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The Structure of (Formato)bis(1,10-phenanthroline)copper(II) Perchlorate, $[Cu(C_{12}H_8N_2)_2(CHO_2)]ClO_4$

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Abstract. $M_r = 568{\cdot}43$, monoclinic, space group $C2/c$, $a = 16{\cdot}7721$ (6), $b = 11{\cdot}5806$ (3), $c = 12{\cdot}5735$ (3) Å, $\beta = 111{\cdot}370$ (2)°, $V = 2274{\cdot}25$ (8) Å^3, $Z = 4$, $D_m = 1{\cdot}658$, $D_x = 1{\cdot}660$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}17$ mm^{-1}, $F(000) = 1156$, $T = 298$ K, $R = 0{\cdot}048$ for 2139 independent reflections with $I > 3\sigma(I)$. The metal ion is hexacoordinated to the four N atoms of the phenanthrolines, and to the oxygen atoms of the formate ion forming a distorted octahedral configuration with bond lengths Cu—N 1·985 (3) and 2·111 (3) Å and Cu—O 2·353 (6) Å. The bidentate formate ion has a twofold symmetry axis with a particularly short C—O distance of 1·189 (6) Å.

Introduction. This structural study is one of a series on compounds obtained at the Department of Chemistry as part of a programme of studies in oxidation of inorganic complexes. It is directed towards the change in copper coordination produced by the replacement of a coordinated chloride ion by a formate ion in an otherwise identical-composition complex (Boys, Escobar & Martínez-Carrera, 1981).

Experimental. Prismatic transparent deep turquoise crystals, D_m by flotation; crystal $0{\cdot}14 \times 0{\cdot}32 \times 0{\cdot}24$ mm, Philips PW 1100 diffractometer, graphite monochromatized Mo $K\alpha$, $\omega/2\theta$ scan; 4553 reflections with $2\theta < 66°$ in the range −25 to 23, 0 to 17, 0 to 19 for h,k,l, respectively, 4219 unique reflections, two standards monitored every 80 reflections constant within ±2%, 34 strong reflections $2\theta < 38°$ for cell determination; Lp correction, absorption ignored, anomalous-dispersion correction for Cu and Cl atoms; systematic absences hkl, $h + k$ odd and $h0l$, l odd; direct methods (*MULTAN*, Main, Lessinger, Woolfson, Germain & Declercq, 1976) and anisotropic full-matrix refinement in both Cc and $C2/c$ indicated centrosymmetric one; H-atom parameters not refined, but included in model with calculated positions [bond distance 0·89 Å, average of C—H distances in phenanthroline given by Simmons, Lundeen & Seff (1978)], isotropic U values ($U = U_{\text{eq}}$ of the corresponding C atom); $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$) minimized with $w = 1$ at the beginning and $w = w_1 w_2$ at the final stages of refinement ($w_1 = 1$ if $\sin\theta > 0{\cdot}25$, otherwise $w_1 = \sin\theta/0{\cdot}25$ and $w_2 = 1$ if $|F_o| < 45$, otherwise $w_2 = 45/|F_o|$); $R = 0{\cdot}048$, $R_w = 0{\cdot}057$, $S = 1{\cdot}44$ for the 2139 (m) reflections with $I > 3\sigma(I)$ used in the refinement of 169 (n) parameters; overdetermination ratio (m/n) is 12·7 and $R = 0{\cdot}071$ for the 4219 unique reflections; mean Δ/σ 0·01, largest 0·15; max. $\Delta\rho$ excursions in final difference Fourier +0·91 e Å^{-3} at 0·95 Å from Cu atom and three peaks less than +0·60 e Å^{-3} near formate O(3) atom, min. −0·34 e Å^{-3};* scattering factors for non-hydrogen neutral atoms and for Cu^{2+} from Cromer & Mann (1968); for H atoms from Stewart, Davidson & Simpson (1965); dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations carried out on an IBM 370/145 computer using XRAY76 (Stewart, 1976), mean planes and torsion angles with *NRC*22 (Ahmed, Hall, Pippy & Huber, 1973).

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* Lists of structure factors, anisotropic thermal parameters, calculated positional parameters for hydrogen atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38806 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Final positional and equivalent isotropic thermal parameters for all non-hydrogen atoms are listed in Table 1.

