Substituted Phenols as Ligands. Part IV.[1] Six- and Four-co-ordinate Copper(II) Complexes with Nitrogen Bases. *X*-Ray Crystal Structure Analysis of Bis-(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II)

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Two groups of six-co-ordinate copper(II) complexes of chloro- or alkoxy-phenolates and a nitrogen base (pyridine, ammonia, or *NNN'N'*-tetramethylethylenediamine) have been identified from their diffuse reflectance electronic spectra. Bis-(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II), (I), has been characterised by an *X*-ray structure analysis [orthorhombic, a = 37·54(2), b = 16·76(1), c = 7·947(5) Å, Z = 8, space group *Pbca*]. Both methoxy-oxygen atoms are co-ordinated at non-equivalent distances [2·46(2) and 2·58(2) Å] with the phenolic oxygen atoms [1·93(2) and 1·95(2) Å] and the pyridine nitrogen atoms [2·05(2) and 2·08(2) Å] completing the co-ordination sphere. This chromophore gives a relatively intense absorption at 13·2 kK in the diffuse reflectance spectrum.

A second group of compounds gives rise to two *d–d* transitions (*ca.* 14 and 17 kK); one of these, (II), bis-(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) hydrate, is known to be six-co-ordinate and contains two molecular types. Both have symmetrically placed methoxy-oxygen atoms [2·321(6) and 2·413(6) Å]. The smaller mean tetragonal distortion is considered to be the determining factor influencing the spectra.

The strong, broad, low-lying charge-transfer absorption (*ca.* 20 kK) obscuring most of the *d–d* transitions, which characterises a third group of compounds with similar ligands, is absent in the above cases. In the third group, bis-(2,4,6-trichlorophenolato)-(*NNN'N'*-tetramethylethylenediamine)copper(II), (III) is known to be square planar. An isomer of bis-(4-formyl-2-methoxyphenolato)(*NNN'N'*-tetramethylethylenediamine)copper(II) has a large tetrahedral distortion.

A NUMBER of copper(II) complexes with substituted-phenolate ligands have been previously reported as hydrates and anhydrates and as adducts of nitrogen bases[2-5] such as pyridine or ammonia. The role of the substituents in the 2,6-positions of the phenols is not clearly understood. A preliminary, single-crystal structure of (III), square-planar bis-(2,4,6-trichlorophenolato)(*NNN'N'*-tetramethylethylenediamine)-copper(II), has been reported.[6] For[1] bis-(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) hydrate, (II), an *X*-ray structure analysis revealed two distinct molecular types within the unit cell. The first had symmetrically placed methoxy-oxygen atoms [Cu–O(Me) 2·413(6) Å] with six-co-ordination completed by two phenolic oxygen atoms [1·941(4) Å] and two pyridine nitrogen atoms [2·043(7) Å]. The corresponding distances for the second molecular type were Cu–O(Me) 2·321(6), Cu–O(phenolic) 1·939(4), and Cu–N(pyridine) 2·061(7) Å.

For hydrated alkoxy-acetate complexes, the Cu–O(R) (R = Me or Et) distances are usually shorter[7] than those in (II) and in a nickel complex[8] the Ni–O(Me) bond is shorter than the Ni–O(OAc) distance. The introduction of a nitrogen base or an ethoxy-group lengthened the Cu–O(Me/Et) distances[9,10] and in[11] bis-(methoxyacetato)tetrakis(imidazole)copper(II) the methoxy-groups were not co-ordinated at all. It would seem reasonable to suppose that atomic separations up to 2·8 Å might affect the energy of the *d–d* transitions since Hathaway and co-workers have used these larger separations (*ca.* 2·6 Å) as an intrinsic feature of their theory of semi-co-ordination[12,13] for copper(II).

Hathaway and co-workers[12,13] have established methods for the analysis of copper(II) electronic spectra which give reliable information with respect to stereochemistry within carefully defined groups of compounds although both McKenzie[14] and Hathaway[15] recognised that such deductions must be made with care and that reference to related compounds of known crystal structure is probably essential. We wished to elucidate the relationship between structure and electronic spectra with special reference to the 2,6-substituents of the phenols.

EXPERIMENTAL

Abbreviations are defined in Tables 1 and 2. Whenever possible Analytical reagent grade materials were used. Most commercially available phenols were recrystallised before use.

Pyridine Complexes.—There were two general methods.

Method (*A*). Pyridine (0·02 mol) was added to a filtered solution of the appropriate phenol (0·021 mol) in aqueous sodium hydroxide (0·02 mol, 100 ml). To this was added, with stirring, copper(II) sulphate pentahydrate (0·01 mol) in distilled water (100 ml). The precipitate was washed

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TABLE 1

(*a*) Analyses for the complexes [a]

