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Bis(4-formyl-2-methoxyphenolato)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II) Tetrahydrate

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Abstract. $C_{22}H_{38}CuN_2O_{10}$; monoclinic; $P2_1/c$; a = 8·3080 (3), b = 15·0715 (6), c = 21·5856 (9) Å, β = 97·158 (3)°; $Z = 4$; D_m = 1·36 (2), D_x = 1·3723 (1) g cm^{-3}; μ(Cu $K\alpha$) = 14·8 cm^{-1}. The structure has been refined to R = 0·034 on 3767 observed reflections. The stereochemistry at Cu is the distorted elongated octahedral CuN_2O_4 chromophore. An O—H···O hydrogen-bond network, including both coordinated and uncoordinated O atoms, is described.

Introduction. As part of a systematic study of the correlation between stereochemistry and solid-state diffuse reflectance spectra in Cu^{II} coordination complexes with nitrogen bases and substituted phenols as ligands (Bullock, Ladd & Povey, 1977), the structures of the title complex and the corresponding anhydrous red isomer (Greenhough & Ladd, 1978) have been investigated. In the present case, tentative spectral evidence for the CuN_2O_4 chromophore, possibly including water coordination, has been given (Bullock, Hobson & Povey, 1974).

A series of Weissenberg photographs provided the Laue symmetry $2/m$, an initial unit cell and the systematic absences $h0l$, $l = 2n$; $0k0$, $k = 2n$, the latter giving the space group as $P2_1/c$. A least-squares analysis of the α_1 and α_2 peaks of 18 reflections (θ = 40–56°) obtained on a Siemens four-circle diffractometer (AED) gave the accurate unit-cell parameters. Intensities were measured to θ = 70° with Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å) and the five-value method (Hoppe, 1965) with variable scan and scan speed. 5067 measurements included 3767 with $I >$ 2·58$\sigma(I)$ (variances based on counting statistics) which were classified as observed. Lorentz and polarization corrections were applied.

All non-hydrogen atoms except for the MEEN* C and water O atoms were located by direct methods; those remaining were located from a Fourier synthesis phased on the known atoms, and all were then refined by a full-matrix least-squares method. The H atoms were located from a difference map, and were assigned isotropic thermal parameters. Scattering factors for H were taken from Stewart, Davidson & Simpson (1965) and all others from Cromer & Mann (1968). The anomalous scattering components given by Cromer & Liberman (1970) were included for Cu. The final refinement included all atomic parameters except the H U-

Table 1. *Final atomic coordinates and least-squares e.s.d.'s for the non-hydrogen atoms*

	x	y	z
Cu	0·15063 (4)	0·20829 (2)	0·15162 (2)
O(11)	0·18597 (21)	0·29184 (11)	0·08518 (7)
O(12)	0·31974 (23)	0·33235 (11)	0·20041 (8)
C(11)	0·20565 (29)	0·37607 (15)	0·09975 (11)
C(12)	0·16088 (32)	0·44388 (17)	0·05683 (12)
C(13)	0·18535 (33)	0·53198 (17)	0·07345 (12)
C(14)	0·25557 (31)	0·55607 (16)	0·13174 (12)
C(15)	0·30212 (31)	0·48983 (16)	0·17622 (12)
C(16)	0·27837 (30)	0·40238 (16)	0·16071 (11)
C(17)	0·27417 (37)	0·64906 (18)	0·14747 (14)
C(18)	0·40533 (48)	0·35307 (21)	0·25974 (15)
O(13)	0·32986 (30)	0·67910 (13)	0·19828 (10)
O(21)	−0·04001 (22)	0·27563 (11)	0·16835 (8)
O(22)	−0·09467 (22)	0·15745 (11)	0·07572 (9)
C(21)	−0·15081 (30)	0·29375 (17)	0·12125 (12)
C(22)	−0·24230 (35)	0·37203 (18)	0·11943 (13)
C(23)	−0·36511 (37)	0·38833 (19)	0·07172 (15)
C(24)	−0·40019 (34)	0·32830 (20)	0·02322 (13)
C(25)	−0·30773 (32)	0·25004 (19)	0·02310 (12)
C(26)	−0·18790 (30)	0·23321 (16)	0·07047 (12)
C(27)	−0·53452 (40)	0·34517 (25)	−0·02529 (17)
C(28)	−0·14604 (39)	0·08624 (19)	0·03401 (14)
O(23)	−0·58367 (30)	0·29536 (20)	−0·06782 (12)
N(31)	0·32711 (25)	0·12500 (13)	0·12792 (10)
N(32)	0·13245 (26)	0·12152 (14)	0·22498 (10)
C(31)	0·31565 (39)	0·10970 (21)	0·05964 (14)
C(32)	0·49009 (34)	0·16159 (21)	0·14872 (14)
C(33)	0·30158 (37)	0·03996 (18)	0·15980 (15)
C(34)	0·27029 (38)	0·05848 (20)	0·22560 (15)
C(35)	−0·02369 (38)	0·07399 (21)	0·21373 (15)
C(36)	0·14138 (44)	0·16537 (23)	0·28661 (14)
O(1)	0·07593 (28)	0·23444 (16)	0·45656 (10)
O(2)	−0·15476 (31)	0·33893 (14)	0·27639 (10)
O(3)	0·39645 (46)	0·40584 (25)	0·40884 (15)
O(4)	0·04074 (38)	0·38948 (16)	0·38643 (12)

