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Crystal and Molecular Structure of the Red Isomer of Bis(4-formyl-2-methoxyphenolato)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II)

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The red isomer of bis(4-formyl-2-methoxyphenolato)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II) is tetragonal with $a = 13{\cdot}8046$ (3), $c = 12{\cdot}1131$ (3) Å, $Z = 4$. The space group is $P4_12_12$ for the crystal used in this investigation. The structure was refined to $R = 0{\cdot}033$ for 1347 counter reflections. The stereochemistry at Cu is the first structurally characterized example of the CuN_2O_4 chromophore in the distorted compressed octahedral configuration. A detailed analysis of the thermal motion is given.

Introduction

In a series of papers entitled 'Substituted Phenols as Ligands', (Bullock & Jones, 1970, 1971; Hobson, Ladd & Povey, 1973; Bullock, Hobson & Povey, 1974; Povey, 1975; Bullock, Ladd & Povey, 1978) attempts were made to correlate the solid-state diffuse reflectance spectra of some Cu^{II} complexes with the stereochemistry of the Cu coordination polyhedron. Hathaway & Tomlinson (1970) and Hathaway & Billing (1970) have established methods whereby stereochemical deductions might be made from the analysis of Cu^{II} reflectance spectra within a closely related group of compounds, although it is stressed by McKenzie (1970) and Hathaway (1972) that it is probably essential to know the crystal structure of at least one member of the related group, and that any deductions should be made with care.

A series of Cu^{II} complexes with N bases and substituted phenols as ligands (Bullock, Hobson & Povey, 1974) has provided a closely related group of compounds within which such correlations between electronic reflectance spectra and stereochemistry may be postulated. The solid-state diffuse reflectance spectra have been characterized into three groups (Bullock, Hobson & Povey, 1974) and structure analysis of one member of each spectral group led to tentative assignments of the Cu coordination polyhedron in other members of the series according to their spectral group. Subsequent structure analysis of bis(2-methoxy-4-nitrophenolato)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II) dihydrate (Povey, 1975) shows that in this case the stereochemical predictions from the solid-state diffuse reflectance spectrum (Bullock, 1975) are essentially correct.

The structures of bis(4-formyl-2-methoxyphenolato)(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)copper(II) tetrahydrate (Greenhough & Ladd, 1978) and the corresponding anhydrous red isomer have been undertaken to provide further evidence whereby the accuracy of the stereochemical predictions of Bullock, Hobson & Povey (1974) might be assessed, the title complex having been assigned as tetrahedrally distorted square planar, but with a large deviation from planarity and with the 2-methoxy substituents not coordinated to Cu.

Experimental

Crystal data

$C_{22}H_{30}CuN_2O_6$, $M_r = 482{\cdot}03$, tetragonal, $a = 13{\cdot}8046$ (3), $c = 12{\cdot}1131$ (3) Å, $V_c = 2308{\cdot}36$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}387$ (0), $D_m = 1{\cdot}37$ (2) g cm^{-3}, μ(Cu $K\alpha$) = 15·2 cm^{-1}, $F(000) = 1012$, $\lambda = 1{\cdot}54178$ Å, space group $P4_12_12$ (or $P4_32_12$).

The title compound was recrystallized from a solution of four parts benzene to one part light petroleum at room temperature. The crystals obtained were either poorly formed, deep-red, square-based pyramids or rectangular blocks. The cell dimensions and choice of space group were determined initially by photographic methods. Refined cell dimensions were obtained by a least-squares analysis of the θ values of twelve reflections measured on a Siemens four-circle diffractometer (AED). The reflections chosen were between $\theta = 43$ and 57°, and in each case the α_1 and α_2 peaks were well resolved giving 24 independent measurements.

Intensities were measured on a crystal $0{\cdot}081 \times 0{\cdot}391 \times 0{\cdot}23$ mm elongated along *b*. No rotation of polarized sodium light could be detected when this or any other crystal was viewed along its optic axis,

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neither could any evidence of chirality be found from a morphological study of the whole batch of crystals. The chirality of the structure determined will depend, therefore, on the crystal chosen, and no correlation with physical properties will be possible. The diffractometer was operated in the θ–2θ scan mode with variable scan range and scan speed out to $\theta = 70°$, the five-value method (Hoppe, 1965) and Ni-filtered Cu $K\alpha$ radiation. The scan speed varied between 2·5 and 10° min^{-1}, with automatic incident beam attenuation to reduce strong intensities to around 4500 c.p.s. Instrumental difficulties prevented the collection of all *hkl*/*khl* reflections and only about half the *khl* data were collected. A periodic check of the 303 reflection showed no significant loss of intensity. Of the 2013 reflections collected, 41 were manually rejected on the grounds of suspicious count totals. Of the remaining 1972 intensities, 1558 had $I/\sigma(I) > 2{\cdot}58$ (observational variances based on counting statistics) and were classified as observed.

Lorentz and polarization corrections were made and the application of an analytical absorption correction was followed by the averaging of symmetry-related pairs of centric reflections, giving a final total of 1690 reflections which included 436 *hkl*/*khl* pairs, 282 averaged centric reflections and 536 unique reflections including 122 of the type *hhl*. Of this final total, 1347 were observed and used in the structure analysis.

Derivation and refinement of the structure

The structure was solved and refined in $P4_12_12$. The Cu atom, on special positions of symmetry 2, was located from a Patterson synthesis. A Fourier synthesis computed with the phases of the Cu atom and an assumed isotropic temperature factor (B = 2·5 Å^2) revealed all the non-hydrogen atoms in the phenolato moiety, and a second Fourier synthesis based on the phases of all the known atoms revealed the remaining non-hydrogen atoms. Scattering factors used were those of Cromer & Mann (1968).