The complex cation $[Cu^{2+}(phen)_2HCOO^-]^+$ is represented in Fig. 1, where the twofold axis (*b* axis) lies along C(13)···Cu. The equatorial plane of the octahedron was taken as the mean plane through the copper atom, the nitrogen atoms N(2) and N(2^{ii}) of the phenanthroline molecules symmetrically related by the twofold axis, and the oxygen atoms O(3), O(3^{ii}) of the formate ion related by this axis. The maximum deviations [±0·168 (5) Å] from this equatorial plane correspond to the oxygen atoms. The N(1)–N(1^{ii}) axis of the octahedron forms an angle of 82·1 (4)° with this plane. The bond lengths and angles are given in Table 2.

Table 1. *Atomic coordinates* (×10^4) *and* U_{eq} (Å^2 ×10^4) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	*y*	*z*	U_{eq}
Cu	5000	7359 (1)	2500	420
Cl	5000	8696 (1)	7500	480
O(1)	5385 (3)	7975 (5)	8457 (4)	1162
O(2)	5628 (3)	9392 (4)	7316 (4)	935
C(13)	5000	5027 (6)	2500	547
O(3)	5450 (3)	5534 (5)	3321 (4)	1194
N(1)	5934 (2)	7350 (3)	1884 (2)	421
N(2)	5911 (2)	8343 (3)	3789 (2)	402
C(1)	5922 (3)	6851 (4)	0928 (3)	511
C(2)	6649 (3)	6770 (4)	0653 (3)	554
C(3)	7402 (3)	7213 (4)	1365 (4)	535
C(4)	7434 (2)	7782 (3)	2370 (3)	446
C(5)	8190 (2)	8287 (4)	3171 (4)	570
C(6)	8176 (2)	8813 (4)	4122 (4)	547
C(7)	7412 (2)	8875 (3)	4374 (3)	443
C(8)	7353 (3)	9395 (4)	5360 (3)	535
C(9)	6595 (3)	9398 (4)	5512 (4)	559
C(10)	5885 (3)	8860 (4)	4716 (3)	501
C(11)	6665 (2)	8366 (3)	3616 (3)	388
C(12)	6677 (2)	7828 (3)	2593 (3)	379