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* Abbreviations used throughout this paper: V = 4-formyl-2-methoxyphenolato; N = 2-methoxy-4-nitrophenolato; MEEN = N,N,N',N'-tetramethylethylenediamine; py = pyridine.

Table 2. *Final positional parameters (e.s.d.'s in parentheses) and isotropic thermal parameters* (Å^2) *for the* H *atoms*

	x	y	z	U
H(12)	0·113 (4)	0·429 (2)	0·019 (1)	0·051
H(13)	0·157 (4)	0·576 (2)	0·043 (1)	0·051
H(15)	0·352 (3)	0·505 (2)	0·215 (1)	0·046
H(17)	0·236 (4)	0·691 (2)	0·114 (1)	0·057
H(181)	0·432 (4)	0·297 (2)	0·279 (2)	0·076
H(182)	0·497 (5)	0·385 (2)	0·257 (2)	0·076
H(183)	0·336 (4)	0·387 (2)	0·285 (2)	0·076
H(22)	−0·219 (4)	0·411 (2)	0·151 (1)	0·057
H(23)	−0·429 (4)	0·441 (2)	0·074 (1)	0·061
H(25)	−0·332 (4)	0·210 (2)	−0·009 (1)	0·051
H(27)	−0·588 (4)	0·402 (2)	−0·020 (2)	0·076
H(281)	−0·082 (4)	0·035 (2)	0·050 (2)	0·063
H(282)	−0·259 (4)	0·072 (2)	0·034 (2)	0·063
H(283)	−0·122 (4)	0·101 (1)	−0·008 (2)	0·063
H(311)	0·394 (4)	0·064 (2)	0·052 (2)	0·063
H(312)	0·205 (4)	0·089 (2)	0·046 (2)	0·063
H(313)	0·339 (4)	0·164 (2)	0·039 (2)	0·063
H(321)	0·574 (4)	0·115 (2)	0·138 (2)	0·061
H(322)	0·497 (4)	0·176 (2)	0·191 (2)	0·061
H(323)	0·504 (4)	0·221 (2)	0·129 (1)	0·061
H(331)	0·206 (4)	0·009 (2)	0·135 (1)	0·061
H(332)	0·397 (4)	0·003 (2)	0·158 (1)	0·061
H(341)	0·240 (4)	0·004 (2)	0·246 (2)	0·063
H(342)	0·364 (4)	0·088 (2)	0·250 (2)	0·063
H(351)	−0·038 (4)	0·045 (2)	0·174 (2)	0·067
H(352)	−0·031 (4)	0·035 (2)	0·246 (2)	0·067
H(353)	−0·116 (4)	0·115 (2)	0·211 (2)	0·067
H(361)	0·136 (4)	0·122 (2)	0·320 (2)	0·072
H(362)	0·241 (4)	0·198 (2)	0·298 (2)	0·072
H(363)	0·055 (4)	0·210 (2)	0·288 (2)	0·072
H(101)	0·102 (4)	0·233 (2)	0·492 (2)	0·076
H(102)	0·145 (4)	0·220 (2)	0·441 (2)	0·076
H(201)	−0·205 (5)	0·299 (2)	0·282 (2)	0·076
H(202)	−0·111 (4)	0·323 (2)	0·249 (2)	0·076
H(301)	0·275 (6)	0·408 (3)	0·391 (2)	0·139
H(302)	0·414 (7)	0·341 (4)	0·417 (2)	0·139
H(401)	0·037 (5)	0·346 (3)	0·411 (2)	0·101
H(402)	0·002 (5)	0·369 (3)	0·352 (2)	0·101

values, and gave $R = 0{\cdot}034$ ($R = \sum|\Delta F|/\sum|F_o|$), the function minimized being $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\{1 + [(|F_o| - 10)/28]^2\}$. The final atomic coordinates are given in Tables 1 and 2.