Full-matrix least-squares refinement with isotropic temperature factors and unit weights gave R = 0·088 ($R = \sum|\Delta F|/\sum|F_o|$) for the observed reflections; anisotropic temperature factors reduced R to 0·063. The presence of some large U_{ij} values up to 0·17 Å^2, particularly in the tetramethylethylenediamine moiety (MEEN) was noted, the large amount of thermal motion having been indicated by an average value of the isotropic temperature factor U over the whole molecule of 6 Å^2 with values as high as 9·2 Å^2 in the MEEN moiety. An attempt was made to discover whether the large temperature factors were due to disorder in the MEEN moiety. Two, seemingly equally plausible, configurations were postulated for this part of the molecule, but, in fact, poorer agreement was obtained and this model was rejected.

All the H atoms associated with the phenolato moiety were located from a difference synthesis and further refinement reduced R to 0·058 with all the H parameters held invariant. The scattering factors for the H atoms were those of Stewart, Davidson & Simpson (1965), and the assigned isotropic temperature factors were those of the C atoms to which they were bonded. The H atoms in the MEEN moiety could not be located satisfactorily: this was attributed to the large amount of thermal motion.

The Cu form factors were corrected for anomalous dispersion (Cromer & Liberman, 1970), and the extinction parameter r^* (Larson, 1970) was included in the refinement which gave R = 0·044. Several peaks on a difference synthesis indicated the remaining H atoms but since most of them were small and ill-defined their expected positions were calculated (Roberts & Sheldrick, 1973) to complete the model. Further refinement of all parameters except the assigned isotropic temperature factors of the H atoms yielded the final R of 0·033 for the observed reflections and the space group

Table 1. *Fractional coordinates* ($\times 10^4$, Cu $\times 10^5$) *and e.s.d.'s for the non-hydrogen atoms*

	x	y	z
Cu	87374 (4)	87374 (4)	$\frac{1}{2}$
O(1)	8746 (2)	8520 (2)	6543 (2)
O(2)	7113 (2)	8749 (3)	5445 (2)
O(4)	4494 (3)	8732 (4)	8625 (3)
C(1)	7933 (3)	8523 (2)	7102 (3)
C(2)	7923 (3)	8383 (3)	8251 (3)
C(3)	7067 (3)	8409 (3)	8828 (4)
C(4)	6179 (3)	8549 (2)	8312 (3)
C(5)	6179 (3)	8664 (3)	7158 (3)
C(6)	7024 (3)	8644 (3)	6585 (3)
C(7)	6259 (4)	8959 (5)	4825 (4)
C(8)	5303 (4)	8556 (4)	8964 (4)
C(9)	10757 (5)	8578 (9)	3923 (7)
C(10)	10792 (5)	8222 (6)	5854 (8)
C(11)	10534 (4)	9838 (4)	5242 (7)
N	10347 (2)	8833 (3)	4984 (3)

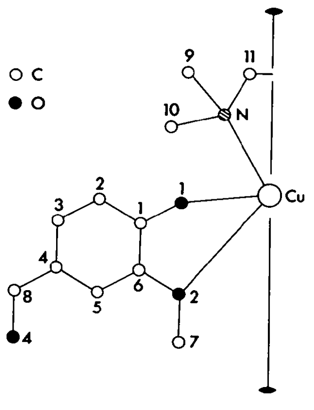

Fig. 1. The atomic numbering.

$P4_12_12$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = X \times Y$ where $X = 1$ for $\sin\theta/\lambda > 0{\cdot}4$, otherwise $X = (\sin\theta/\lambda)/0{\cdot}4$; and $Y = 1$ for $|F_o| < 50$, otherwise $Y = 50/|F_o|$. An analysis confirmed the suitability of the chosen weights, the final value of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ being 0·036 for the observed reflections. The final value of r^* was $1{\cdot}624 \times 10^3$ and the goodness-of-fit $\{\mathrm{GOF} = [\sum w(|F_o|^2 - |F_c|^2)^2/(m - s)]^{1/2}\}$ was 1·005. A final difference synthesis showed no deviations $> \pm 0{\cdot}15$ e Å^{-3}.

Refinement of the enantiomorph in $P4_32_12$ yielded $R = 0{\cdot}034$ and $R_w = 0{\cdot}038$, the Hamilton test (Hamilton, 1965) indicating that $P4_12_12$ is the correct space group at a confidence level well above 99·5%.

Fig. 1 shows the atomic numbering. The positional parameters of the non-hydrogen atoms are listed in Table 1, the coordinates and isotropic U values of the H atoms in Table 2. The observed and calculated U_{ij} values (see next section) are in Table 4.*

Thermal-motion analysis

The thermal motion of the molecule was analysed in terms of rigid-body translation and libration (Schomaker & Trueblood, 1968) as available in the program *XANADU* (Roberts & Sheldrick, 1973). Different groups of atoms contributing to the assumed rigid body were inspected, omitting H atoms. The r.m.s. deviation in U_{ij} was reduced from 0·024 Å^2 for the whole molecule (63% of the average U_{ij}), the agreement between observed and calculated U_{ij} being particularly poor in the MEEN moiety, to 0·020 Å^2 for MEEN + Cu [rigid body (I)] and 0·013 Å^2 for Cu + bis-phenolato (II). The results for (I) are included in Table 3.

The MEEN moiety

The MEEN moiety was further divided into the Cu—N—C(9)—C(10)—C(11) fragment (III) and the symmetry-related fragment containing the same Cu atom (IV). The r.m.s. deviation in U_{ij} was reduced markedly from 0·020 (I) to 0·005 Å^2 for each of these assumed rigid bodies. Results for (III) are included in Table 3.

