

## Bis(2-dimethylaminopyridine 1-oxide)copper(II) Diperchlorate

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**Abstract.**  $[\text{Cu}(\text{C}_7\text{H}_{10}\text{N}_2\text{O})_2](\text{ClO}_4)_2$ ,  $\text{C}_{14}\text{H}_{20}\text{CuN}_4\text{O}_2^+ \cdot 2\text{ClO}_4^-$ ,  $M_r = 538.8$ , monoclinic,  $P2_1/c$ ,  $a = 8.3147$  (7),  $b = 10.3410$  (7),  $c = 15.1192$  (8) Å,  $\beta = 127.74$  (1)°,  $Z = 2$ ,  $D_c = 1.74$ ,  $D_m = 1.74$  (2)  $\text{Mg m}^{-3}$ ;  $R = \sum |\Delta F| / \sum |F_o| = 0.029$  for 1715 reflections used in the refinement. In this centrosymmetric complex 2-dimethylaminopyridine 1-oxide acts as a bidentate ligand with Cu coordinated in a square-planar configuration to *trans* oxygen and amine N donor atoms. Bond lengths from Cu to O(1) and N(2) are 1.897 and 2.052 (2) Å, and they make an angle of 83.2 (1)° at Cu. The  $\text{ClO}_4^-$  anions are above and below the coordination plane with a shortest Cu–O contact of 2.656 (2) Å. This Cu–O contact makes an angle of 81.5° with the coordination plane.

**Introduction.** Violet crystals of the title compound were obtained by evaporation of nitromethane solutions. A small amount of yellow-brown solid usually formed as well and was considered to be a decomposition or solvation product. A fragment measuring 0.23 (parallel to final mount)  $\times$  0.26  $\times$  0.30 (2) mm was cut from a larger crystal and used for data collection. An initial mount afforded precession and cone-axis photographs which revealed a monoclinic cell with systematic absences ( $k$  odd for  $0k0$  and  $l$  odd for  $h0l$ ) consistent with space group  $P2_1/c$ . The crystal was remounted, transferred to a Picker FACS-I fully automated diffractometer ( $b^*$  axis coincident with  $\varphi$  axis), and lattice constants were determined from 12 intense reflections by a least-squares fit of carefully measured  $\pm 2\theta$  values ( $72^\circ < 2\theta < 78^\circ$ ) for the Cu  $K\alpha_1$ – $K\alpha_2$  doublet [ $\lambda(\text{Cu } K\alpha_1) = 1.54050$ ,  $\lambda(\text{Cu } K\alpha_2) = 1.54434$  Å].

Intensity data were collected to a  $2\theta_{\text{max}}$  of 50° with Zr-filtered Mo  $K\alpha$  radiation, using a fixed  $\theta:2\theta$  scan rate of 1°  $\text{min}^{-1}$ . A variable scan width, 1.6° + 0.48°  $\tan \theta$ , and 10 s background measurements at

both extremities of the scan were used to measure 1941 independent reflections. Periodically measured reference reflections showed an average intensity decrease of only 2% over the five-day data-collection period. Intensities were corrected for absorption as a function of  $\varphi$  angle setting from a  $\varphi$  scan measurement of the 040 reflection at  $\chi = 90^\circ$ . The ratio of observed intensity extremes for the 040 reflection was 1.06, compared to 1.07 calculated from transmission factors of cylindrical crystals with diameters of 0.26 and 0.33 mm and  $\mu(\text{Mo}) = 1.31 \text{ mm}^{-1}$ . Intensities were also corrected for Lorentz and polarization effects and then converted to structure amplitudes. A total of 1715 reflections for which  $|F| > 3\sigma(F)$  were used for the structure determination and refinement.