Discussion. The molecular structure of bis(4-formyl-2-methoxyphenolato)(*N,N,N',N'* - tetramethylethylene - diamine)copper(II) tetrahydrate, hereinafter Cu(V)$_2$-MEEN.4H$_2$O, is shown in Fig. 1. Bond distances and angles are given in Tables 3–5; further data including additional bond angles and distances and least-squares planes calculations have been deposited.*

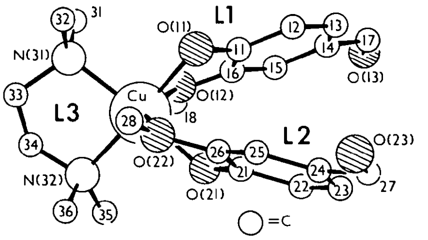

Fig. 1. Perspective view of the molecular structure. H atoms are omitted. The ligands are numbered L_1, L_2 and L_3.

Table 3. *Bond distances* (Å), *not involving water molecules, with e.s.d.'s in parentheses*

Ligands numbered as in Fig. 1.

Ligand L_1		Ligand L_2	
Cu–O(11)	1·958 (2)	Cu–O(21)	1·952 (2)
Cu–O(12)	2·492 (3)	Cu–O(22)	2·568 (4)
O(11)–C(11)	1·313 (3)	O(21)–C(21)	1·312 (4)
C(11)–C(12)	1·398 (3)	C(21)–C(22)	1·401 (4)
C(12)–C(13)	1·379 (4)	C(22)–C(23)	1·378 (5)
C(13)–C(14)	1·387 (4)	C(23)–C(24)	1·387 (4)
C(14)–C(15)	1·406 (4)	C(24)–C(25)	1·408 (4)
C(15)–C(16)	1·368 (3)	C(25)–C(26)	1·359 (4)
C(16)–C(11)	1·434 (4)	C(26)–C(21)	1·430 (4)
C(14)–C(17)	1·446 (4)	C(24)–C(27)	1·454 (5)
C(17)–O(13)	1·223 (4)	C(27)–C(23)	1·217 (5)
C(16)–O(12)	1·376 (3)	C(26)–O(22)	1·376 (3)
O(12)–C(18)	1·420 (4)	O(22)–C(28)	1·432 (4)
	Ligand L_3		
Cu–N(31)	2·043 (2)	Cu–N(32)	2·074 (2)
N(31)–C(31)	1·483 (4)	N(32)–C(36)	1·479 (4)
N(31)–C(32)	1·479 (4)	N(32)–C(35)	1·475 (4)
N(31)–C(33)	1·482 (4)	N(32)–C(34)	1·487 (4)
C(33)–C(34)	1·502 (5)		

Table 4. *Bond angles* (°) *subtended at Cu, with e.s.d.'s in parentheses*

O(11)–Cu–O(12)	72·48 (6)	O(12)–Cu–N(32)	103·96 (7)
O(21)–Cu–O(22)	71·06 (7)	O(22)–Cu–N(31)	101·20 (8)
O(11)–Cu–N(31)	91·95 (8)	O(12)–Cu–O(21)	87·67 (7)
O(21)–Cu–N(32)	102·79 (8)	O(22)–Cu–O(11)	84·50 (8)
O(11)–Cu–N(32)	175·39 (8)	O(12)–Cu–O(22)	148·70 (7)
O(21)–Cu–N(31)	171·80 (8)	O(11)–Cu–O(21)	90·02 (7)
O(12)–Cu–N(31)	100·51 (7)	O(12)–Cu–N(31)	100·51 (7)
O(22)–Cu–N(32)	99·88 (8)		

The stereochemistry at Cu is distorted elongated octahedral with the phenolic O(ph) and MEEN N atoms coordinated to Cu in a pseudo square-planar arrangement, the methoxy O(Me) completing the coordination sphere. The deviation of the O(Me) atoms from the z axis of the Cu–N–O(ph) plane is approximately 17°, similar to that found in the related

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33547 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Hydrogen-bond parameters*