Compound	Found (%)				Calc. (%)			
(i) Group (1)	Cu	C	H	N	Cu	C	H	N
$Cu(monp)_2(py)_2$ [b]	11·4	51·7	3·9	9·8	11·4	51·65	3·95	10·05
$Cu(eofp)_2(py)_2$ [c]	11·7	60·8	5·6	5·1	11·45	60·7	5·45	5·05
$Cu(tclp)_2(py)_2$ [d, e]	10·5	43·6	2·6	4·5	10·35	43·0	2·3	4·55
$Cu(pclp)_2(py)_2$ [c, f]	8·4	36·0	1·4	3·8	8·45	35·1	1·35	3·7
(ii) Group (2)								
$Cu(fomp)_2(py)_2,H_2O$ [g]	11·6	57·9	4·8	5·3	11·7	57·6	4·85	5·15
$Cu(fomp)_2(py)_2,C_6H_6$	10·5	64·1	5·0	4·7	10·55	63·85	5·0	4·65
$Cu(fomp)_2(NH_3)_2$	15·9	47·8	5·1	6·9	15·9	48·05	5·05	7·0
$Cu(eofp)_2(NH_3)_2$	14·6	50·8	5·7	6·4	14·85	50·5	5·65	6·55
$Cu(monp)_2(NH_3)_2,(H_2O)_2$ [h]	13·4	35·9	4·0	11·8	13·5	35·8	4·7	11·9
$Cu(monp)_2(meen),H_2O$	11·9	45·1	5·5	10·7	11·9	45·0	5·65	10·5
$Cu(fomp)_2(meen),(H_2O)_4$ [i]	11·5	47·8	5·5	5·0	11·45	47·7	6·9	5·05

(*b*) Diffuse reflectance spectra (room temperature on upper line, liquid–nitrogen temperature on lower line, with shoulders in parentheses)

Compound	Electronic spectra (kK) *d–d*	Other bands
$Cu(monp)_2(py)_2$	13·2 (10·7), 13·3, (15·5)	(20·3,) 21·7, (23·8), 26·7 (20·5), 21·8, (24·0), 26·1
$Cu(eofp)_2(py)_2$	13·1, (15·8) 13·2, (15·5)	20·6, (21·4), 23·7, (29·2) 20·7, (21·6), 23·3, (29·0)
$Cu(tclp)_2(py)_2$	13·2, (16·7) (10·7), 13·4, (15·5), (17·6)	21·4, (24·9) 20·0, (24·9)
$Cu(pclp)_2(py)_2$	13·0, (15·3) 13·0, 16·0, 17·5	22·3, 27·1, (28·1) 22·3, 27·0, (29·3)
$Cu(fomp)_2(py)_2,H_2O$	12·5, 16·4 12·7, 16·7, (18·1)	21·0, (24·1) 21·3, (24·2)
$Cu(fomp)_2(py)_2,C_6H_6$	12·9, (16·6—17·7) 13·1, 16·8	21·4, 22·4, 24·2, 29·3 21·4, 22·6, 24·2, 29·1
$Cu(fomp)_2(NH_3)_2$	13·1, 16·4 (11·0), 13·0, 16·6	(21·7), 24·0, 28·6 (21·7), 24·4, 28·6
$Cu(eofp)_2(NH_3)_2$	(14·2), (17·6) 14·1, 17·4	20·9, (22·5), 25·4 20·9, 22·3, 25·5
$Cu(monp)_2(NH_3)_2,(H_2O)_2$	14·0, 17·5 14·2, 18·0	20·8 21·3, (22·9), 28·9
$Cu(monp)_2(meen),H_2O$	(13·9), 18·5 (13·8), (16·0), 18·4	21·2, (23·5), 27·6 21·3, (23·1), 27·6
$Cu(fomp)_2(meen),(H_2O)_4$	(14·2), (16·5) 13·8, 16·7	20·4, (22·4) 20·2, (21·3), (23·0)

[a] Ligand abbreviations: monp = 2-methoxy-4-nitrophenolato, eofp = 2-ethoxy-4-formylphenolato, tclp = trichlorophenolato, pclp = pentachlorophenolato, fomp = 4-formyl-2-methoxyphenolato, py = pyridine, meen = *NNN'N'*-tetramethylethylenediamine. [b] Recrystallised from benzene–chlorobenzene (1 : 1). [c] Recrystallised from benzene. [d] Cl: Found 34·4, calc. 34·6%. [e] Recrystallised from benzene–light petroleum (b.p. 100—120 °C), (1 : 9). [f] Cl: Found 46·7, calc. 47·1%. [g] Recrystallised from water–pyridine (4 : 1). [h] H_2O: Found 7·6, calc. 7·65%. [i] H_2O: Found 13·0, calc. 13·0%.

TABLE 2

Analyses and diffuse reflectance spectra for group (3) complexes [a]

