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## Di- $\mu$ -(pyridine oxide)-bis[dichloro(dimethyl sulfoxide)copper(II)]\*

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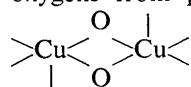
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**Abstract.**  $[(C_5H_5NO)(C_2H_6SO)CuCl_2]_2$ , monoclinic,  $P2_1/c$ ,  $a = 7.17$  (1),  $b = 15.444$  (7),  $c = 11.183$  (4) Å,  $\beta = 104.8$  (1)°;  $d_{obs} = 1.77$ ,  $d_{calc} = 1.72$  g cm<sup>-3</sup> for  $Z = 4$ . The compound was prepared by recrystallizing  $CuCl_2 \cdot (pyridine\ oxide)$  in dimethyl sulfoxide (DMSO). The structure was determined from X-ray diffraction data for 2860 independent reflections ( $R = 0.072$ , observed reflections only). The molecule is dimeric with two  $CuCl_2 \cdot DMSO$  groups bridged together by two oxygens from pyridine oxide ligands. The resulting



bridge is planar with two non-crystallographically equivalent Cu-O distances of 2.050 (6) Å and angles O-Cu-O, 70.8 (3)° and Cu-O-Cu, 109.2 (3)°. The O-O and Cu-Cu distances across the bridge are 2.38 (1) and 3.342 (3) Å respectively and other bond distances are: Cu-Cl(1) 2.260 (4); Cu-Cl(2) 2.243 (3) and Cu-O(DMSO) 2.278 (6) Å.

**Introduction.** A light-green needle-shaped crystal of the compound with dimensions  $0.25 \times 0.29 \times 0.90$  mm was mounted along the needle axis for data collection. Three-dimensional intensity data were measured for levels  $0kl$  to  $7kl$  with a Philips Pailred diffractometer using equi-inclination geometry and the continuous  $\omega$ -scan technique. Mo  $K\alpha$  radiation, a silicon monochromator ( $d_{111} = 3.1355$  Å) and a scintillation detector were utilized to measure the intensities of 2860 unique reflections to a maximum  $2\theta$  of 55°; 1696 of these had  $I > 3\sigma(I)$ , and only these were used in the subsequent refinement. The standard deviation,  $\sigma(I)$ , of the intensity of each reflection was estimated by:  $\sigma(I) = [N_p + tN_B + [0.02(N_p - tN_B)]^2]^{1/2}$ , where  $N_p$  = the total scan count,  $tN_B$  = the normalized background count and 0.02 is an empirical error parameter.

Absorption corrections were applied to the data assuming a cylindrical crystal with  $\mu r = 0.438$  (*International Tables for X-ray Crystallography*, 1959). The maximum error in an individual observed structure

factor caused by this approximation is less than 5%.

Systematic extinctions  $0k0$ ,  $k = 2n$ ,  $h0l$ ,  $l = 2n$  indicate space group  $P2_1/c$ . The unit-cell dimensions were measured from  $hk0$  Weissenberg and  $l$  axis layer-line photographs calibrated by superimposed NaCl powder lines [ $\lambda(\text{Mo } K\alpha_1) = 0.70926$  Å].

The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique. The function minimized was  $\sum w(F_o - F_c)^2$  where  $w$  is the weight of an individual  $F$  derived from  $\sigma(I)$  (Stout & Jensen, 1968) and  $F_c^*$ , containing an extinction parameter, has been previously defined (Williams, Cromer & Larson, 1971). Anisotropic refinement yielded  $R = 0.072$  for non-zero reflections where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . The largest parameter shift after refinement was 3% of its estimated deviation.

A list of final positional and thermal parameters with estimated standard deviations is given in Table 1.† The final value of the refined extinction parameter,  $g$ , is  $1.297(1) \times 10^{-6}$ . The maximum extinction correction was 11% in intensity for the 202, 102 and 132 reflections. Atomic scattering factors for  $Cu^{2+}$ ,  $Cl^-$ , S, O, N and C were taken from Cromer & Waber (1965). Anomalous scattering corrections were applied to the scattering factors of all atoms (Cromer & Liberman, 1970).