The structure was solved by the Fourier synthesis method. Structure refinement utilized full-matrix least-squares calculations which minimized the function  $\sum w(|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2$  and  $\sigma^2(F_o) = (F_o/2I_n)^2 [I_s + (t_s/t_b)^2 I_b + (0.02I_n)^2]$ ;  $I_s$ ,  $I_b$  and  $I_n$  are scan, background and net intensities, and  $t_s$  and  $t_b$  are scan and background times. Scattering factors for neutral nonhydrogen atoms were taken from tabulations of Cromer & Waber (1965), and from Stewart, Davidson & Simpson (1965) for the H atoms. Anomalous-dispersion corrections for real and imaginary terms were applied to Cu and Cl structure factors (Cromer & Liberman, 1970). When Cu was placed at the origin, all nonhydrogen atoms were readily located in sequential Fourier syntheses; anisotropic refinement on these atoms resulted in  $R = 0.053$ . A difference electron density map showed peaks corresponding to the expected positions of the ten H atoms. These were included in structure factor calculations and refined with isotropic temperature factors. The average H temperature factor is 3.0 (6) Å<sup>2</sup>; the maximum is 3.7 (6) Å<sup>2</sup> for H''(C7). The final  $R$  values ( $\sum w||F_o| - |F_c|| / \sum w|F_o|$ ) are  $R = 0.029$  ( $w = 1.0$ )

Table 1. *Final positional parameters*

Estimated standard deviations are in parentheses.

	x	y	z
Cu	0.0	0.0	0.0
Cl	0.31626 (9)	-0.28573 (6)	0.01655 (5)
O(1)	0.26329 (24)	0.06699 (17)	0.06569 (13)
O(2)	0.14145 (29)	-0.23081 (20)	0.00122 (16)
O(3)	0.38389 (34)	-0.19756 (22)	-0.02750 (19)
O(4)	0.47115 (31)	-0.30565 (20)	0.13192 (14)
O(5)	0.25982 (33)	-0.40574 (20)	-0.04192 (16)
N(1)	0.40195 (28)	0.00547 (19)	0.16312 (15)
N(2)	0.12770 (28)	-0.05197 (20)	0.16159 (14)
C(1)	0.34189 (34)	-0.05900 (24)	0.21618 (18)
C(2)	0.48509 (39)	-0.11991 (26)	-0.31522 (20)
C(3)	0.68637 (41)	-0.11571 (27)	0.35821 (21)
C(4)	0.74196 (42)	-0.04963 (29)	0.30180 (22)
C(5)	0.59686 (38)	0.01023 (28)	0.20351 (22)
C(6)	0.08886 (46)	0.05618 (31)	0.21240 (23)
C(7)	0.04461 (46)	-0.17491 (30)	0.16934 (24)
H(C2)	0.447 (4)	-0.163 (2)	0.353 (2)
H(C3)	0.773 (4)	-0.165 (3)	0.424 (2)
H(C4)	0.868 (4)	-0.045 (2)	0.327 (2)
H(C5)	0.623 (4)	0.061 (3)	0.161 (2)
H(C6)	0.147 (4)	0.135 (3)	0.207 (2)
H'(C6)	0.155 (4)	0.036 (2)	0.292 (2)
H''(C6)	-0.051 (5)	0.059 (3)	0.176 (2)
H(C7)	-0.098 (4)	-0.164 (2)	0.126 (2)
H'(C7)	0.074 (4)	-0.246 (3)	0.135 (2)
H''(C7)	0.092 (4)	-0.191 (3)	0.243 (2)

Table 2. *Bonding distances (Å) and angles (°) in the perchlorate anion of bis(2-dimethylaminopyridine 1-oxide)copper(II) diperchlorate*

Cl—O(2)	1.4410 (20)	O(2)—Cl—O(3)	108.60 (13)
Cl—O(3)	1.4316 (21)	O(2)—Cl—O(4)	108.89 (13)
Cl—O(4)	1.4119 (18)	O(2)—Cl—O(5)	109.05 (13)
Cl—O(5)	1.4262 (20)	O(3)—Cl—O(4)	110.28 (14)
		O(3)—Cl—O(5)	109.86 (14)
		O(4)—Cl—O(5)	110.12 (13)