Compound	Calc. (%)					Found (%)					CT * and *d–d* absorptions (kK)	
	Cu	C	H	N	Cl	Cu	C	H	N	Cl	RT †	LT ‡
$Cu(tclp)_2(meen)$	11·1	37·75	3·5	4·9		11·0	38·0	3·6	4·9		(27·5), (20·8), 13·4sh	(27·5), (20·9), 14·2sh
$Cu(fomp)_2(meen)$ [b]	13·2					13·0					(24·7), (19·5), 13·5sh	(24·7), (19·4), 13·6—14·9sh
$Cu(mnp)_2(meen)$	13·15	49·65	5·85	11·6		13·0	49·3	5·9	11·6		(23·8), (21·7), (19·4), 14·1	(23·6), (21·9), (18·7), 14·2
$Cu(monp)_2(meen),H_2O,C_6H_6$ [c]	10·4	51·0	5·95	9·15		10·3	51·0	5·7	9·1		(21·3), (19·0sh), 14·2sh	(21·4), (19·3sh), 14·5sh
$Cu(tclp)_2(NH_3)_2$	12·95	29·4	2·05	5·7	43·35	13·1	29·4	2·1	5·5	43·3	(23·0), (20·8sh), 14·5sh	(23·1), (21·0sh), 17·7sh, 14·3sh
$Cu(pclp)_2(NH_3)_2$	10·1	22·95	0·95	4·1	56·45	10·2	23·0	1·3	4·5	56·4	(21·6), 14·7sh, 11·6sh	(21·7), 14·9sh 12·1
$Cu(monp)_2(NH_3)_2$	14·65	38·75	4·2	12·9		14·5	38·7	4·2	12·9		(19·4), 17·7sh 14·3sh	(19·3), 18·0sh 14·9sh
$Cu(fomp)_2(meen)$ [d]	13·2	54·8	6·25	5·8		13·1	54·7	6·3	5·9		(20·3), 13·5, 10·2, 7·0	(20·3), 13·8, 10·7, 9·7sh, 6·7

[a] mnp = 2-methyl-4-nitrophenolato. [b] Black; satisfactory analyses were obtained for the parent tetrahydrate. [c] From T.G.A.: $H_2O + C_6H_6$ = 15·0% (calc., 15·7%). [d] Red.

* CT = Charge transfer, values given in parentheses. † Room temperature. ‡ Liquid–nitrogen temperature.

with distilled water (4 × 20 ml), and dried *in vacuo* ($CaCl_2$). $Cu(fomp)_2(py)_2,H_2O$ was dried at atmospheric pressure. Yields >85%.

Method (*B*). Pyridine (0·021 mol) was added to copper(II) sulphate pentahydrate (0·01 mol) in distilled water (50 ml). To this was added, with stirring, the appropriate phenol (0·021 mol) in ethanol (96%, 50 ml) and aqueous sodium hydroxide (0·02 mol, 100 ml). The precipitate was washed with ethanol (96%)–water (3 × 10 ml, 1 : 1), and dried *in vacuo* ($CaCl_2$). Yields >90%. The complexes were recrystallised from appropriate solvents (see Table 1).

The complex $Cu(fomp)_2(py)_2,C_6H_6$ was prepared by the recrystallisation of the hydrate from benzene solution. It was stored at atmospheric pressure (P_4O_{10}).

Tetramethylethylenediamine Complexes.—The ligand meen (0·011 mol) was added to a filtered solution of the appropriate phenol (0·021 mol) in ethanol (96%, 20 ml) and aqueous sodium hydroxide (0·02 mol, 100 ml). To this was added, with stirring, copper(II) sulphate pentahydrate (0·01 mol) in distilled water (100 ml). The precipitate was washed with distilled water (4 × 20 ml), and dried (*vide infra*). Yields >80%. Necessary modifications to the method for particular complexes are as follows.

(*a*) $Cu(mnp)_2(meen)$ was not washed after filtration; it was dried *in vacuo* (P_4O_{10}).

(*b*) $Cu(monp)_2(meen),H_2O,C_6H_6$ was prepared as a monohydrate which on recrystallisation from benzene yielded the required product; no drying agent used.

(*c*) $Cu(monp)_2(meen),C_6H_4Me_2$ was prepared as a monohydrate which on recrystallisation from xylene yielded the required product; no drying agent used.

(*d*) Isomers of $Cu(fomp)_2(meen)$. The general method gave a tetrahydrate, which on dehydration *in vacuo* (P_4O_{10}) gave bluish black crystals. In a dry atmosphere these changed over a period of months to give the red isomer. A more convenient method for obtaining the red isomer was to dissolve the black isomer (1·50 g) in benzene (40 ml) with heating to give a red solution. Light petroleum (60 ml, b.p. 80—100°) was added with stirring to the hot solution. On cooling a red crystalline solid was produced, which was dried *in vacuo* (P_4O_{10}). It was stable in air.

Ammine Complexes.—Concentrated aqueous ammonia was added dropwise to copper(II) sulphate pentahydrate (0·01 mol) in distilled water (100 ml) until the initial pale blue precipitate dissolved and a deep blue solution was obtained. To this was added, with stirring, a solution of the appropriate phenol (0·021 mol) in ethanol (96%, 20 ml). The resulting precipitate was washed with distilled water (2 × 10 ml), then ethanol (96%, 3 × 10 ml). The products were initially air-dried and then dried over calcium chloride. Yields 60—95%.

(*a*) $Cu(monp)_2(NH_3)_2$ prepared by the general method was a dihydrate which was dehydrated *in vacuo* (P_4O_{10}) to give a brown crystalline solid.

(*b*) $Cu(eofp)_2(NH_3),H_2O$ was prepared by the general method but for the anhydrous compound $Cu(eofp)_2(py)_2$ (2·40 g) was dissolved in chlorobenzene (300 ml) with gentle heating. The cool solution was filtered and treated with ammonia gas when a green precipitate slowly appeared. This was dried under dry nitrogen.