A difference Fourier synthesis was calculated after refinement to check the accuracy of the final model. The only significant detail was near the Cu atom position with peak densities of 1.37, 1.04,  $-1.23$  and  $-1.16$  e Å<sup>-3</sup>. No significant densities were found near what would be reasonable hydrogen atom positions; no attempt was therefore made to assign and refine hydrogen atoms.

The computer programs for data reduction and absorption correction were from the T.C.U. Crystallo-

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31055 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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graphic Program Package (Stemple, 1970). Those for the full-matrix anisotropic refinement, Fourier syntheses and calculation of distances and angles were from the *LASL* System (Larson, 1970).

**Discussion.** There have been a number of recent reports concerning the structural and magnetic properties of complexes formed between aromatic *N*-oxides and copper(II) salts (Watson, 1969). A number of these complexes exhibit magnetic moments which are considered abnormally low (Kato, Jonassen & Fanning, 1964) owing to a magnetic interaction between pairs of  $\text{Cu}^{\text{II}}$  ions bridged together (Watson, 1969). One class of low-moment complexes which have not been structurally characterized are the adducts of 1:1 aromatic *N*-oxide- $\text{Cu}^{\text{II}}$  salts with small polar solvent molecules like DMSO, DMF,  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ . The title compound is such a complex and its structure determination was therefore undertaken.

A drawing of the structure viewed along the *c* axis is shown in Fig. 1. Table 2 lists bond distances and angles with estimated standard deviations. The compound exists as a dimer consisting of two distorted

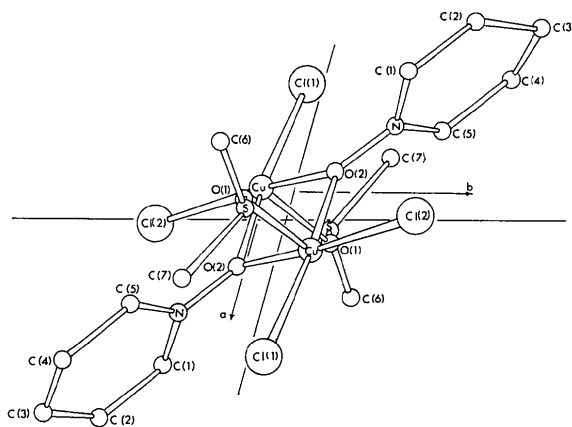


Fig. 1. A drawing of the structure of  $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$  viewed along the *c* axis.

Table 2. Bond distances (Å) and angles (°) for  $[(\text{C}_5\text{H}_5\text{NO})(\text{C}_2\text{H}_6\text{SO})\text{CuCl}_2]_2$

Primed atoms are related to corresponding unprimed atoms by a center of symmetry.