The **L** and **T** tensors for (III) and (IV) are non-positive definite, possibly due to the very large e.s.d.'s on the elements which in turn are probably due to the rigid body being only one atom over-determined. Indeed, the only significant elements of the tensors are L_{11} and T_{11} for (III) and the symmetry-related L_{22} and T_{22} in (IV). There seems little doubt, however, that the thermal motion in the MEEN moiety is better represented by the two rigid bodies (III) and (IV), although the representation quadrics themselves are poorly determined. The least-squares r.m.s. $\sigma(U_{ij})$ is 0·0041 Å^2 for the atoms in each model, comparison of which with the r.m.s. ΔU_{ij} (0·0052 Å^2) suggests that the rigid-body models give a good approximation to the thermal motion. The major librations in rigid bodies (I), (III) and (IV) are represented schematically in Fig. 2.

In model (I) the main librations take place about axes parallel to the twofold axis along [110] and approximately parallel to $[1\bar{1}0]$, which is as expected if an attempt is made to combine the two individual but symmetry-related librations in (III) and (IV), approximately parallel to [100] and [010] respectively, into one description. These two related librations are about axes approximately parallel to Cu—N and Cu—N^{i}, and are consistent with the twofold symmetry of the MEEN ligand if the librations are in the same sense parallel to Cu—N and Cu—N^{i}. The Cu atom itself however undergoes a motion forbidden by its twofold site symmetry when the rigid bodies (III) and (IV) are considered independently. The combined effect of the two rigid-body motions, however, maintains the symmetry at Cu,

Table 2. *Fractional coordinates* (×10^3) *and U values* (Å^2) *of the* H *atoms*

	x	y	z	U
H(2)	860 (4)	836 (3)	860 (3)	0·0659
H(3)	694 (3)	837 (3)	955 (4)	0·0722
H(5)	570 (3)	875 (4)	682 (3)	0·0583
H(8)	534 (3)	837 (3)	976 (4)	0·0760
H(71)	650 (4)	905 (4)	412 (5)	0·0925
H(72)	588 (4)	850 (4)	496 (5)	0·0925
H(73)	594 (4)	959 (4)	511 (4)	0·0925
H(11)	1027 (4)	996 (4)	620 (5)	0·1140
H(12)	1125 (5)	1008 (4)	496 (5)	0·1140
H(91)	1148 (5)	854 (5)	401 (5)	0·1267
H(92)	1044 (5)	875 (7)	338 (6)	0·1267
H(93)	1059 (5)	795 (5)	378 (6)	0·1267
H(101)	1084 (5)	881 (6)	638 (6)	0·1267
H(102)	1148 (5)	835 (5)	585 (6)	0·1267
H(103)	1067 (5)	764 (5)	551 (6)	0·1267

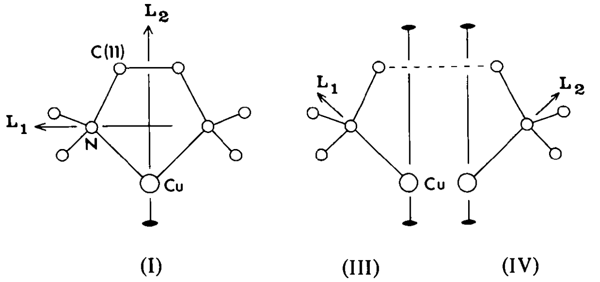

Fig. 2. The directions of the main principal libration axes in rigid-body models (I), (III) and (IV).

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33553 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected results from the thermal-motion analysis*

Model (I): full MEEN fragment, Cu(NC$_3$)$_2$

L (rad^2)	0·0233 (49)	−0·0056 (30)	0·0013 (18)
		0·0233 (49)	−0·0013 (18)
			0·0035 (33)
T (Å^2)	0·0468 (77)	−0·0009 (75)	0·0019 (78)
		0·0468 (77)	−0·0019 (78)
			0·0456 (113)

Principal axes and direction cosines

L	i	L_i (rad^2)	L_i r.m.s. amplitude (°)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·0290	9·76	0·7053	−0·7053	0·0718
	2	0·0177	7·62	0·7071	0·7071	0·0000
	3	0·0034	3·34	−0·0506	0·0506	0·9974

T	i	T_i (Å^2)	T_i r.m.s. amplitude (Å)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·0495	0·222	0·5839	−0·5839	0·5640
	2	0·0459	0·214	0·7071	0·7071	0·0000
	3	0·0438	0·209	−0·3988	0·2988	0·8258

r.m.s. ΔU_{ij} = 0·0196 Å^2 [$\Delta U_{ij} = U_{ij}$ (observed) − U_{ij} (calculated from the rigid-body motion)]

r.m.s. $\sigma(U_{ij})_{\text{obs}}$ = 0·0043 Å^2 (least-squares e.s.d.'s, see Table 4).

