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Structure of Hexakis(pyridine *N*-oxide)copper(II) Nitrate Dihydrate, $[Cu(C_5H_5NO)_6](NO_3)_2.2H_2O$

By J. S. Wood

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, *USA*

C. P. Keijzers

Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 *ED Nijmegen, The Netherlands*

and R. O. Day

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, *USA*

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Abstract. $M_r = 794\cdot2$, monoclinic, $P2_1/c$, $a = 9\cdot556$ (2), $b = 9\cdot924$ (2), $c = 18\cdot658$ (3) Å, $\beta = 100\cdot43$ (3)°, $V = 1740\cdot2$ (1) Å^3, $Z = 2$, $D_x = 1\cdot515$, $D_m = 1\cdot50$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 7\cdot38$ cm^{-1}, $F(000) = 822$, $T = 295$ K. Final $R = 0\cdot042$ for 2798 non-zero reflections. The $[Cu(C_5H_5NO)_6]^{2+}$ cation exhibits a statically distorted Jahn–Teller geometry at room temperature with Cu—O distances of 1·954 (2), 1·970 (2) and 2·478 (2) Å in contrast to the anhydrous complex, which has previously been shown to undergo a dynamic Jahn–Teller distortion. The cations pack in a pseudo-ferrodistortive arrangement and EPR measurements indicate no exchange between the two magnetically distinct complexes in the unit cell.

Introduction. The series of hexakis(pyridine *N*-oxide) complexes, $[Cu(C_5H_5NO)_6]X_2$ ($X = ClO_4^-$, BF_4^-, NO_3^-) crystallize in the trigonal space group $R\bar{3}$ and exhibit dynamic Jahn–Teller distortions above *ca* 50 K and static-cooperative Jahn–Teller effects below this temperature. The detailed forms of the low-temperature structures depend on the nature of the anion, X. They have been extensively examined, using a combination of diffraction and EPR techniques both by ourselves and by other workers (Wood, Keijzers, de Boer & Buttafava, 1980; Keijzers, McMullan, Wood, van Kalkeren, Srinivasan & de Boer, 1982; Reinen & Krause, 1979; Day & Wood, 1981). In studying the nitrate complex, we found that a monoclinic modification cocrystallized alongside the trigonal form when aqueous ethanol was used for crystal growing and that it reverted to the latter form on grinding. Since EPR measurements indicated that this low-symmetry form contained tetragonally elongated $[Cu(C_5H_5NO)_6]^{2+}$ complex ions, we undertook a structure analysis in order to be able to compare the details of the geometry of the statically distorted complex and its packing, with those proposed for the low-temperature modifications of the trigonal complexes and specifically with that of the nitrate complex. EPR measurements on the trigonal form of the latter complex indicate an antiferrodistortive arrangement of tetragonal complexes at low temperature, *i.e.* one in which the tetragonal axes of nearest neighbor ions are mutually orthogonal (Wood *et al.*, 1980).

Experimental. Crystals of title compound prepared as previously described (Wood *et al.*, 1980). Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator; cell dimensions obtained from 25 reflections in range $21 \leq 2\theta \leq 28°$. Density measured by flotation; crystal dimensions 0·2 × 0·25 × 0·2 mm. No absorption corrections made. Total of 3053 independent reflections (h 0–11, k 0–11, l −22–21) measured in range $2 \leq 2\theta \leq 50°$ using ω–2θ scan technique. Five standards monitored, no significant variation with time. Standard deviations assigned as $\sigma(I) = [\sigma^2_{\rm count} + (0\cdot05\,I)^2]^{1/2}$; 2798 reflections with net non-zero intensity used for refinement. Structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971); least-squares refinement carried out using *LINEX*, a modified version of *ORFLS* (Busing, Martin & Levy, 1962); function minimized $\sum w(|F_o| - |F_c|)^2$ with weights $w = [2{\rm Lp}F_o/\sigma(I)]^2$. Pyridine-ring H atoms included as fixed contributions, with C—H set at 1·05 Å. At convergence, all $\Delta p_i \leq 0\cdot1\sigma(p_i)$ with $R = 0\cdot042$, $R_w = 0\cdot066$, $S = 2\cdot05$ for 241 variables refined. Max. and min. values in final difference density map 0·73 and −0·6 e Å^{-3} respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); anomalous-dispersion correction for Cu included (Cromer & Liberman, 1970). Calculations carried out on a CDC-Cyber 175 computer.

