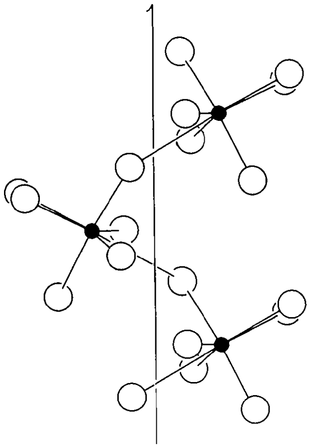

Fig. 3. Chain of U bipyramids along 2_1 axis in α-UO_2SeO_4.

Fig. 2 shows that the main difference between β-UO_2SO_4 and α-UO_2SeO_4 is a slight change in the orientation of the bipyramids and tetrahedra. As we assume the structure of β-UO_2SeO_4 to be identical to that of β-UO_2SO_4 it appears that the phase transition between α- and β-UO_2SO_4, although accompanied by a sizeable increase in cell volume, from a structural point of view only involves minor rotation of the coordination polyhedra.

The authors thank Professor Dr E. H. P. Cordfunke of ECN, Petten, for providing the sample of β-UO_2SO_4 and the chemical analyses. The step-scanned X-ray and neutron data were kindly collected by the staff of the neutron physics department of ECN, Petten.

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Dimeric Dibromo(2,3-butanedione dioximato)copper(II)

By H. Endres

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, *D*-6900 *Heidelberg, Federal Republic of Germany*

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Abstract. $C_4H_8N_2O_2CuBr_2$, FW 339·5, triclinic $P\bar{1}$, $a = 7{\cdot}759\,(1)$, $b = 8{\cdot}594\,(1)$, $c = 8{\cdot}273\,(1)$ Å, $\alpha = 71{\cdot}56\,(1)$, $\beta = 69{\cdot}08\,(1)$, $\gamma = 101{\cdot}20\,(1)°$, $V = 458{\cdot}5\,(1)$ Å, $Z = 2$, $D_c = 2{\cdot}46$ g cm^{-3}. There is one centrosymmetric dimer in the unit cell, bridged by two Br atoms. Chains are formed along x by hydrogen bridges (2·886 Å) between oxime O atoms of adjacent dimers. The coordination around each Cu is approximately square-pyramidal, the base formed by N and two strongly bonded Br atoms, the apex by a weakly bonded (2·883 Å) Br, belonging to the other Cu. The Cu—Cu distance is 3·599 Å. Atomic coordinates taken from the analogous chloro compound were refined by least squares to $R = 0{\cdot}066$, based on 1696 observed reflections.

Introduction. Bridged Cu complexes have received much interest in recent years because of magnetic exchange between the paramagnetic Cu ions. [Reviews have been given by Hatfield (1974) and Hodgson (1975).] For a better understanding of the correlation between structural and magnetic properties it is desirable to have a series of compounds where only the bridging atoms are changed. In dealing with halide-bridged systems, there are a few pairs of compounds with amine or pyridine ligands and Cl or Br bridges (Table 2 and the references therein). Besides these ligands, halide-bridged complexes with dioximato ligands constitute another series of closely related compounds. Nevertheless, there is only one structure known, dimeric dichloro(2,3-butanedione dioximato)-

copper(II) (Svedung, 1969), and Br-bridged dioxime complexes seem not to have been prepared hitherto.

In a recent paper, Mégnamisi-Bélombé & Novotny (1978) describe the preparation and magnetic and EPR properties of dimeric dibromo(2,3-butanedione dioximato)copper(II), which, from its IR spectrum and its lattice constants, was supposed to be isostructural with the chloro compound (Svedung, 1969).

The structure determination was undertaken to prove the dimeric nature of the compound, establish the tetragonal-pyramidal coordination around the Cu, and reveal the exact geometry of the Cu_2Br_2 core. This could lead to a better understanding of the differences in the magnetic behaviour of the chloro and the bromo compound (Mégnamisi-Bélombé & Novotny, 1978).