Model (III): CuNC(9)C(10)C(11) half MEEN

L (rad^2)	0·0451 (56)	−0·0063 (117)	0·0132 (100)
		0·0073 (48)	0·0078 (63)
			0·0042 (61)
T (Å^2)	0·0704 (124)	0·0182 (185)	−0·0288 (154)
		0·0121 (488)	−0·0601 (635)
			0·0357 (529)

Principal axes and direction cosines

L	i	L_i (rad^2)	L_i r.m.s. amplitude (°)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·0494	12·63	−0·9598	−0·0948	0·2642
	2	0·0134	6·63	−0·0782	0·8137	0·5760
	3	−0·0062	–	−0·2696	−0·5735	0·7736

T	i	T_i (Å^2)	T_i r.m.s. amplitude (Å)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·1124	0·335	0·6278	0·4807	−0·6122
	2	0·0433	0·208	−0·7772	0·4305	−0·4589
	3	−0·0375	–	0·0430	0·7639	0·6439

r.m.s. ΔU_{ij} = 0·0052 Å^2

r.m.s. $\sigma(U_{ij})_{\text{obs}}$ = 0·0041 Å^2

Table 3 (*cont.*)

Model (VII): Cu + phenolato – O(4), C(7)
[Cu, O(1), O(2), C(1) → C(6), C(8)]

L (rad^2)	0·0082 (12)	0·0010 (8)	−0·0074 (11)
		0·0018 (4)	−0·0010 (8)
			0·0108 (8)
T (Å^2)	0·0469 (19)	−0·0003 (21)	−0·0056 (17)
		0·0315 (38)	−0·0026 (20)
			0·0513 (18)

Principal axes and direction cosines

L	i	L_i (rad^2)	L_i r.m.s. amplitude (°)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·0171	7·50	−0·6409	−0·0915	0·7622
	2	0·0020	2·58	0·7052	0·3220	0·6317
	3	0·0016	2·31	−0·3032	0·9423	−0·1419

T	i	T_i (Å^2)	T_i r.m.s. amplitude (Å)	θ_{xi}	θ_{yi}	θ_{zi}
	1	0·0553	0·235	−0·5515	−0·0838	0·8300
	2	0·0433	0·208	0·8312	−0·1396	0·5382
	3	0·0311	0·176	0·0707	0·9866	0·1468

r.m.s. ΔU_{ij} = 0·0040 Å^2

r.m.s. $\sigma(U_{ij})_{\text{obs}}$ = 0·0019 Å^2

and it is perhaps useful to consider torsional oscillations of the N—C$_3$ groups about the Cu—N bonds with a stationary Cu atom. Since Cu—N is almost parallel to [100] (the angle is 3°) and since L_{11} is the only significant component in **L** for rigid body (III), the description of two symmetry-related torsional oscillations about the Cu—N bonds seems reasonably well justified. Indeed, it is perhaps best, in view of the indeterminacy of the **L** and **T** components in (III) and (IV), simply to describe the thermal motion in the MEEN ligand as made up of only two librations, of magnitude in the region of L_{11} for (III) and L_{22} for (IV), both representing torsional oscillation of the N—C$_3$ groups.

Observed and calculated U_{ij} values for the rigid body (III) are included in Table 4 and the resulting bond-length corrections in Table 5, along with those obtained by approximating (III) to a simple torsional oscillation represented by L_{11}. While the torsional oscillations do not allow the C(11)—C(11$^{\text{i}}$) bond to remain rigid, a correction has been derived with this assumption since only a slight deformation of the N—Cu—N$^{\text{i}}$ angle is required, and the **L** tensors in (III) and (IV) contain sufficient error to allow this possibility. The U_{ij} for C(11) have been resolved on to three mutually perpendicular directions (Cruickshank, 1956), parallel to [110], which is a principal libration axis by symmetry, and parallel and perpendicular to C(11)—C(11$^{\text{i}}$). The correction has then been calculated solely from libration about the twofold axis since the origin is not known and the magnitudes and directions of the principal axes of **L** vary greatly with choice of origin, except for the libration about the axis parallel to the vector of displacement of the origin (Schomaker & Trueblood, 1968), which by symmetry lies on [110] here. The N—C$_3$ torsional oscillations suggest that the relative motion of C(11) and C(11$^{\text{i}}$) is reasonably well described by a large libration $L_{[110]}$ about the symmetry

Table 4. *Observed and calculated* U_{ij} ($Å^2 \times 10^4$)

(*a*) From model (III)

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Cu U_o	456 (3)	−2 (4)	−22 (3)	456	22	600 (4)
U_c	488	10	−75	456	30	605
C(9)	700 (42)	−33 (50)	179 (39)	1680 (87)	−601 (65)	1292 (58)
	657	−40	228	1743	−474	1231
C(10)	563 (33)	33 (36)	−277 (43)	1175 (57)	264 (49)	1601 (68)
	571	72	−315	1126	325	1618
C(11)	608 (30)	−173 (26)	−163 (36)	772 (34)	−2 (37)	1550 (60)
	605	−151	−138	742	−136	1495
N	494 (18)	−14 (18)	14 (19)	653 (22)	74 (26)	797 (21)
	500	−80	30	669	13	891

(*b*) From model (VII)

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
Cu U_o	456 (3)	−2 (4)	−22 (3)	456	22	600 (4)
U_c	528	1	22	539	33	610
O(1)	461 (15)	27 (15)	−11 (15)	694 (19)	79 (13)	630 (13)
	465	23	−46	584	53	616
O(2)	577 (17)	30 (19)	−58 (12)	820 (21)	44 (17)	477 (14)
	497	14	−52	748	28	519
C(1)	436 (22)	−13 (16)	−25 (17)	386 (21)	9 (16)	601 (21)
	470	3	−65	394	5	541
C(2)	511 (25)	26 (18)	−98 (20)	608 (26)	11 (18)	569 (23)
	534	5	−90	715	51	547
C(3)	614 (28)	−50 (21)	−28 (21)	629 (30)	−14 (18)	483 (22)
	589	−30	−55	563	−15	512
C(4)	503 (22)	9 (20)	13 (20)	396 (20)	−49 (16)	563 (18)
	539	−15	−10	402	−63	534
C(5)	442 (21)	19 (23)	−93 (17)	462 (21)	−20 (18)	558 (18)
	473	19	−38	562	−22	542
C(6)	515 (21)	−9 (20)	−41 (16)	434 (22)	−32 (18)	454 (18)
	464	5	−54	404	−19	513
C(7)	731 (22)	−92 (31)	−198 (29)	994 (43)	18 (25)	607 (25)
	–	–	–	–	–	–
C(8)	653 (30)	−26 (25)	45 (22)	640 (30)	−77 (22)	609 (23)
	609	11	68	614	−78	611
O(4)	656 (20)	86 (25)	58 (17)	1397 (32)	3 (26)	829 (21)
	–	–	–	–	–	–