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Discussion. The final atomic coordinates are listed in Table 1.* Fig. 1 contains an *ORTEP* view (Johnson, 1965) of the statically distorted $[Cu(C_5H_5NO)_6]^{2+}$ complex ion projected along the pseudo-[111] direction of the CuO_6 octahedron. Comparison with the similar view for the trigonal modification of the nitrate complex (Day & Wood, 1981) indicates that the crystallographically imposed $\bar{3}$ symmetry of the latter is destroyed, not only by the distortion to the tetragonal geometry in which Cu—O(3) is the pseudo-fourfold axis of the coordination polyhedron, but also by angular distortions of the polyhedron from 90° and appreciable changes in the orientations of the ligand rings relative to the Cu—O bonds. In addition, the Cu—O—N angle for the pyridine *N*-oxide ligand in the tetragonal position is appreciably smaller [114·6 (1)°] than those for the other two ligands [average 119·7 (1)°], a result which is consistent with the rigid-body analysis of the ligand motion derived from the low-temperature neutron structure results for the trigonal perchlorate complex (Keijzers *et al.*, 1982). The weaker coordination of the 'axial' ligand is also evident in the ligand N—O distances, the average for the two in-plane ligands being 1·341 (3) Å while that for the axial ligand [1·314 (3) Å] is more in keeping with the distance of 1·297 (1) Å found for NO_2—C_5H_5NO at low temperature (Coppens & Lehmann, 1976).

The Cu—O distances given in Table 2 yield a Jahn–Teller radius of 0·59 Å {calculated as $[\sum_{i=1}^{6}(d_{\rm ave}-d_i)^2]^{1/2}$} which is appreciably larger than that of 0·40 Å estimated from the room-temperature r.m.s. amplitudes of the O atoms in the trigonal modification. This larger value is attributable to the rather long Cu—O(3) bond. The stability of this monoclinic modification of the nitrate complex appears to arise from the presence of the two water molecules of crystallization per molecule of complex, which are involved in hydrogen bonds to two of the nitrate O atoms, O(5) and O(6), as illustrated in Fig. 2. The O···O distances involving the hydrogen bonds are 2·900 (4) and 2·935 (4) Å for O(5)···O(7) and O(6)···O(7) respectively, while the angle O(5)—O(7)—O(6) is 117·3 (2)°. Powdering the monoclinic crystals apparently causes loss of the water molecules and conversion to the trigonal modification, since EPR measurements on such powders indicate a gradual change from a static to a dynamic spectrum at room temperature. In addition to showing the hydrogen bonding, Fig. 2 gives the relative orientations of the two CuO_6 moieties in the unit cell and shows that their

Table 1. *Positional* (× 10^4) *and equivalent isotropic thermal* ($Å^2$ × 10^3) *parameters for the non-*H *atoms of* $[Cu(C_5H_5NO)_6](NO_3)_2.2H_2O$ *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Cu	$\frac{1}{2}$	$\frac{1}{2}$	0	31·8 (4)
O(1)	4616 (2)	6944 (2)	57 (1)	39 (1)
N(1)	5497 (2)	7849 (2)	−151 (1)	31 (2)
C(11)	6154 (3)	8724 (3)	349 (2)	39 (2)
C(12)	7019 (3)	9715 (3)	151 (2)	47 (2)
C(13)	7204 (4)	9800 (3)	−561 (2)	50 (2)
C(14)	6528 (4)	8892 (3)	−1057 (2)	53 (2)
C(15)	5655 (3)	7916 (3)	−851 (1)	44 (2)
O(2)	7035 (2)	5403 (2)	175 (1)	39 (1)
N(2)	7930 (2)	4485 (2)	−24 (1)	33 (2)
C(21)	8430 (3)	3493 (3)	437 (2)	45 (2)
C(22)	9418 (3)	2602 (3)	240 (2)	60 (3)
C(23)	9854 (3)	2739 (3)	−417 (2)	59 (3)
C(24)	9296 (3)	3758 (4)	−877 (2)	59 (3)
C(25)	8337 (3)	4641 (3)	−672 (2)	43 (2)
O(3)	4916 (2)	5047 (2)	1319 (1)	43 (2)
N(3)	5493 (2)	6121 (2)	1664 (1)	36 (2)
C(31)	6924 (3)	6258 (3)	1809 (2)	43 (2)
C(32)	7539 (3)	7387 (3)	2165 (2)	50 (2)
C(33)	6702 (4)	8387 (3)	2375 (2)	55 (3)
C(34)	5239 (4)	8206 (3)	2228 (2)	53 (2)
C(35)	4657 (3)	7086 (3)	1873 (2)	45 (2)
N(4)	628 (3)	5507 (3)	7094 (2)	60 (2)
O(4)	201 (3)	5446 (4)	7681 (2)	85 (2)
O(5)	1708 (3)	6164 (3)	7041 (2)	84 (2)
O(6)	−8 (4)	4908 (3)	6556 (2)	99 (3)
O(7)	2380 (3)	6733 (4)	3128 (2)	92 (2)