Crystals were kindly supplied by Dr M. Mégnamisi-Bélombé. A 'coffin'-like crystal with approximate dimensions 0·1 × 0·1 × 0·2 mm was mounted on the top of a glass capillary. Orientation matrix and lattice constants were determined from the setting angles of 15 reflections, centered on an automatic four-circle single-crystal diffractometer (Syntex $P2_1$, Mo $K\alpha$ radiation, graphite monochromator). Data collection (θ–2θ scans, background–peak–background step scan mode, $2\theta_{\max} = 60°$, about 3050 reflections) yielded 1804 observed reflections with intensities at least three times their standard deviations. They were corrected for Lorentz and polarization factors only, and weights based on F^2 statistics were applied.

Comparison of the lattice constants with those of the chloro analogue (Svedung, 1969) indicated that the two compounds are isomorphous. A Patterson synthesis could be explained using the same space group ($P\bar{1}$) and the heavy-atom positions of the chloro compound. Therefore, the published coordinates of the atoms of the chloro compound were taken as trial coordinates and refined by a least-squares procedure. Isotropic refinement converged with $R = 0{\cdot}13$, mixed refinement with anisotropic temperature factors for Cu and Br with $R = 0{\cdot}078$, and anisotropic refinement with $R = 0{\cdot}072$. As there were a number of reflections with observed structure factors just above the statistical threshold, and with much lower calculated ones, reflections with $I < 3{\cdot}5\sigma(I)$ were discarded, leaving 1703 observed reflections. R dropped to 0·069. Then seven more low-index reflections apparently greatly affected by absorption or extinction, were discarded too. Thus, the final refinement was based on 1696 reflections. R was 0·066 (weighted R = 0·079, maximum shift/error = 0·15). H positions were sought on a difference Fourier synthesis, but they could not be located unambiguously and were not included in the calculations. The positional parameters are given in Table 1.* Calculations were performed with programs of the *Structure Determination Package* (Enraf–Nonius) on a PDP 11/45 computer (Department of Chemistry, Stanford University). Scattering factors were derived from *International Tables for X-ray Crystallography* (1974) and anomalous terms were included. Plots were performed with the PDP 11/45–Versatec plotter adaption of *ORTEP* (Johnson, 1965).

Table 1. *Positional parameters*

	x	y	z
Br(1)	0·9565 (1)	0·2148 (1)	0·5003 (1)
Br(2)	0·3405 (1)	0·1288 (1)	0·6131 (2)
Cu(1)	0·0001 (2)	0·9879 (2)	0·7211 (2)
O(1)	0·1394 (9)	0·770 (1)	0·977 (1)
O(2)	0·5613 (9)	0·899 (1)	0·833 (1)
N(1)	0·981 (1)	0·796 (1)	0·946 (1)
N(2)	0·709 (1)	0·853 (1)	0·876 (1)
C(1)	0·812 (1)	0·682 (1)	0·073 (1)
C(2)	0·650 (1)	0·719 (1)	0·036 (1)
C(3)	0·783 (2)	0·529 (2)	0·238 (2)
C(4)	0·436 (1)	0·613 (2)	0·167 (2)

Discussion. The structure of the title compound is similar to that of its chloro analogue (Svedung, 1969). The numbering scheme, bond lengths and angles are displayed in Fig. 1. Fig. 2 shows an *ORTEP* plot of the centrosymmetric dimer. The center of symmetry of the dimer lies on the crystallographic inversion center at 0,0,½. The dimers form chains along the x direction, held together by hydrogen bonds between oxime O atoms of adjacent dimers, 2·886 (8) Å apart. The fact that just one of the two oxime H atoms of each dimer is involved

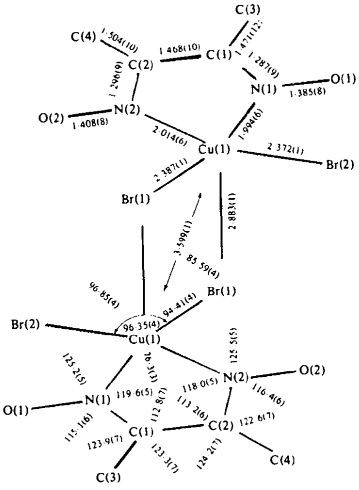

Fig. 1. Bond lengths (Å) and angles (°) in dimeric dibromo(2,3-butanedione dioximato)copper(II).