O–H···O	O···O (Å)	O–H (Å)	O···H (Å)	∠H (°)*
O(2)–H(201)···$O(13)^{ii}$	2·901 (3)	0·75 (4)	2·15 (4)	175
O(2)–H(202)···O(21)	2·795 (4)	0·77 (4)	2·04 (4)	168
O(1)–H(101)···$O(11)^{iii}$	2·840 (4)	0·77 (4)	2·08 (4)	170
O(1)–H(102)···$O(23)^{i}$	2·975 (4)	0·73 (4)	2·30 (4)	154
O(3)–H(301)···O(4)	2·945 (5)	1·04 (5)	1·95 (5)	159
O(3)–H(302)···O(23)	3·075 (5)	1·01 (5)	2·07 (5)	172
O(4)–H(401)···O(1)	2·780 (3)	0·85 (4)	1·95 (4)	165
O(4)–H(402)···O(2)	2·811 (5)	0·83 (4)	2·01 (4)	161

Symmetry code

(i) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.
(ii) $x, y - \frac{1}{2}, \frac{1}{2} - z$.
(iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

* E.s.d. 3–4°.

complexes $Cu(V)_2(py)_2H_2O$ (Hobson, Ladd & Povey, 1973) and $Cu(N)_2(py)_2$ (Bullock, Hobson & Povey, 1974). In the corresponding anhydrous red isomer $Cu(V)_2$MEEN(red), however, the octahedron is compressed and the axial O(ph) [Cu–O(ph) = 1·901 (3) Å] are displaced from the z axis by only 7° (Greenhough & Ladd, 1978). While the CuN_2O_4 geometries here and in $Cu(N)_2(py)_2$ (Bullock, Hobson & Povey, 1974) [Cu–O(Me) = 2·46, 2·58 Å; Cu–O(ph) = 1·93, 1·95 Å; Cu–N = 2·05, 2·08 Å] are very similar, the solid-state diffuse-reflectance spectra are markedly different; clearly other factors play a role in determining these spectra. The angle between the two phenolato ligands, 31° here and 61° in $Cu(N)_2(py)_2$ (Bullock, Hobson & Povey, 1974), and the bidentate and chelating MEEN ligand and the hydrogen bond to O(ph) here may all be important factors. There are no significant (3σ) differences between the phenolato ligands L_1 and L_2 and both show distortions consistent with chelation, with, for example, in L_1, C(16)–C(11)–C(12) = 116·9 (2), C(11)–C(16)–O(12) = 113·8 (2) and C(15)–C(16)–O(12) = 124·7 (2)° and C(11)–C(16) = 1·434 (4) Å. The parameters of the hydrogen-bond network, given in Table 5 and illustrated in Fig. 2, show the chain O(21)(ph)–O(2)–O(4)–O(1)–O(11)(ph) linking molecules in the c direction, with weaker hydrogen bonds involving O(3) and the aldehydic O(13) and O(23). While the O–H distances are generally shorter than the standard value of 0·96 Å (Sutton, 1965), the average O–H in O–H···O [excluding O(3) which is at best very weakly hydrogen bonded] is 0·79 Å which compares well with the values of Hoge & Nordman (1974), Smith, Fitzgerald, Caughlan, Kerr & Ashmore (1974) and Berking & Mootz (1971) who give 0·80, 0·79 and 0·82 Å respectively for O–H in O–H···O. The only non-bonded contact <3·4 Å is C(18)–O(30) at 3·32 Å.

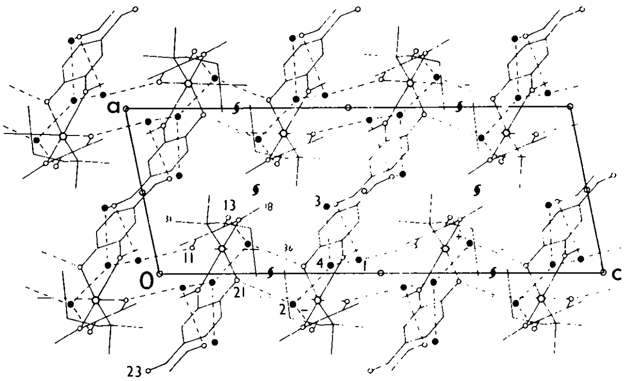

Fig. 2. Molecular packing viewed parallel to b. The larger open circles are Cu, the smaller are periodic methoxy and aldehydic O atoms and the filled circles are water. Large numerals identify O and small numerals refer to C atoms. Numbered atoms are in the molecule given in Table 1. Hydrogen bonds are denoted by dashed lines. The + and – signs indicate a hydrogen bond from one unit cell to the next in the $+b$ and $-b$ directions, respectively. O(13) and O(11) have been displaced slightly, for clarity, from the phase of the ligand L_1.

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