Physical Methods.—Spectra were obtained by use of a Unicam SP 700 C spectrophotometer. Magnetic susceptibilities were determined by use of a Newport Instruments variable-temperature Gouy balance. Thermogravimetric analyses were performed under dry nitrogen by use of a modified Stanton HT D thermobalance.

X-*Ray Crystal Structure Analysis of* $Cu(monp)_2(py)_2$, (I)

Crystals of the dark green solid decomposed rapidly in the *X*-ray beam. Additionally, single crystals proved very difficult to grow (the only three obtained coming from the slow evaporation of chloroform–benzene solutions). In view of these difficulties, and since the primary purpose of the analysis was to obtain estimates of the Cu–O and Cu–N distances, a lower level of convergence than would be normally expected was accepted. Unit-cell and space-group data were obtained by Weissenberg and precession methods. Cell parameters were refined by least-squares methods from the θ(Cu-K_α) values measured on a Siemens four-circle diffractometer for *ca.* 20 reflections.

Crystal Data.—$C_{24}H_{22}CuO_8N_4$, $M = 558·01$, Orthorhombic, $a = 37·54(2)$, $b = 16·76(1)$, $c = 7·947(5)$ Å, $U = 5002·94$ Å^3, $D_m = 1·48$ (by flotation), $Z = 8$, $D_c = 1·482$, $F(000) = 2296$. Space group, *Pbca*, from systematic absences: $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd. Cu-K_α radiation, $\lambda = 1·5418$ Å; μ(Cu-K_α) = 18 cm^{-1}. A total of 2550 reflections with $\sin\theta/\lambda < 0·497$ were measured on a Siemens four-circle diffractometer by the θ—2θ scanning method. Of these, only 884 having $I > 2\sigma(I)$ were considered observed, and were used in the subsequent analysis. Because of decomposition, two crystals (0·56 × 0·22 × 0·05 and 0·44 × 0·17 × 0·4 mm) were used, each mounted with the *c* axis parallel to the spindle axis of the diffractometer. The two portions of data collected from the two crystals were treated as separate scale groups but were also manually scaled to reference reflections collected from both crystals. No absorption or extinction corrections were applied.

Structure Analysis.—The structure was solved by a combination of the heavy-atom method and Fourier syntheses. The F^2 Patterson synthesis yielded the coordinates of the copper atom both from its general peak and the relevant Harker sections. However, subsequent Fourier synthesis with the structure factors phased by the copper atom failed to reveal any of the molecular structure. The positional and anisotropic thermal parameters of the copper atoms were refined by full-matrix least-squares methods after which successive Fourier syntheses enabled location of all remaining non-hydrogen atoms.

The structure was refined by full-matrix least-squares methods, with isotropic temperature factors for the light atoms, to *R* 0·124. The introduction of anisotropic thermal parameters for the light atoms resulted in nonpositive definite temperature factors. Convergence was reached at *R* 0·111 for 884 observed reflections. The mean value of ΔF showed an irregular variation over ranges of F_0 therefore unit weighting was employed. On the final cycle of refinement no parameter shift was $>0·30\sigma$. A final difference Fourier synthesis showed small random fluctuations (up to ±0·12 carbon atoms) and did not enable location of hydrogen atoms. Final positional and thermal parameters are in Table 3.*

RESULTS AND DISCUSSION

Structural Aspects of (I).—An abbreviated description of the structure will be given. The structure consists of discrete six-co-ordinate molecules. The molecular structure and atomic numbering are shown in Figure 1,

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* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 27091 (13 pp., 1 microfiche). See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

TABLE 3

Final positional (fractional, × 10^4) and thermal parameters, with standard deviations in parentheses

Atom	*x*	*y*	*z*	*U*/ Å × 10^3
Cu	1175(1)	4842(2)	5397(5)	*
O(1)	1239(5)	3894(9)	6787(21)	50(6)
O(2)	1124(4)	5807(8)	4090(17)	24(4)
O(3)	1802(6)	4260(10)	4908(24)	69(6)
O(4)	0577(4)	5374(9)	5953(18)	37(5)
O(5)	2836(6)	3418(12)	8516(26)	83(7)
O(6)	2583(6)	2824(12)	0565(27)	89(7)
O(7)	−0038(16)	8007(12)	7164(27)	80(8)
O(8)	0291(5)	8870(12)	5837(23)	70(7)
N(1)	1377(6)	5517(10)	7321(25)	33(6)
N(2)	0959(5)	4174(10)	3440(21)	18(5)
N(3)	2593(7)	3226(13)	9227(29)	50(7)
N(4)	0211(7)	8146(14)	6370(28)	53(7)
C(1)	1319(6)	5359(12)	8920(27)	21(7)
C(2)	1450(8)	5799(15)	0309(35)	50(8)
C(3)	1690(8)	6300(17)	9933(37)	64(10)
C(4)	1804(7)	6513(16)	8234(36)	58(9)
C(5)	1654(7)	6061(14)	6925(32)	37(8)
C(6)	0730(7)	4512(12)	2396(28)	21(7)
C(8)	0614(8)	3251(15)	1046(33)	52(9)
C(9)	0870(8)	2920(16)	2112(35)	51(9)
C(10)	1032(6)	3372(12)	3422(26)	16(6)
C(11)	2102(9)	4448(18)	3910(40)	81(11)
C(12)	1575(9)	3742(16)	7331(38)	56(9)
C(13)	1874(7)	3934(12)	6441(29)	16(6)
C(14)	2204(6)	3745(12)	7096(27)	19(7)
C(15)	2212(7)	3362(13)	8638(28)	26(7)
C(16)	1924(7)	3167(12)	9626(31)	29(7)
C(17)	1589(7)	3386(14)	8986(31)	39(8)
C(18)	0279(7)	5161(15)	7004(30)	42(8)
C(19)	0916(7)	6364(14)	4678(33)	41(8)
C(20)	0591(7)	6185(13)	5571(30)	27(7)
C(21)	0360(7)	6763(14)	6255(29)	34(7)
C(22)	0464(7)	7572(13)	5747(29)	30(7)
C(23)	0753(7)	7768(13)	4758(31)	34(7)
C(24)	0983(6)	7189(12)	4156(25)	16(7)