Table 5. *Bond-length corrections and corrected bond lengths* (Å)

(*a*) From rigid-body model (VII)

	Uncorrected	Correction	Corrected
Cu–O(1)	1·892 (2)	0·009 (1)†	1·901
Cu–O(2)	2·306 (3)	0·011	2·317
C(1)–O(1)	1·311 (5)	0·004	1·315
C(6)–O(2)	1·394 (4)	0·006	1·400
C(1)–C(2)	1·405 (6)	0·007	1·412
C(2)–C(3)	1·374 (7)	0·004	1·378
C(3)–C(4)	1·389 (6)	0·013	1·402
C(4)–C(5)	1·407 (5)	0·007	1·414
C(5)–C(6)	1·358 (6)	0·004	1·362
C(6)–C(1)	1·412 (5)	0·013	1·425
C(4)–C(8)	1·445 (6)	0·004	1·449
C(8)–O(4)*	1·214 (6)	0·011	1·225
C(7)–O(2)*	1·428 (6)	0·013	1·441

(*b*) From rigid-body model (III)

	Uncorrected	Correction	Corrected
Cu–N	2·226 (3)	0·014 (5)†	2·240
N–C(9)	1·448 (10)	0·037	1·485
N–C(10)	1·483 (10)	0·030	1·513
N–C(11)	1·445 (7)	0·033	1·478
C(11)–C(11$^{\text{i}}$)‡	1·480 (9)	0·018	1·498

(*c*) $CuNC_3$ corrections from simple torsional oscillation of $N–C_3$§

	Uncorrected	Correction	Corrected
Cu–N	2·226 (3)	0	2·226
N–C(9)	1·448 (10)	0·028 (5)†	1·476
N–C(10)	1·483 (10)	0·029	1·512
N–C(11)	1·445 (9)	0·031	1·476

* C(7), O(4) not included in the rigid-body model.

† E.s.d.'s: model (VII): 0·001 Å; model (III) and torsional model: 0·005 Å.

‡ See text. Symmetry code (i) *y*, *x*, 1 − *z*.

§ **L** approximated to L_{11} [rigid-body model (III)] directed along Cu–N.

axis [110]. The values of u^2 for C(11), parallel and perpendicular to C(11)–C(11$^{\rm i}$), are 0·141 and 0·089 Å^2 respectively, giving $L_{[110]}$ = 0·024 rad^2 and a bond-length correction (Busing & Levy, 1964) of 0·018 Å. Calculation of the correction from rigid bodies (I) and (III) gives 0·018 and 0·019 Å respectively.

Errors on the corrected bond lengths are difficult to assess, but the error in L_{11} suggests an error in the N–C corrections of 0·004 Å for the corrections derived from the simple torsional representation, so the original e.s.d. + 0·005 Å would seem to provide a reasonable estimate. Rigid body (III) gives an average corrected N–C of 1·492, the approximation to L_{11} gives 1·488 and the uncorrected average is 1·459 Å. While the corrections themselves are not significant (3σ) in some cases, the corrected bond distances are in general considered to be an improvement over the uncorrected values, and those from rigid-body model (III), together with that derived for C(11)–C(11$^{\rm i}$) are considered the better estimates.

The bis-phenolato moiety

This molecular fragment was also considered in two symmetry-related halves containing the same Cu atom, and improvements in the agreement between U_{ij}(obs) and U_{ij}(calc), similar to those obtained in the MEEN ligand, suggested that the thermal motion was again better described in terms of two rigid bodies (V and VI, r.m.s. ΔU_{ij} 0·006 Å^2) rather than the whole bis-phenolato ligand (model II, r.m.s. ΔU_{ij} 0·013 Å^2). Exclusion of C(7) and O(4) further reduced the r.m.s. ΔU_{ij} to 0·004 Å^2, and these models (VII and VIII) were considered unacceptable approximations to rigid bodies, each having r.m.s. $\sigma(U_{ij})_{\rm obs}$ = 0·0019 Å^2. Results for (VII) are included in Table 3, the observed and calculated U_{ij} in Table 4, and resulting bond-length corrections in Table 5. The principal libration axis lies approximately parallel to the plane of the assumed rigid body in a direction deviating from a line joining Cu and C(4) by only 3·5°; translational motion is roughly isotropic. Symmetry considerations concerning the Cu atom and the two symmetry-related **L** and **T** tensors in models (VII) and (VIII) are as given in the thermal-motion analyses for the MEEN ligand. By considering the errors on the components of **L**, an estimate of the error in the bond-length corrections of about 0·001 Å may be obtained, and this added to the original e.s.d. is considered to be a reasonable estimate of the errors in the corrected bond lengths.

The r.m.s. ΔU_{ij} value of 0·024 Å^2 for the whole molecule rigid-body approximation, compared to an r.m.s. $\sigma(U_{ij})$ value of 0·003 Å^2, has indicated a large amount of internal thermal motion which has been somewhat accounted for by division of the molecule into four fragments, two symmetry-related pairs, each approximated to a rigid body. The resulting thermal-motion analyses suggest that this approximation is satisfactory, and provides a general description of a large torsional oscillation of the NC_3 groups about Cu–N, with a similar but smaller libration for each phenolato ligand about axes nearly parallel to Cu–C(4). Corrections to atomic positions, bond angles and C–H distances have not been calculated.