Bridge and Cu coordination sphere		Dimethyl sulfoxide	
Cu—Cl(1)	2.260 (4)	O(1)—S—C(6)	104.8 (5)
Cu—Cl(2)	2.243 (3)	O(1)—S—C(7)	106.9 (5)
Cu—O(1)	2.279 (6)	C(6)—S—C(7)	99.9 (6)
Cu—O(2)	2.050 (7)		
Cu—O(2')	2.050 (6)	Pyridine ring	
O(2)—O(2')	2.380 (10)	O(2)—N	1.362 (9)
Cu—Cu'	3.342 (3)	N—C(1)	1.39 (1)
		C(1)—C(2)	1.40 (1)
		C(2)—C(3)	1.40 (1)
		C(3)—C(4)	1.36 (2)
		C(4)—C(5)	1.40 (1)
		C(5)—N	1.36 (1)
O(2)—Cu—O(2')	70.8 (2)	O(2)—N—C(1)	116.5 (8)
Cu—O(2)—Cu'	109.2 (3)	O(2)—N—C(5)	118.9 (8)
O(1)—Cu—O(2)	92.3 (3)	C(1)—N—C(5)	124.7 (9)
O(1)—Cu—O(2')	89.7 (3)	N—C(1)—C(2)	116.8 (9)
O(1)—Cu—Cl(1)	101.4 (2)	C(1)—C(2)—C(3)	120 (1)
O(1)—Cu—Cl(2)	102.4 (2)	C(2)—C(3)—C(4)	120 (1)
O(2)—Cu—Cl(1)	93.9 (2)	C(3)—C(4)—C(5)	121 (1)
O(2)—Cu—Cl(2)	94.6 (2)	C(4)—C(5)—N	117 (1)
O(2')—Cu—Cl(1)	159.6 (2)		
O(2')—Cu—Cl(2)	94.6 (2)	Dimethyl sulfoxide	
O(1')—Cu—Cl(2)	161.6 (2)	O(1)—S	1.546 (6)
Cl(1)—Cu—Cl(2)	97.1 (1)	S—C(6)	1.82 (1)
		S—C(7)	1.84 (1)

square-based pyramidal copper(II) polyhedra joined at one edge of their base so that their apices are *trans*. This common edge is composed of oxygen atoms from the two pyridine oxide molecules. Two chloride ions form the remainder of each base with a dimethyl sulfoxide molecule coordinated through the oxygen atom at each apex. The bridge, similar structurally to that found in  $[(\text{C}_5\text{H}_5\text{NO})\text{CuCl}_2]_2$  (Sager, Williams & Watson, 1967), is required by crystallographic symmetry to be planar and contains two non-crystallographically equivalent Cu—O bond distances of 2.050 (6) and 2.050 (7) Å and bond angles O(2)—Cu—O(2') 70.8 (3) and Cu—O(2)—Cu' 109.2 (3)°. These appear to be bond-angle compromises between the 90° O(2)—

Table 1. Positional and thermal parameters ( $\times 10^4$ ) with standard deviations for  $[(\text{C}_5\text{H}_5\text{NO})(\text{C}_2\text{H}_6\text{SO})\text{CuCl}_2]_2$

Anisotropic temperature factors have the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	839 (2)	425 (1)	1408 (1)	142 (2)	25 (1)	56 (1)	16 (2)	56 (2)	-4 (1)
Cl(1)	3892 (3)	4606 (1)	7615 (2)	141 (6)	40 (1)	89 (2)	0 (5)	17 (6)	5 (3)
Cl(2)	109 (4)	6626 (1)	2786 (2)	207 (7)	31 (1)	95 (2)	-32 (4)	42 (7)	32 (2)
S	336 (4)	4462 (1)	1324 (2)	185 (6)	27 (1)	54 (2)	2 (4)	98 (6)	-2 (2)
O(1)	570 (9)	4356 (3)	2732 (5)	212 (16)	39 (3)	68 (5)	24 (11)	92 (15)	-4 (5)
O(2)	1380 (9)	5448 (3)	5162 (5)	216 (16)	39 (2)	77 (5)	-68 (12)	38 (15)	1 (6)
N	2732 (11)	6091 (4)	5454 (4)	142 (19)	33 (3)	75 (6)	-25 (12)	70 (18)	13 (7)
C(1)	4193 (15)	6073 (6)	4858 (8)	198 (30)	39 (4)	103 (9)	-7 (18)	83 (28)	43 (10)
C(2)	4378 (15)	3290 (6)	4816 (10)	180 (30)	40 (4)	147 (12)	-32 (19)	44 (30)	0 (12)
C(3)	4494 (17)	2667 (6)	3930 (9)	209 (31)	39 (4)	116 (10)	-39 (19)	25 (31)	11 (11)
C(4)	4012 (17)	7322 (6)	6621 (9)	252 (33)	36 (4)	102 (9)	-66 (19)	47 (29)	-2 (10)
C(5)	2538 (14)	6700 (5)	6300 (7)	251 (29)	27 (3)	69 (7)	-8 (17)	64 (24)	14 (8)
C(6)	2233 (17)	3788 (6)	983 (9)	311 (36)	57 (5)	131 (11)	90 (23)	245 (34)	-20 (13)
C(7)	1796 (16)	6169 (6)	9462 (9)	264 (36)	46 (5)	131 (11)	-67 (21)	3 (32)	-26 (12)