* Anisotropic thermal parameters in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	32(4)	29(2)	42(2)	−1(2)	−8(3)	5(2)

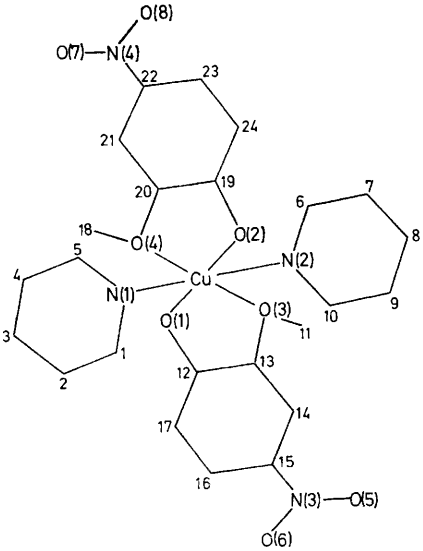

FIGURE 1 Molecular structure and numbering scheme for $Cu(monp)_2(py)_2$, (I)

bond lengths and angles in Table 4, and a perspective drawing in Figure 2. The configuration about copper is asymmetric and the unit cell contains four of each enantiomorph.

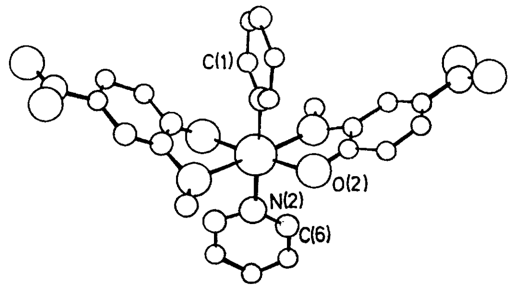

FIGURE 2 Perspective drawing of $Cu(monp)_2(py)_2$

The phenolic oxygen atoms and the pyridine nitrogens form a square plane about copper with a very distorted

TABLE 4

Bond distances (Å) and angles (°). Standard deviations are *ca.* 0·03 Å and 1—3° for light atoms only. Those involving copper are *ca.* 0·02 Å and 0·7°

(*a*) Distances

Cu–O(1)	1·95	C(20)–C(21)	1·41
Cu–O(2)	1·93	C(21)–C(22)	1·47
Cu–O(3)	2·58	C(22)–C(23)	1·38
Cu–O(4)	2·46	C(23)–C(24)	1·38
Cu–N(1)	2·05	C(24)–C(19)	1·45
Cu–N(2)	2·08	C(11)–O(3)	1·41
C(1)–C(2)	1·42	C(12)–O(1)	1·36
C(2)–C(3)	1·27	C(13)–O(3)	1·36
C(3)–C(4)	1·46	C(18)–O(4)	1·44
C(4)–C(5)	1·41	C(19)–O(2)	1·30
C(6)–C(7)	1·39	C(20)–O(4)	1·39
C(7)–C(8)	1·38	C(1)–N(1)	1·32
C(8)–C(9)	1·40	C(5)–N(1)	1·42
C(9)–C(10)	1·43	C(6)–N(2)	1·32
C(12)–C(13)	1·37	C(10)–N(2)	1·37
C(13)–C(14)	1·38	C(15)–N(3)	1·52
C(14)–C(15)	1·38	C(22)–N(4)	1·44
C(15)–C(16)	1·37	N(3)–O(5)	1·12
C(16)–C(17)	1·41	N(3)–O(6)	1·26
C(17)–C(12)	1·45	N(4)–O(7)	1·15
C(19)–C(20)	1·45	N(4)–O(8)	1·30