Results and discussion

Bond distances which have been corrected for thermal motion and are referred to here are given in Table 5(*a*) and (*b*); the errors quoted include an estimate of the error in the libration correction. The uncorrected C–H distances are given in Table 6 and bond angles in Table 7. One molecule viewed down the twofold symmetry axis is shown in Fig. 3.

The stereochemistry at Cu is distorted compressed octahedral with twofold symmetry, the N atoms in the CuN_2O_4 chromophore being both in-plane and *cis* with $\mathrm{Cu{-}O_{axial}} < \mathrm{Cu{-}O_{in\text{-}plane}}$. The methoxy O(2) and the MEEN N atoms are coordinated in an approximate

Table 6. C–H *lengths* (Å)

C(2)–H(2)	1·03 (5)	C(9)–H(91)	1·00 (7)
C(3)–H(3)	0·90 (5)	C(9)–H(92)	0·82 (7)
C(5)–H(5)	0·78 (4)	C(9)–H(93)	0·91 (7)
C(7)–H(71)	0·93 (6)	C(10)–H(101)	1·03 (7)
C(7)–H(72)	0·84 (6)	C(10)–H(102)	0·96 (7)
C(7)–H(73)	1·04 (5)	C(10)–H(103)	0·93 (7)
C(11)–H(11)	1·23 (6)	C(11)–H(12)	1·10 (6)
C(8)–H(8)	1·00 (5)		

Table 7. *Bond angles* (°)

(*a*) At Cu

O(1)–Cu–O(2)	77·1 (1)	N–Cu–N$^{\rm i}$	83·2 (1)
O(1)–Cu–N	90·7 (1)	N–Cu–O(1$^{\rm i}$)	98·6 (1)
O(1)–Cu–O(2$^{\rm i}$)	94·4 (1)		
O(2)–Cu–N	166·5 (1)	O(2)–Cu–O(2$^{\rm i}$)	93·9 (1)
O(1)–Cu–O(1$^{\rm i}$)	167·7 (1)	N–Cu–O(2$^{\rm i}$)	92·8 (1)

(*b*) Other bond angles

Cu–O(1)–C(1)	120·3 (2)	C(3)–C(4)–C(5)	117·6 (4)
Cu–O(2)–C(7)	133·0 (3)	C(4)–C(5)–C(6)	120·3 (4)
Cu–O(2)–C(6)	108·5 (2)	C(5)–C(6)–C(1)	122·7 (3)
O(1)–C(1)–C(6)	122·1 (3)	C(6)–C(1)–C(2)	116·5 (4)
O(1)–C(1)–C(2)	121·3 (4)		
C(7)–O(2)–C(6)	118·0 (3)	C(9)–N–C(10)	109·3 (6)
O(2)–C(6)–C(1)	111·9 (3)	C(9)–N–C(11)	110·9 (6)
O(2)–C(6)–C(5)	125·4 (3)	C(10)–N–C(11)	108·6 (5)
C(5)–C(4)–C(8)	122·8 (4)	Cu–N–C(9)	112·5 (4)
C(3)–C(4)–C(8)	119·5 (4)	Cu–N–C(10)	111·9 (3)
C(4)–C(8)–O(4)	125·9 (4)	Cu–N–C(11)	103·5 (3)
C(1)–C(2)–C(3)	120·6 (4)	N–C(11)–C(11$^{\rm i}$)	114·9 (5)
C(2)–C(3)–C(4)	122·2 (4)		

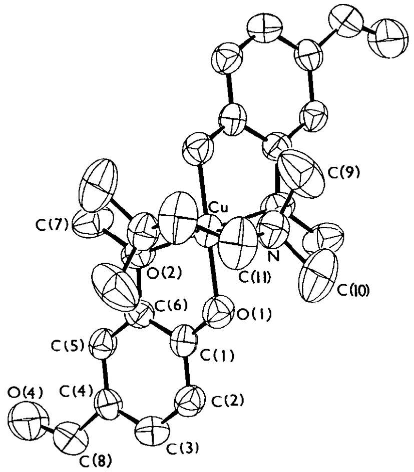

Fig. 3. The molecular structure viewed parallel to the molecular symmetry axis. The thermal ellipsoids are drawn at the 50% probability level (*ORTEP*; Johnson, 1965). H atoms omitted.

Table 8. *Some best least-squares planes expressed in the form $PI + QJ + RK = S$ (orthogonal ångström space)*

	Plane (1)	Plane (2)	Plane (3)		Plane (4)	
P	0·0962	0·9868	0·1340		−0·0193	
Q	0·9868	0·0962	−0·1340		0·9969	
R	0·1300	−0·1300	0·9819		0·0766	
S	13·7834	12·2087	5·9470		12·2360	
Atoms defining the plane and distances from the plane in Å (all atoms unit weight)	Cu	0·068	Cu	0·0	Cu	0·019
	O(1)	0·016	N	0·261	O(1)	−0·137
	O(2)	−0·063	O(2)	0·227	O(2)	0·119
	O(4)	0·067	N^i	−0·261	N	0·106
	C(1)	0·000	$O(2^i)$	−0·227	$O(1^i)$	−0·106
	C(2)	−0·012				
	C(3)	0·001				
	C(4)	−0·007				
	C(5)	−0·032				
	C(6)	−0·037				
	C(7)	0·012				
	C(8)	−0·012				
σ*	0·0383	0·0383	0·2443		0·1183	

Acute angles between the planes (°)

(1)–(2)	80·0	(2)–(3)	89·5
(1)–(3)	89·5	(2)–(4)	86·2
(1)–(4)	7·3	(3)–(4)	86·5

* σ is the e.s.d. from the plane of the atoms defining the plane.