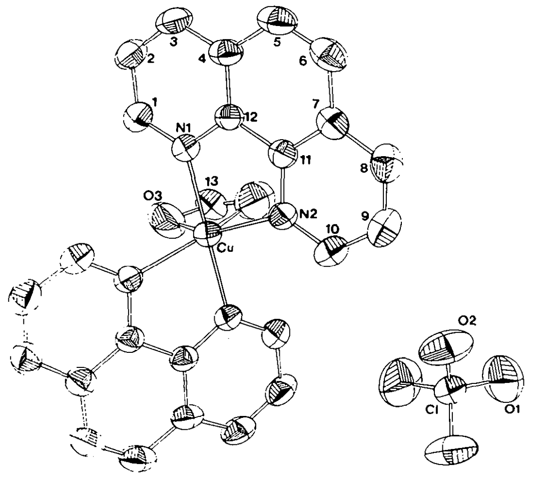

Fig. 1. Structure of the complex cation and perchlorate anion with the atom-numbering scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(*a*) Metal coordination			
Cu–N(1)	1·985 (3)		
Cu–N(2)	2·111 (3)		
Cu–O(3)	2·353 (6)		
In-plane angles		Out-of-plane angles	
N(2)–Cu–O(3)	97·0 (1)	N(1)–Cu–N(2)	81·3 (1)
O(3)–Cu–O(3^{ii})	52·1 (2)	N(1)–Cu–N(2^{ii})	99·0 (1)
N(2)–Cu–O(3^{ii})	148·1 (1)	N(1)–Cu–N(1^{ii})	179·4 (5)
N(2)–Cu–N(2^{ii})	114·6 (1)	N(1)–Cu–O(3)	89·7 (2)
		N(1)–Cu–O(3^{ii})	89·8 (2)
(*b*) Formate ion			
C(13)–O(3)	1·189 (6)	Cu–O(3)–C(13)	93·5 (4)
		O(3)–C(13)–O(3^{ii})	120·8 (7)
(*c*) Phenanthroline molecule			
N(1)–C(1)	1·327 (5)	C(4)–C(12)	1·397 (6)
N(1)–C(12)	1·358 (4)	C(5)–C(6)	1·349 (7)
N(2)–C(10)	1·325 (5)	C(6)–C(7)	1·430 (6)
N(2)–C(11)	1·359 (5)	C(7)–C(8)	1·413 (6)
C(1)–C(2)	1·387 (7)	C(7)–C(11)	1·398 (4)
C(2)–C(3)	1·354 (5)	C(8)–C(9)	1·353 (7)
C(3)–C(4)	1·409 (6)	C(9)–C(10)	1·394 (5)
C(4)–C(5)	1·427 (5)	C(11)–C(12)	1·436 (5)
Cu–N(1)–C(1)	127·0 (3)	C(4)–C(5)–C(6)	120·8 (4)
Cu–N(1)–C(12)	114·1 (2)	C(5)–C(6)–C(7)	121·8 (3)
Cu–N(2)–C(10)	132·3 (3)	C(6)–C(7)–C(11)	118·6 (4)
Cu–N(2)–C(11)	110·1 (2)	C(8)–C(7)–C(11)	116·6 (4)
C(1)–N(1)–C(12)	118·7 (3)	C(7)–C(8)–C(9)	119·6 (3)
C(10)–N(2)–C(11)	117·6 (3)	C(8)–C(9)–C(10)	119·9 (4)
N(1)–C(1)–C(2)	122·0 (3)	C(9)–C(10)–N(2)	122·7 (4)
C(1)–C(2)–C(3)	120·2 (4)	N(2)–C(11)–C(7)	123·6 (3)
C(2)–C(3)–C(4)	119·4 (4)	C(7)–C(11)–C(12)	119·5 (4)
C(3)–C(4)–C(12)	117·3 (3)	N(1)–C(12)–C(4)	122·4 (3)
C(5)–C(4)–C(12)	118·8 (4)	C(4)–C(12)–C(11)	120·5 (3)
(*d*) Perchlorate ion			
Cl–O(1)	1·413 (5)	Cl–O(2)	1·411 (5)
O(1)–Cl–O(1^{ii})	107·5 (3)	O(1)–Cl–O(2)	109·9 (3)
O(2)–Cl–O(1^{ii})	109·5 (3)	O(2)–Cl–O(2^{ii})	110·3 (3)

The three coordination distances of the Cu^{2+} ion are significantly different. They may be compared with the mean values of the short Cu–N, intermediate Cu–N and long Cu–*X* distances found in other complexes of the type $[Cu(phen)_2X].ClO_4$. These mean values are: 1·995 (6), 2·107 (6) and 2·298 (2) for $X = Cl$ (Boys, Escobar & Martínez-Carrera, 1981); 2·000 (4), 2·114 (4) and 2·321 (4) for $X = CH_3CO_2$ (Clifford, Counihan, Fitzgerald, Seff, Simmons, Tyagi & Hathaway, 1982); 2·013 (13), 2·062 (13) and 2·328 (12) Å for *X* = phen (Anderson, 1973). The N(1)–Cu–N(2) bite angle of 81·3 (1)° for the present complex ($X = HCO_2$) is between the values of 80·5 (2) and 81·7 (2)° given independently for *X*=Cl.

The phenanthroline molecule is planar within a root-mean-square deviation of 0·015 (3) Å from the mean plane calculated with all its atoms. The major deviation corresponds to N(2) with −0·026 (3) Å. The molecule shows the usual C_{2v} symmetry. The differences between equivalent bonds (Table 2) are not significant and these bonds agree well with the weighted mean values (and also with the calculated MO lengths) reported for molecular 1,10-phenanthroline (Nishigaki, Yoshioka & Nakatsu, 1978). The major discrepancies correspond to the symmetry unpaired bonds: C(5)–C(6) = 1·349 (7) instead of 1·331 (9) Å (calculated

1·368 Å) and C(11)—C(12) = 1·436 (5) instead of 1·454 (6) Å (calculated 1·445 Å).

The perchlorate ion exhibits twofold symmetry with Cl—O distances of 1·413 (5) and 1·411 (5) Å and interbond angles varying from 107·5 (3) to 110·3 (3)°. These values together with its thermal parameters [$B_{\text{eq}} = 9{\cdot}2$ (2) and 7·4 (2) Å^2 for the oxygen atoms] indicate an unusually ordered perchlorate ion, which is not coordinated to the copper atom.