(*b*) Angles

N(1)–Cu–N(2)	178·6	C(15)–C(16)–C(17)	116
O(1)–Cu–O(2)	177·5	C(16)–C(17)–C(12)	118
O(3)–Cu–O(4)	178·1	C(17)–C(12)–C(13)	123
N(1)–Cu–O(1)	88·9	C(19)–C(20)–C(21)	125
N(1)–Cu–O(2)	88·6	C(20)–C(21)–C(22)	111
N(1)–Cu–O(3)	89·1	C(21)–C(22)–C(23)	126
N(1)–Cu–O(4)	90·2	C(22)–C(23)–C(24)	121
N(2)–Cu–O(1)	91·9	C(23)–C(24)–C(19)	117
N(2)–Cu–O(2)	90·6	C(24)–C(19)–C(20)	119
N(2)–Cu–O(3)	92·3	Cu–O(1)–C(12)	117
N(2)–Cu–O(4)	88·5	Cu–O(2)–C(19)	118
O(1)–Cu–O(3)	70·5	Cu–O(3)–C(13)	101
O(2)–Cu–O(4)	72·7	Cu–O(4)–C(20)	106
N(1)–C(1)–C(2)	126	O(1)–C(12)–C(13)	124
C(1)–C(2)–C(3)	114	C(12)–C(13)–O(3)	113
C(2)–C(3)–C(4)	126	O(2)–C(19)–C(20)	122
C(3)–C(4)–C(5)	116	C(19)–C(20)–O(4)	110
C(4)–C(5)–N(1)	118	Cu–O(3)–C(11)	137
C(5)–N(1)–C(1)	118	Cu–O(4)–C(18)	136
N(2)–C(6)–C(7)	121	C(11)–O(3)–C(13)	116
C(6)–C(7)–C(8)	121	C(18)–O(4)–C(20)	113
C(7)–C(8)–C(9)	117	C(16)–C(15)–N(3)	122
C(8)–C(9)–C(10)	122	C(23)–C(22)–N(4)	124
C(9)–C(10)–N(2)	116	O(5)–N(3)–O(6)	127
C(10)–N(2)–C(6)	123	O(5)–N(3)–C(15)	125
C(12)–C(13)–C(14)	119	O(7)–N(4)–O(8)	121
C(13)–C(14)–C(15)	117	O(7)–N(4)–C(22)	126
C(14)–C(15)–C(16)	127		

octahedral configuration being completed by the phenolic methoxy-oxygen atoms which are co-ordinated at an angle of *ca.* 70° to the plane containing the phenolic oxygen and pyridine nitrogen atoms, and are at a greater distance than the in-plane phenolic oxygens. For the donor oxygen atoms to subtend angles of 90° at copper the Cu–O(methoxy) bond lengths would need to be similar to the Cu–O(phenolic) bond lengths (*ca.* 1·95 Å).

The differences between the two Cu–N and the two Cu–O(phenolic) bond lengths are not statistically significant. However, the Cu–O(methoxy) bond lengths are different: O(4) shows a smaller temperature factor than O(3), suggesting the former to be more strongly bonded to copper. No simple explanation suggests itself for this.

As Figure 2 shows, neither the pyridine nor the phenolate ligands are co-planar, unlike[1] the situation in (II), $Cu(fomp)_2(py)_2,H_2O$. It is unlikely that this is due to intermolecular repulsion since there are no intermolecular contacts <3·2 Å and the distortion of the phenolate rings relative to the O(1)—(4) plane is in the same sense for molecules related by the *c* glide. If the pyridine molecules are fixed by their bonding role to copper, then this could explain the relative orientation of the phenolate ions. There is no immediate reason to suppose that the bonding roles of pyridine in (I) and (II) should be different.

Further structural details, for instance, the least-squares planes, are available from the authors.

Crystal Structure of $Cu(tclp)_2meen$, (III).—The preliminary report[6] gave neither the Cu–Cl distances nor the Cl–Cu–Cl angle for the *o*-chlorine atoms nearest to copper. We have calculated these from a set of atomic co-ordinates[16] by use of a local program. Selected crystal data * and relevant bond lengths and angles are: $C_{18}H_{20}Cl_6CuN_2O_2$, Monoclinic, space group $C2/c$, $Z = 12$, $a = 26·76(2)$, $b = 18·28(2)$, $c = 15·93(2)$ Å, $\beta = 70·62(9)°$.

Mean bond lengths (Å) and angles (°) (standard deviations[16] *ca.* 0·02 Å and 2°): Cu–O 1·91, Cu–N 2·05, Cu–Cl 3·07; O–Cu–N 168, Cl–Cu–Cl 138. Mean polar angle,[17] α 84°.

These results show that the stereochemistry at copper is best described as distorted square-planar with a *cis*-configuration imposed by the bidentate ligand.

Results of Magnetic Measurements for (I), (II), *and* (III).—The compounds obey the Curie law within the given temperature range. (I): μ_{eff} (291 K) 1·92, (89 K) 1·90 B.M., θ 1°; (II): μ_{eff} (292 K) 1·87, (89 K) 1·89 B.M., θ −3°; (III): μ_{eff} (293 K) 1·89, (90 K) 1·88 B.M., θ 2°.