square-planar arrangement [Cu–O(2) = 2·317 (4), Cu–N = 2·240 (8) Å] with axial phenolic O(1) atoms completing the coordination sphere at distances of 1·901 (3) Å from Cu. To the best of our knowledge this is the first structurally characterized example of the CuN_2O_4 chromophore in the distorted compressed octahedral configuration, although electronic and ESR spectroscopy results for polycrystalline samples of some members of a series of N-base adducts of Cu^{II} α-nitroketonates have been interpreted as indicative of the presence of such a configuration (Attanasio, Collamati & Ercolani, 1974). On the basis of electronic spectra, elongated tetragonal structures have been suggested for many complexes having the CuN_2O_4 chromophore (*e.g.* Attanasio, Collamati, Ercolani & Rotilio, 1973), and structures revealing this configuration *via* X-ray methods include bis(2-methoxy-4-nitrophenolato)-bis(pyridine)copper(II) $[\mathrm{Cu}(N)_2(\mathrm{py})_2]$* (Bullock, Hobson & Povey, 1974) and bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) monohydrate $[\mathrm{Cu}(V)_2(\mathrm{py})_2.\mathrm{H_2O}]$* (Hobson, Ladd & Povey, 1973), both of which are members of the same series as the title complex, $\mathrm{Cu}(V)_2$MEEN(red). Even for other sets of ligands and a different chromophore the compressed octahedral configuration is unusual, two examples being the CuF_6 chromophore in K_2CuF_4 (Knox, 1959) with two F at 1·95 and four F at 2·08 Å and CuO_6 in $\mathrm{Cu(methoxyacetate)_2.2H_2O}$ (Prout *et al.*, 1968) with 2O at 1·93, 2O at 2·13 and 2O at 2·15 Å. While neither the Cu–methoxy O nor the Cu–phenolic O atom coordination distance in $\mathrm{Cu}(V)_2$MEEN(red) is unusual, the Cu–N distance of 2·240 (8) Å is longer than that usually found for N coordinating to Cu^{II}, 1·9–2·1 Å (Hathaway & Billing, 1970; Hobson, Ladd & Povey, 1973; Bullock, Hobson & Povey, 1974), although in $\mathrm{Cu(dien)_2(NO_3)_2}$, which has the compressed rhombic octahedral CuN_6 chromophore (Stephens, 1969), the average in-plane Cu–N distance is 2·22 Å.

The equations of some least-squares planes are given in Table 8, showing that the equatorial plane is a poorer approximation to a plane than is that containing the phenolic O atoms. The phenolic O atoms are removed from the *z* axis of the equatorial Cu–N–O(methoxy) pseudo plane by 7°, smaller than that found in the elongated configuration in the related complexes $\mathrm{Cu}(V)_2(\mathrm{py})_2.\mathrm{H_2O}$ (Hobson, Ladd & Povey, 1973) and $\mathrm{Cu}(N)_2(\mathrm{py})_2$ (Bullock, Hobson & Povey, 1974) where the angles are 15 (average) and 20° respectively and the axial atoms are O(methoxy). Since $\mathrm{Cu}(N)_2$-MEEN.$2H_2O$ (Povey, 1975) and preliminary results for $\mathrm{Cu}(V)_2$MEEN.$4H_2O$ (Greenhough & Ladd, 1978) both show the CuN_2O_4 chromophore in the distorted elongated octahedral configuration, and since marked differences between the electronic spectra of the red and black isomers of $\mathrm{Cu}(V)_2$MEEN suggest different structures (Bullock, Hobson & Povey, 1974), even a tentative assignment of stereochemistry on the basis of the ligands present does not seem possible, even when the state of hydration is considered. Furthermore, a re-examination of the electronic spectra themselves is required since the stereochemistry found here bears little resemblance to the predicted tetrahedrally distorted square-planar CuN_2O_2 chromophore with the

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* py = pyridine; N = 2-methoxy-4-nitrophenolato; V = 4-formyl-2-methoxyphenolato.

methoxy substituents not coordinated, even though Bullock, Hobson & Povey (1974) suggest that the observed spectrum is readily classified with the known tetrahedral systems.

The angle between the mean planes through the symmetry-related phenolato ligands (including Cu) is 80°, the largest deviations being for Cu, O(2) and O(4) (0·06–0·07 Å). The aromatic ring itself is distorted with C(1)–C(6) = 1·425 (6) and C(5)–C(6) = 1·362 (7) Å, both significantly different [3σ level: $\sigma = (\sigma_A^2 + \sigma_B^2)^{1/2}$, Cruickshank, 1949] from the standard value of 1·395 (3) Å (Sutton, 1965). The average C–C distance in the ring is 1·399 Å and the average C–C–C bond angle is 120·0°, the largest deviations from which are C(2)–C(1)–C(6) [116·5 (4)°] and C(1)–C(6)–C(5) [122·7 (3)°]. The major distortions are thus centred on C(1) and C(6) and are probably due to chelation, a further illustration of which is provided by the O(2)–C(6)–C(1) [111·9 (3)°] and O(2)–C(6)–C(5) [125·4 (3)°] angles which distort so as to allow O(2) to approach closer to Cu.

In the MEEN ligand the corrected C(11)–C(11$^{\text{i}}$) distance of 1·498 (14) Å exhibits an electron excess similar to that found in the same bond in the related complex Cu(N)$_2$MEEN.2H$_2$O (Povey, 1975) where the value is 1·506 Å. Both N–C(9) and N–C(11), 1·485 (15) and 1·478 (12) Å, agree with the expected value of about 1·48 Å (Sutton, 1965) as found in related complexes, but N–C(10), 1·513 (15) Å, is somewhat in excess of this value but not significantly so. The average of angles centred on N is 109·5° with deviations of up to 6° occurring where Cu is involved; the N–C(11)–C(11$^{\text{i}}$) angle of 114·9 (5)° appears to be significantly larger than the expected tetrahedral value, although the error is probably underestimated since the C(11) atoms are symmetry-related.