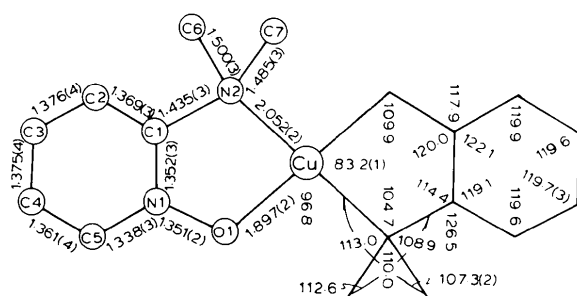


Fig. 1. A schematic diagram of the bis(2-dimethylaminopyridine 1-oxide)copper(II) cation with bond distances (Å) and angles (°) indicated. The e.s.d.'s of angles are 0.3° in the pyridine ring, 0.1° in the chelate ring, and 0.2° for non-ring angles. The diagram shows the e.s.d. of only one angle in each section.

and  $R_w = 0.031$  ( $w = 1/\sigma^2$ ), and the goodness-of-fit is 1.76. The final difference electron density map was featureless and contained a maximum peak of 0.3 e Å<sup>-3</sup>. The fractional coordinates of all atoms are listed

in Table 1, and bond lengths and angles are shown in Fig. 1 and Table 2.\*

**Discussion.** The preparation and characterization of a series of transition-metal complexes containing 2-dimethylaminopyridine 1-oxide has been reported (Kohrman, Phadtare & West, 1975a,b). The compounds are of particular interest because they display wide differences in the ratio of their ligand to metal content ( $L/M = 2, 3, 4$  or 5) and degree of hydration. The bis(ligand)copper(II) complex is unique in two respects: it has the lowest  $L/M$  ratio and is anhydrous. Accordingly, the coordination sphere of Cu could contain a bidentate ligand, coordinated  $\text{ClO}_4^-$ , or both; or, the substituent methyl groups could sterically prevent coordination to amino and/or  $\text{ClO}_4^-$  donor atoms. A determination of the structure was undertaken to resolve which of these possibilities is present in the crystal.

The structure of the centrosymmetric formula unit is shown in Fig. 2. Cu is coordinated to two chelated ligands in a *trans* square-planar configuration and equivalent  $\text{ClO}_4^-$  groups are located on either side of the coordination plane. The shortest copper—perchlorate O atom contact is 2.656 (2) Å, to O(2), and it makes an angle of 81.5° to the plane. This type of 4 + 2 coordination is common in Cu complexes and is one in which the  $\text{ClO}_4^-$  groups are said to be semicoordinated. Clearly the substituent methyl groups do not prevent coordination of the amino N or semicoordination of the  $\text{ClO}_4^-$  groups in the crystal.

In the coordination plane, Cu is bonded to O(1) and N(2) with bond lengths of 1.897 (2) and 2.052 (2) Å respectively. This is a longer Cu—(tertiary amine) bond distance than is found in a series of *N,N,N',N'*-tetramethylethylenediamine complexes (Brown, Miller & Pavkovic, 1977). The donor atoms are separated by a 'bite' distance of 2.624 (3) Å and they subtend an angle of 83.2° at Cu. The chelate ring almost has an

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34744(10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

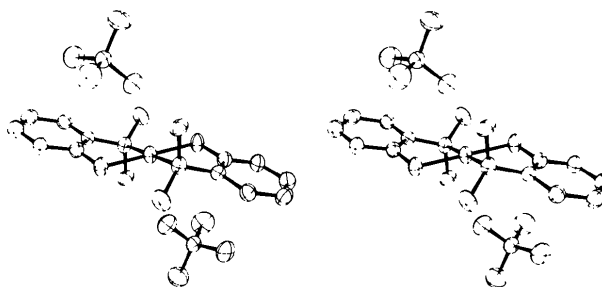


Fig. 2. A stereoview of the bis(2-dimethylaminopyridine 1-oxide)copper(II) diperchlorate formula unit (Johnson, 1965).

envelope conformation as shown by the small O(1)-N(1)C(1)N(2) torsion angle of  $-1.4(3)^\circ$ . Within the ring, angles about vertex atoms C(1) and N(2) of  $114.4$  and  $104.7^\circ$  are significantly smaller than expected for  $sp^2$  and  $sp^3$  hybridized atoms. This may be due to steric factors in that methyl-group atoms C(6) and C(7) have close contact distances of  $3.14$  and  $3.15 \text{ \AA}$  to the semi-coordinated O(2) atom, or to ring conformation.