Six-co-ordinate Complexes: Diffuse Reflectance Spectra.—The markedly different axial bond lengths [Cu–O(Me) 2·46 and 2·58 Å] in (I), the presence of two distinct molecular types in (II) with Cu–OMe 2·33 and 2·42 Å, and the positioning of the axial ligand atoms away from the copper atom *z* axis in both structures immediately illustrate the essential difficulty of relating stereochemistry to electronic spectra for copper(II). None of these features could have been predicted from the spectroscopic study alone, not withstanding the wealth of information available.[12,13]

The group (2) complexes (Table 1), typified by (II), have the two-band spectrum often observed for tetragonally distorted six-co-ordinate copper(II) complexes. The energy separation of the two bands is larger than is often observed. Since there is an off-*z*-axis positioning of the methoxy-oxygen atoms in (II), similarities between the phenolate ligands probably cause this to be a feature of all group (2) complexes. Similar findings[15] are reported for other potentially bidentate oxygen donor ligands. However, the results[1] for (II) do not necessarily imply that two distinct molecular types are present in the other group (2) complexes. Indeed, this would be unlikely for the non-hydrated complexes. The diffuse reflectance spectra may indicate a mean axial bond length of *ca.* 2·37 Å. For $Cu(monp)_2(meen),H_2O$ a strong ligand band from monp complicates the spectra at 19 kK, but the better resolution obtained at liquid-nitrogen temperature suggests that this complex may have a structure intermediate between those of groups (1) and (2).

Two of the hydrates, $Cu(monp)_2(NH_3)_2(H_2O)_2$ and $Cu(fomp)_2(meen)(H_2O)_4$ may have co-ordinated water molecules since marked changes in the diffuse reflectance spectra were found on dehydration. The new spectra were typical of four-co-ordination (*vide infra*). On the other hand, the water molecules could hydrogen bond to give a stable six-co-ordinate chromophore involving the phenol and nitrogen base only. Nitroguaiacolate probably has only weak donor properties for the methoxy-oxygen atom when compared with the other methoxy-compounds and $Cu(fomp)_2(meen)(H_2O)_4$ must be very sterically hindered.

Literature data for the CuO_4N_2 chromophore are sparse.

The group (1) complexes (Table 1) have a single peak in the diffuse reflectance spectrum near 13 kK which sometimes has poorly resolved shoulders. $Cu(monp)_2(py)_2$ is six-co-ordinate with non-equivalent axial bond lengths. This is not necessarily the case for the other group (1) complexes and this type of spectrum may indicate mean tetragonal bond lengths of *ca.* 2·5 Å for the CuO_4N_2 chromophore. The deviation from the *z* axis in the methoxy-group co-ordination is much the same in the two groups, perhaps suggesting that this may be a ligand requirement.

The complexes of the chlorophenolates may have polymeric structures since the *ortho*-chloro-substituents are unlikely to co-ordinate even though pyridine is less sterically hindering than *NNN'N'*-tetramethylethylenediamine. The bridges would presumably be made by the phenolic oxygen atoms and would necessarily be

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* The unit cell contains non-equivalent copper atoms (eight on general positions, four on special positions) but bond length and angle differences are not statistically significant.

[16] L. H. Vogt, personal communication.

[17] N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, 1968, **10**, 259.

asymmetric since the spectral classification of a large tetragonal distortion requires this to be the case.

The spectrum of Cu(tclp)$_2$(py)$_2$ in benzene solution was very similar to those recorded for the solid state. However, the resolved bands at 22·2 and 13·1 kK did not obey the Beer–Lambert law which may be further evidence for a polymeric structure.

The stereochemical deductions have been made within a closely related set of complexes with reference to *X*-ray crystal structures. These results confirm the suspicion that only gross estimates of stereochemistry can be made from non-crystallographic methods and that other methods for determining detailed arrangements within copper(II) chromophores are probably unreliable, especially when non-equivalent sets of donor atoms are present. For example, even within the present groups, the spectra of Cu(eofp)$_2$(NH$_3$),H$_2$O and of Cu(monp)$_2$(meen),xylene are not readily classified and further crystallographic work is required to elucidate the structures.

Four-co-ordinate Complexes: Diffuse Reflectance Spectra.—The compounds (Table 2) have a very broad, intense, charge-transfer absorption centred near 20 kK, the tail of which partially obscures the *d–d* transitions (Figure 3). It is known [18] that the energy of the charge-transfer transitions depends upon the co-ordination number of the metal for a given metal and ligands. For ligand-to-metal charge-transfer the energies of the bands would be expected to decrease with decreasing co-ordination number. The spectrum of Cu(tclp)$_2$(meen) in benzene solution is identical to that recorded for the solid state. The absorption at 20·3 kK obeys the Beer–Lambert Law with ε 2780 ± 80 l mol^{-1} cm^{-1}. On heating the wine-red solution of Cu(tclp)$_2$(meen) in chloroform this absorption gradually decreases as the solution becomes green; from this solution a pale-coloured phenolic polymer may be isolated leaving the copper in solution. Neither the parent phenol, its sodium salt, nor the octahedral Co(tclp)$_2$(meen) have intense absorptions near 20 kK. We consider it unlikely that the readily reducible copper(II) ion and the oxidisable phenols would give rise to low-energy metal-to-ligand charge-transfer.