The cohesion of the crystal is provided fundamentally by ionic forces, but some interactions with distances smaller than the sum of the van der Waals radii of the involved atoms were detected. These proximities are shown in Fig. 2.

The formato group, being symmetrically coordinated to the metal atoms, shows total resonance. The C—O bond length [1·189 (6) Å] appears shorter than the double bond in formic acid [1·222 (2) Å] (Nahringbauer, 1978) and it is in the range of short C—O distances for bidentate bridging formato groups [1·18 (4)–1·21 (4) Å] found in diammonium uranyl tetraformate (Mentzen, Puaux & Sautereau, 1978). In that work, these short C—O distances were associated with an infrared band at 1744 cm^{-1} and the usual C—O distances (1·24–1·30 Å) with a band at 1600–1560 cm^{-1}. The IR spectrum of the present complex exhibits this last band, but not the first one.

From Table 1 it can be seen that the temperature factor of O(3) [$B_{\text{eq}} = 9{\cdot}4$ (2) Å^2] is unexpectedly large: it is larger than the temperature factor of the oxygen atoms of the non-coordinated perchlorate group. The C(13) atom, however, is not particularly agitated [$B_{\text{eq}} = 4{\cdot}3$ (2) Å^2], less, in fact, than some carbon atoms of the phenanthroline molecule. The r.m.s. displacements in the principal directions are 0·21, 0·23, 0·26 Å for atom C(13) and 0·22, 0·27, 0·49 Å for atom O(3). The direction of the largest displacement of O(3) makes an angle of ~85° with the C(13)—O(3) bond, but only ~5° with the Cu—O(3) bond. The r.m.s. displacements of O(3) towards the C(13) and Cu atoms are 0·13 and 0·45 Å, respectively. This preferential vibration along the metal–ligand bond suggests a contribution of disorder to the r.m.s. displacements of the formato O atoms in the equatorial plane. On the other hand, it was not possible to find a reasonable model for a bond-length correction on the assumption that all the r.m.s. displacements are thermal displacements.

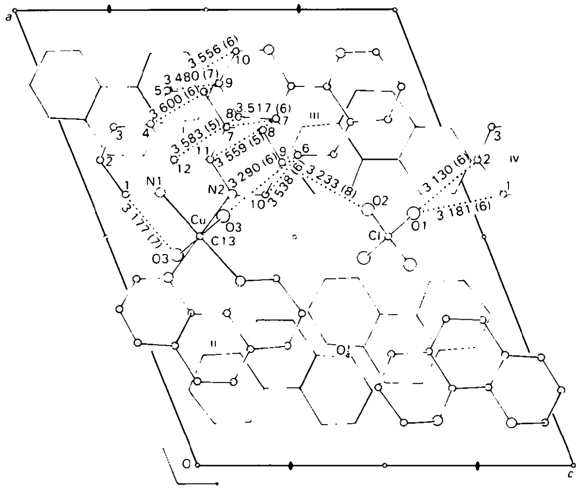

Fig. 2. Crystal structure as viewed along the *b* axis. The shortest distances (Å) between neighboring molecules are shown. The perchlorate and formate ions and the copper atom are plotted only once. Atom C(13) below Cu atom is not plotted. Symmetry code: None *x, y, z*; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iv) $x, y, 1+z$.

The behavior of the formate oxygen atoms is similar to the behavior of the acetate oxygen atoms in the [Cu(phen)$_2$CH$_3$COO]ClO$_4$ and [Cu(phen)$_2$CH$_3$COO].BF$_4$.2H$_2$O complexes (Clifford *et al.*, 1982). In that work, a fluxional disorder of the whole CuN$_4$O$_2$ chromophore is proposed, which would be consistent with ESR results for these complexes. In the meantime, the structures of other *cis*-distorted octahedral Cu$^{\text{II}}$ complexes exhibiting this disorder in the oxygen atoms of their chelating O*X*O$^-$ groups have been determined and a general explanation has been made in terms of a pseudo Jahn–Teller formalism (Simmons, Seff, Clifford & Hathaway, 1983). According to that explanation, each cation in the present structure has an asymmetric form which changes dynamically to a stereochemically equivalent one, so that the binary axis is an average symmetry element. The origin of this dynamic disorder is vibronic, *i.e.* it is due to a coupling between electronic motions and nuclear vibrational modes in the cations.