Cu–O(2') angle expected for a tetragonal pyramidal Cu coordination and the 120° Cu–O(2)–Cu' angle expected for a normal  $sp^2$  hybridized oxygen coordination. These angles cause the O(2)–O(2') distance to be much less than the Cu–Cu' distance across the bridge, 2.38 (1) and 3.34 (3) Å respectively. Distances and angles involving the chloride ions are distorted by the geometrical requirements of the bridge (Sager, Williams & Watson, 1967). Those for the pyridine ring appear normal. The DMSO molecule is coordinated through oxygen to the Copper(II) ion as expected (Cotton, Francis & Horrocks, 1960). The resulting Cu–O(1) distance of 2.279 (6) Å is normal for apical coordination. This coordination causes a slight lengthening of the S–O bond in the DMSO group to 1.546 (6) Å over that found in free DMSO (Thomas, Shoemaker & Eriks, 1966), 1.531 (8) Å and is consistent with a slight decrease in  $d \rightarrow p\pi$  bonding from sulfur to oxygen caused by coordination (Bennett, Cotton, Weaver, Williams & Watson, 1967).

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## Refinement of the Crystal Structure of Lithium Chromate

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**Abstract.**  $\text{Li}_2\text{CrO}_4$  crystallizes with the phenacite structure (type  $S1_3$ ), rhombohedral,  $R\bar{3}(C_{3i}^2)$ ,  $a = 14.005(10)$ ,  $c = 9.405(5)$  Å,  $Z = 18$  (hexagonal cell),  $D_m = 2.426$ ,  $D_c = 2.427$  g cm $^{-3}$ . The sample was prepared by heating  $\text{Li}_2\text{Cr}_2\text{O}_7(\text{H}_2\text{O})_2$  and recrystallizing from the melt.

**Introduction.** A cylindrical crystal 0.15 mm in diameter and 0.20 mm long was sealed inside a quartz capillary. The measured density was taken from Hartford, Costa & Moore (1952). The unit-cell parameters and intensities were measured on a Syntex  $P\bar{1}$  diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) and a  $\theta$ – $2\theta$  scan. No systematic absences were found for the rhombohedral setting. A total of 2751 intensity measurements in the region  $2\theta \leq 55^\circ$  were reduced to 825 by averaging reflexions related by the threefold axis. Of these, 152 were less than  $3\sigma$ , the standard error derived from counting statistics. A cylindrical absorption correction ( $\mu = 3.01$  mm $^{-1}$ ) was applied and the intensities were reduced to structure factors by applying Lorentz and polarization correc-

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tions. We assumed that  $\text{Li}_2\text{CrO}_4$  has the phenacite structure (Martin & Durif, 1964) which we refined by least-squares calculations using the local program *CUDLS* to give  $R_1$  (all reflexions) = 0.075 and  $R_2$  (weighted) = 0.054. In the final round an extinction correction,  $F^* = F[1 + 0.12 \times 10^{-6} \beta(2\theta)F^2]^{-1/2}$  (Larson, 1967), was applied and the reflexions were weighted by the function  $\omega = (151.2 - 2.18F + 0.00844F^2)^{-1/2}$  except that for the 97 reflexions for which  $I_o < 3\sigma$  and  $F_c < F_o$ ,  $\omega$  was set equal to zero. The atomic parameters are given in Table 1.†

**Discussion.** The phenacite structure ( $S1_3$  type) was first proposed for  $\text{Li}_2\text{CrO}_4$  by Martin & Durif (1964) on the basis of powder diagrams. Their cell constants agree with ours given above.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31045 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.