There are few reports of solid-state reflectance spectra for compounds of the type CuO$_2$N$_2$ with known crystal structure. Table 5 correlates some results for compounds with increasing tetrahedral distortion. The mean polar angle, α, is a measure [17] of the distortion since α is 90° for a regular square plane and 54° 44′ for a regular tetrahedron. The *d–d* transitions clearly move to lower energy as α decreases. The same result has been found [19,20] for the copper(II) chloride complexes. These observations strongly suggest that the compounds of group (3) in Table 2 [except the red isomer of Cu(fomp)$_2$(meen)] have structures very closely related to that of Cu(tclp)$_2$(meen) in which α is 84°, since the band positions and profiles of the group are so similar and the ligand systems are comparable. It would seem likely that the *ortho*-substituents are not co-ordinated although we have shown earlier that is probably the exception rather than the rule for 2-methoxy-substituents in complexes with nitrogen donor ligands with a low steric requirement (*vide supra*).

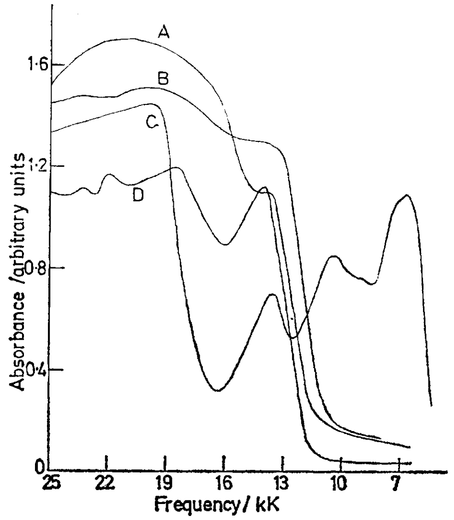

FIGURE 3 Diffuse reflectance spectra: A, Cu(tlcp)$_2$(meen); B, black Cu(fomp)$_2$(meen); C, red Cu(fomp)$_2$(meen); and D, Cu(mnp)$_2$(meen)

TABLE 5

Some four-co-ordinate CuN$_2$O$_2$ chromophores

Copper(II) complex	α (°)	Electronic spectrum (kK)
Bis(salicylaldiminato)	90 [a]	18·5, 16·5 [b]
Bis-(*N*-n-propylsalicylaldiminato)	90 [c]	16·7—15·2 [c]
NN′-Ethylenebis(acetylacetoneiminato)	*d*	18·2 (CT?), 16·4sh, 13·9sh [e]
NN′-(2,2-Biphenyl)bis(salicylaldiminato)	76·5 [f]	20·8 (CT), 15·2, 11·5sh [g]
Bis-(*N*-t-butylsalicylaldiminato)	70·7 [h]	21·0 (CT), 13·6sh, 8·5sh [e]
Bis-(*N*-isopropylsalicylaldiminato)	68·7 [i]	21·0 (CT), 13·6sh, 8·5sh [e]

[a] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 680. [b] J. Ferguson, *J. Chem. Phys.*, 1961, **35**, 1612. [c] R. J. Dudley, R. J. Fereday, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 1341 (bands just resolved from CT absorptions). [d] D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 1963, 5897 (very slight distortion from square-planar stereochemistry). [e] B. N. Figgis, M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc.* (*A*), 1968, 2028. [f] T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1966, 1396. [g] Footnote (*f*), p. 694 (solution spectrum). [h] Footnote (*f*), p. 685. [i] P. L. Orioli and L. Sacconi, *J. Amer. Chem. Soc.*, 1966, **88**, 277. CT, literature assignments.

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[18] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, London, 1968, ch. 8.

[19] R. D. Willett, O. L. Liles, jun., and C. Michelson, *Inorg. Chem.*, 1967, **6**, 1885.

[20] W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 841.

The compound Cu(mnp)(meen) has a resolved band near 14·1 kK (Figure 3), unlike most of the other complexes, but the general similarity of the spectra and the presence of the non-co-ordinating 2-methyl-substituent allow the classification of the complex within this group.

Structure of the Red Isomer of Cu(fomp)(meen).—More regular tetrahedral complexes of copper(II) have *d–d* transitions at lower energy. Thus the compounds[20] Cs_2CuX_4 have their lowest energy bands at 4·5 kK ($X = Cl$, $\alpha = 62°$) and 4·6 kK ($X = Br$, $\alpha = 64°$) whilst the spectra of copper(II) occupying the tetrahedral holes in the spinel[21] $CuAl_2O_4$ and in[22] $Cu_{0\cdot05}Zn_{1\cdot95}SiO_4$ are similar with absorptions near 6·7 and 7·5 kK respectively with high- and low-frequency shoulders. The marked differences in the spectra of the two forms of Cu(fomp)(meen) (Figure 3) suggest different structures, and we suggest that the red isomer has a very large tetrahedral distortion in which the 2-methoxy-substituents are not co-ordinated. The observed spectrum is readily classified with the known distorted tetrahedral systems (see also Table 5).

The charge-transfer band at 20 kK moves little with change in distortion for the two isomers. This is also shown in Table 5, and was found[19] for the copper(II) chloride complexes.

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[22] O. Schmitz-DuMont, H. Fendel, M. Hassanein, and H. Weissenfeld, *Monatsh.*, 1966, **97**, 1660.