We are grateful to Professor W. Zamudio for proposing this structural study and to Mrs R. Barahona who prepared the crystals and kindly supplied them with the measured density. We are indebted to Mrs E. Spodine (Facultad de Ciencias Básicas y Farmacéuticas) for the infrared spectra and valuable discussions and to the Instituto de Química Física 'Rocasolano', Madrid, Spain, for intensity-data collection. This work was partially supported by a grant from the Departamento de Desarrollo de la Investigación de la Universidad de Chile (E938–8235).

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The Structure of (4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane-$N,N',O^4,O^{13},O^{16},O^{21}$)nickel(II) Nitrate, $[Ni(C_{16}H_{32}N_2O_5)].(NO_3)_2$

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Abstract. $M_r = 515{\cdot}16$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}374\,(2)$, $b = 13{\cdot}862\,(2)$, $c = 16{\cdot}442\,(2)$ Å, $V = 2136{\cdot}8\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}601$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}79$ cm^{-1}, $F(000) = 1088$, 163 K, $R = 0{\cdot}042$ for 2139 ($I \geq 3\sigma_I$) of 3533 unique reflections. The Ni^{2+} ion resides inside the cryptand cavity but is coordinated to only six of the seven potential donor atoms. The Ni—O distances are 2·054 (4), 2·072 (3), 2·093 (3) and 2·106 (4) Å. The Ni—N distances are 2·114 (4) and 2·180 (5) Å. The nitrate ions are not bound to the nickel.

Introduction. Diazapolyoxamacrobicyclic ligands (a type of cryptand) have been shown by X-ray crystallography to encapsulate transition-metal ions in only four cases (Mathieu & Weiss, 1973; Hart, Hursthouse, Malik & Moorhouse, 1978; Ciampolini, Dapporto & Nardi, 1979; Burns, 1979) although there is considerable evidence for complexation in solution (for example, Arnaud-Neu, Spiess & Schwing-Weill, 1977; Cox, Firman & Schneider, 1982). The cavity of the cryptand *C*221 is approximately the correct size to accommodate divalent first-row transition-metal ions inside the cavity without gross distortion. Therefore, as part of our survey of the binding of polyether ligands to first-row transition-metal ions, we prepared the complex Ni(*C*221)$(NO_3)_2$ for which a single-crystal X-ray diffraction study is presented.

Experimental. Prepared by addition of cryptand *C*221 to a solution of $Ni(EtOH)_6(NO_3)_2$ in a mixture of ethanol and triethyl orthoformate; yellowish brown crystalline blocks formed, sensitive to atmospheric moisture. Single crystal mounted in Lindemann capillary; details of data collection and structure refinement appear in Table 1; systematic absences $h00$, h odd; $0k0$, k odd; $00l$, l odd; data corrected for Lorentz and polarization effects, absorption and decay. Ni atom located by Patterson methods. *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) gave same Ni position but also two sets of peaks related by a mirror plane. Ni-phased heavy-atom map produced a similarly mirrored set of peaks attributed to the presence of both enantiomorphs. Location of remaining non-hydrogen atoms required careful selection of peaks from several subsequent difference maps so as to enhance only one enantiomorph. Hydrogen atoms located in a difference map as peaks of 0·3–0·6 e Å^{-3}, but idealized positions [d(C—H) = 1·0 Å] used in model with U fixed at 0·038 Å^2; non-hydrogen positions and anisotropic thermal parameters refined, $R = 0{\cdot}0423$.* Refinement of enantiomorph gave $R = 0{\cdot}051$; Hamilton's test (Hamilton, 1965) suggests that this configuration can be rejected at the 99·5% confidence level; hydrogen scattering factors from Stewart, Davidson & Simpson (1965); other scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). Principal computer programs given by Riley & Davis (1976); parameter and geometry tables generated by *FUER* by S. B. Larson.

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* Lists of anisotropic thermal parameters, H-atom calculated positions, miscellaneous interatomic distances, least-squares planes and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38784 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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