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

Table 2. *Bond distances* (Å) *and angles* (°) *for the coordination polyhedron*

Cu—O(1)	1·970 (2)	O(1)—Cu—O(2)	88·9 (1)
Cu—O(2)	1·954 (2)	O(1)—Cu—O(3)	83·6 (1)
Cu—O(3)	2·478 (2)	O(2)—Cu—O(3)	92·4 (1)

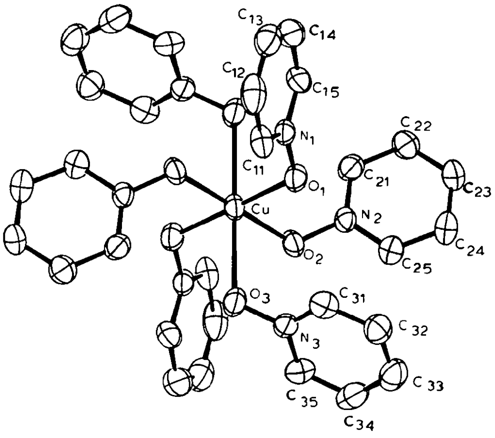

Fig. 1. A perspective view of the $[Cu(C_5H_5NO)_6]^{2+}$ complex ion projected onto one of the (111) planes of the CuO_6 pseudo-octahedron. The thermal ellipsoids are at the 50% probability level.

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* Lists of anisotropic thermal parameters, H-atom coordinates, observed and calculated structure factors, ligand bond distances and angles and least-squares-planes' data for the pyridine rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39040 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

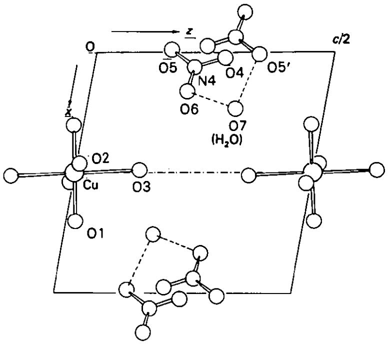

Fig. 2. Projection onto the (010) plane of the CuO_6 coordination polyhedra, the nitrate ions and water-molecule O atoms.

pseudo-fourfold axes are almost collinear, the angle between them being 2·2 (3)°. This result means that the $[Cu(C_5H_5NO)_6]^{2+}$ ions pack in what may be termed a pseudo-ferrodistortive fashion with all coordination polyhedra axes approximately parallel. Since the packing of complex ions within any one (001) plane closely resembles that for the low-temperature ferrodistortive forms of the trigonal complexes, the magnetic exchange between nearest neighbors within these planes is expected to be very similar to the intralayer exchange in the latter. This explains the disappearance of the Cu hyperfine splitting in all EPR spectra. While the interlayer exchange is not known for the trigonal complexes, it is expected to be small (van Kalkeren, Keijzers, Srinivasan, de Boer & Wood, 1983). EPR measurements for this monoclinic form at both *X*- and *Q*-band frequency indicate that there is in fact no magnetic exchange between the two magnetically inequivalent molecules in the unit cell. Two distinct signals are seen with a *g*-value separation that is consistent with an exchange constant no larger than 10^{-3} cm^{-1}. In summary, these crystallographic results again demonstrate the sensitivity of the cooperative Jahn–Teller coupling forces to the presence of solvent molecules in the lattice and to the nature of the counterions. In the present example, the water molecule appears to be instrumental in giving the pseudo-ferrodistortive arrangement since the low-temperature anhydrous form adopts the energetically more favorable antiferrodistortive arrangement (Keijzers *et al.*, 1982).

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Exemple d'une Caractérisation par Rayons X d'un Composé Moléculaire du Fer(III) Contenant Trois Ligands Chlorure: *mer*-Trichlorotris(isonicotinonitrile)fer(III), $[FeCl_3(C_6H_4N_2)_3]$

Par Jean-Claude Daran, Yves Jeannin et Liliana Martin

Laboratoire de Chimie des Métaux de Transition, ERA 608, *Université Pierre et Marie Curie*, 4 *place Jussieu*,
75230 *Paris CEDEX* 05, *France*

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Abstract. $M_r = 474·5$, monoclinic, $P2_1/c$, $a = 10·152\ (11)$, $b = 12·216\ (4)$, $c = 16·906\ (8)$ Å, $\beta = 97·4\ (1)°$, $Z = 4$, $V = 2079\ (12)$ Å^3, $D_m = 1·53\ (1)$, $D_x = 1·52$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 1·15 mm^{-1}, room temperature, $F(000) = 1164$, $R = 0·045$, $R_w = 0·05$ for 2324 reflexions. Ligand geometry around Fe is meridional; pyridine rings are in a propeller-like arrangement.

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