The average C–H distance is 0·97 Å, the largest deviations from which are for C(5)–H(5) [0·78 (4) Å] and C(11)–H(11) [1·23 (6) Å]; the H thermal parameters are unrefined and isotropic (hence no C–H distance corrections for thermal motion have been calculated) and the e.s.d.'s for C–H are almost certainly underestimated. This also applies to bond angles involving H although only C(2)–C(3)–H(3) [131 (3)°], H(91)–C(9)–H(92) [129 (6)°], C(11)–C(11$^{\text{i}}$)–H(11$^{\text{i}}$) [95 (3)°], and all angles involving H(101) are more than 3σ from their expected values. The angles involving H(101) are particularly poor and this atom cannot be considered satisfactorily located.

Table 9. *Selected non-bonded contacts* (Å), *uncorrected for thermal motion*

(*a*) Intramolecular

O(1)–O(2)	2·636 (4)	O(1)–N$^{\text{i}}$	3·129 (4)
O(1)–N	2·938 (4)	O(2)–O(2$^{\text{i}}$)	3·371 (5)
N–N$^{\text{i}}$	2·955 (4)	O(2)–N$^{\text{i}}$	3·282 (5)
O(1)–O(2$^{\text{i}}$)	3·094 (4)		

(*b*) Intermolecular (X–X < 3·4 Å, X–H < 2·8 Å, H–H < 2·6 Å)

C(3)–O(4$^{\text{ii}}$)	3·347 (6)	H(3)–O(4$^{\text{ii}}$)	2·63 (5)
C(8)–O(4$^{\text{ii}}$)	3·210 (6)	H(12)–H(2$^{\text{iii}}$)	2·57 (7)
H(8)–O(4$^{\text{ii}}$)	2·60 (5)	H(72)–H(93$^{\text{iv}}$)	2·54 (9)

Symmetry code

(ii) $\frac{3}{2} - y, \quad \frac{1}{2} + x, \quad \frac{1}{4} + z$
(iii) $2 - y, \quad 2 - x, \quad \frac{3}{2} - z$
(iv) $-\frac{1}{2} + x, \quad \frac{3}{2} - y, \quad \frac{3}{4} - z$

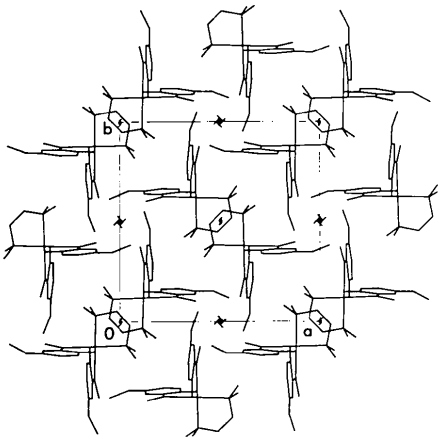

Fig. 4. Molecular packing viewed parallel to c.

Some selected non-bonded contacts are given in Table 9; the C(8)–H(8)···O(4$^{\text{ii}}$) angle of 119° and the H(8)···O(4$^{\text{ii}}$) distance 2·60 Å indicate that there is no hydrogen-bonding in this structure. The molecular packing, viewed parallel to c, is shown in Fig. 4.

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Structures of Polyether Complexes.
III.* Molecular and Crystal Structure of Bis[(*o*-methoxyphenoxy)ethoxy]ethane–Sodium Isothiocyanate

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$C_{20}H_{26}O_6$.NaSCN crystallizes from methanol/ethyl acetate in space group $P2_12_12_1$ with $a = 10{\cdot}146\ (3)$, $b = 15{\cdot}171\ (4)$, $c = 14{\cdot}855\ (4)$ Å, $Z = 4$. The structure was solved from 2054 X-ray diffractometer data by direct methods and refined to $R_w = 7{\cdot}0\%$. Starting with one oxyanisole residue the polyether ligand is wrapped around the Na^+ ion in a planar, annular structure with the C—O torsion angles *trans* and ethylenedioxy C—C angles *gauche*. To avoid a collision between the two oxyanisole residues, the two C—O bonds near the second oxyanisole residue are *gauche*, giving rise to a helical structure of the ligand with the normals to the phenyl rings forming an angle of 116°. The Na^+ ion is coordinated to all six O atoms of the ligand with $Na^+\cdots O$ distances ranging from 2·33 to 2·54 Å and is also connected to the N atom of the isothiocyanate group, $Na^+\cdots N = 2{\cdot}33$ Å.

Introduction

Cyclic crown ethers and cryptates have been of considerable interest as analogues of cyclic ionophore antibiotics (Ovchinnikov, Ivanov & Shkrob, 1974; Pedersen & Frensdorff, 1972; Lehn, 1973; Christensen, Eatough & Izatt, 1974) and have found application in preparative organic chemistry (Vögtle & Neumann, 1973). Recently, linear polyethers with good cation complexing properties have been synthesized (Vögtle & Weber, 1975; Vögtle & Sieger, 1977; Tümmler, Maass, Weber, Wehner & Vögtle, 1977). The structure analysis of bis(8-quinolyloxyethoxyethyl) ether–RbI (I.RbI; Saenger, Brand, Vögtle & Weber, 1977) revealed a helical complex structure. The present study

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* Part II: Saenger, Brand, Reddy, Suh & Weber (1978).

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