The aromatic ring of the ligand is almost exactly planar, the six atoms having mean and maximum distances of  $0.002$  and  $0.004 \text{ \AA}$  from the best least-squares plane through them. The oxide and amine atoms O(1) and N(2) lie  $0.008$  and  $0.27 \text{ \AA}$  on one side of the ring plane, and the ring is inclined to the coordination plane by  $24.5^\circ$ . Bonding distances and angles within the ring are essentially the same as those found in other complexes containing the pyridine *N*-oxide moiety (Estes & Hodgson, 1976; Al-Karaghoulí & Wood, 1979).

The perchlorate group is approximately tetrahedral with average bond length and angle values of  $1.427(12) \text{ \AA}$  and  $109.5(7)^\circ$ . Its distortion may be attributed to interaction with Cu, and is best evidenced by the semi-coordinated O(2) having the longest Cl—O bond of  $1.441(2) \text{ \AA}$ . Apparently the  $\text{ClO}_4^-$  groups may

assume other bonding roles in this compound under slightly different conditions, since significant changes are observed in  $\text{ClO}_4^-$  IR frequencies after sample preparation by grinding or pressing techniques (West, 1978).

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### Trichlorobis(4-pyridinecarbonitrile 1-oxide-O)thallium

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**Abstract.**  $[\text{Tl}(\text{C}_6\text{H}_4\text{N}_2\text{O})_2\text{Cl}_3]$ ,  $\text{C}_{12}\text{H}_8\text{Cl}_3\text{N}_4\text{O}_2\text{Tl}$ ,  $M_r = 550.95$ , monoclinic,  $C_c$ ,  $a = 7.0295(5)$ ,  $b = 26.887(8)$ ,  $c = 8.8436(8) \text{ \AA}$ ,  $\beta = 105.85(5)^\circ$ ,  $Z = 4$ ,  $D_c = 2.28 \text{ Mg m}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 10.66 \text{ mm}^{-1}$ . The crystal consists of individual molecules held together by van der Waals contacts. The Tl atom is at the center of a distorted trigonal bipyramid, with the three Cl atoms in equatorial positions and the O atoms axial. The coordination appears new for Tl, its geometry being: Tl—Cl =  $2.364(5)$ – $2.452(4) \text{ \AA}$ , Tl—O =  $2.36(1)$ ,  $2.40(1) \text{ \AA}$ , Cl—Tl—Cl =  $140.2(2)$ ,  $112.9(2)$ ,  $106.6(2)^\circ$  and O—Tl—O =  $168.9(5)^\circ$ .

**Introduction.** Some attempts have been made to elucidate the stereochemistries of Tl trihalide complexes with donor molecules by spectroscopic techniques (Walton, 1968). Five different structural models have been proposed. However, evidence from X-ray diffraction has only been obtained for the compound  $\text{TlCl}_3$ -(1,10-phenanthroline) (Baxter & Gafner, 1972). In the present paper, the structure of the complex of  $\text{TlCl}_3$  with  $\text{C}_6\text{H}_4\text{N}_2\text{O}$  is reported.

Samples were provided by Departamento de Química Inorgánica from the University of Santiago de Compostela (Spain). A pale-yellow prismatic crystal  $0.26 \times 0.13 \times 0.08 \text{ mm}$  was used to collect the data. 3055 reflexions were measured in the  $\omega/2\theta$  scan mode on a PW 1100 four-circle diffractometer, with graphite-

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