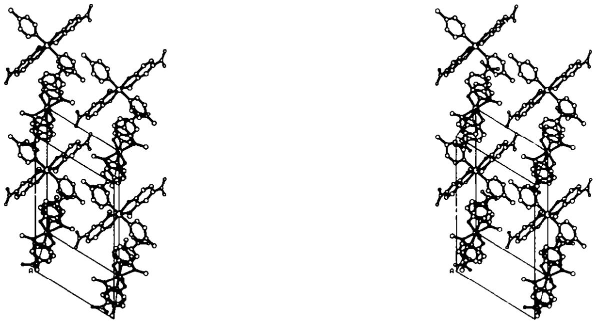

Fig. 4. Stereoview of the molecular packing in CUNPIC, as seen along *x*. Molecules have been omitted from some corners of the unit cell so as to show the different orientations of the molecules.

values involving H atoms whose positions were determined from a difference synthesis are clearly inaccurate, but this is not surprising as some of the peaks were very broad; moreover, the e.s.d.'s of the C atoms in these isolated methyl groups are about twice those of the other atoms, thus increasing the uncertainty.

Table 9. *Bond lengths* (Å) *and angles* (°) *for* H *atoms in CUNPIC*

	Molecule (1)	Molecule (2)
C(2)–H(1)	1·06	1·00
C(3)–H(2)	1·10	1·01
C(5)–H(3)	1·01	1·00
C(8)–H(4)	1·01	1·00
C(9)–H(5)	1·03	1·01
C(11)–H(6)	1·06	1·02
C(12)–H(7)	1·17	1·01
C(7)–H(8)	1·05	1·16
C(7)–H(9)	1·09	1·02
C(7)–H(10)	1·01	1·03
C(13)–H(11)	0·87	0·98
C(13)–H(12)	0·90	1·04
C(13)–H(13)	0·93	0·78
C(1)–C(2)–H(1)	118·2	118·6
C(3)–C(2)–H(1)	118·6	120·0
C(2)–C(3)–H(2)	118·8	125·8
C(4)–C(3)–H(2)	122·7	114·1
C(4)–C(5)–H(3)	120·3	127·6
C(6)–C(5)–H(3)	120·5	113·3
N(2)–C(8)–H(4)	118·0	118·7
C(9)–C(8)–H(4)	119·0	118·6
C(8)–C(9)–H(5)	121·1	120·8
C(10)–C(9)–H(5)	119·7	119·2
C(10)–C(11)–H(6)	119·1	118·7
C(12)–C(11)–H(6)	120·1	119·8
C(11)–C(12)–H(7)	120·4	124·4
N(2)–C(12)–H(7)	117·4	112·1
O(2)–C(7)–H(8)	112·4	89·5
O(2)–C(7)–H(9)	108·6	113·7
O(2)–C(7)–H(10)	111·8	118·6
H(8)–C(7)–H(9)	107·2	108·1
H(8)–C(7)–H(10)	108·6	112·1
H(9)–C(7)–H(10)	108·1	103·6
C(10)–C(13)–H(11)	99·0	113·5
C(10)–C(13)–H(12)	107·3	106·9
C(10)–C(13)–H(13)	118·2	109·3
H(11)–C(13)–H(12)	116·3	72·7
H(11)–C(13)–H(13)	114·6	117·2
H(12)–C(13)–H(13)	100·8	137·0

The Cu atom shows the expected distorted-octahedral coordination, the Cu–N and shorter Cu–O bonds having lengths similar to those in CUTP. The longer Cu–O bonds are, as expected, shorter than the Cu–Cl bonds in CUTP, though the values in the two molecules are slightly different (2·46 and 2·40 Å). As predicted from the reflectance spectra, these values are somewhat greater than the 2·37 Å in bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) monohydrate (Hobson, Ladd & Povey, 1973).

Other bond lengths and angles are comparable with those in related compounds (Bullock, Hobson & Povey, 1974). The molecular packing is illustrated in Fig. 4, which shows the different orientation of the two unique molecules.

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Hall, 1972) on the CDC 7600 computer at the University of London Computer Centre, which supplemented local facilities.

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The Structures of Methyl 3-Phenyldithiocarbazate and Its Derivative, Square-Planar Bis(methyl N'-phenyldiazenecarbodithioato-N',S)platinum

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Abstract

The crystal structures of the title compounds, $C_8H_{10}N_2S_2$, (I), monoclinic, $a = 10{\cdot}262\,(2)$, $b = 5{\cdot}939\,(1)$, $c = 17{\cdot}363\,(4)$ Å, $\beta = 108{\cdot}48\,(2)^\circ$, $Z = 4$, space group $P2_1/c$, 934 reflections, $R = 0{\cdot}030$, and its neutral platinum complex $[Pt(C_8H_8N_2S_2)_2]$, (II), triclinic, $a = 5{\cdot}883\,(2)$, $b = 8{\cdot}426\,(4)$, $c = 9{\cdot}767\,(3)$ Å, $\alpha = 72{\cdot}43\,(3)$, $\beta = 91{\cdot}42\,(2)$, $\gamma = 92{\cdot}96\,(2)^\circ$, $Z = 1$, space group $P\bar{1}$, 3492 reflections, $R = 0{\cdot}036$, have been determined from diffractometer data. The molecules of (I) have a *trans–cis* conformation and are coupled in dimers. The complex unit of (II) is monomeric: Pt occupies a centre of symmetry within a square-planar S_2N_2 environment of two ligands in a *cis–cis* conformation.

Introduction

As part of an investigation on the methyl esters of the N-substituted dithiocarbazic acid R_1R_2N—NR_3—

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