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* Lists of structure factors, anisotropic thermal parameters and deviations from mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33794 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in this hydrogen bond can clearly be seen in the splitting of the O—H absorption in the infrared spectrum (Svedung, 1969; Mégnamisi-Bélombé & Novotny, 1978).

The dioxime ligand is roughly planar (maximum deviation 0·06 Å), the Cu atom being well in this plane (deviation 0·04 Å). Another plane can be laid through the N and Br atoms of the monomer. The two planes include a dihedral angle of 5 °; the Cu atom sticks out of the second plane by 0·16 Å in the direction of the axially bound Br. The coordination sphere around each Cu can thus be described as tetragonal-pyramidal. Geometric details may be taken from Fig. 1 and Table 2. The dimer is formed by sharing a base to apex edge of the coordination pyramids. The resulting Cu—Cu distance is 3·599 (1) Å.

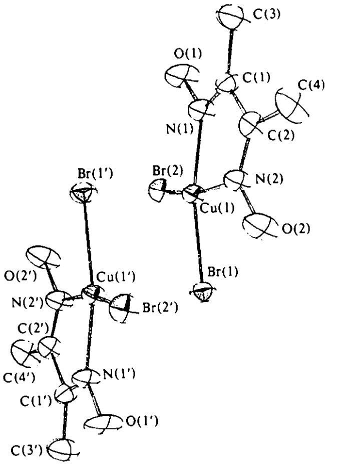

Fig. 2. *ORTEP* plot of dimeric dibromo(2,3-butanedione dioximato)copper(II).

For the understanding of the magnetic properties, the Cu_2Br_2 core is the most interesting part of the structure. This core is completely planar, as imposed by the inversion center midway between the two Cu atoms. In the case described here it forms an angle of 87° with the basal plane of the coordination pyramid. A comparison of geometries of this core in different Cl and Br bridged complexes is given in Table 2. (This table includes also compounds with trigonal bipyramidal and distorted octahedral coordinations.) Comparing Cl to Br compounds, the Cu—halogen distances increase by roughly 0·16 Å with only one exception, which corresponds to the difference in the covalent radii of the two halogens (Pauling, 1960). The angles at the bridging halogens tend to be smaller for Br, reflecting the higher 'softness' of the electronic system of bromine.

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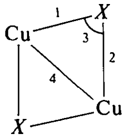
Table 2. *Comparison of geometries of the* Cu_2X_2 *cores in* $(LL)CuX_2$ *compounds* (*lengths in* Å, *angles in* deg)



LL	*X* = Br (1)	(2)	(3)	(4)	*X* = Cl (1)	(2)	(3)	(4)
a	2·422	3·260	80·77	3·737†				
b	2·435	3·109	87·56	3·866†				
c	2·468	2·802	92·14	3·803‡		*		
d	2·463	2·868	83·71	3·570	2·309	2·734	86·13	3·458
e	2·42	3·20	95·6	4·20				
f	2·43	3·87	100·4	4·93	2·26	3·37	101	4·41
g	2·46	3·19	93	4·04†	2·28	3·05	92	3·87†
h	2·387	2·883	85·59	3·599	2·24	2·70	88	3·445

Ligands and references: (*a*) 2-(2-Aminoethyl)pyridine: Helis, Goodman, Wilson, Morgan & Hodgson (1977). (*b*) 2-Methyl-1,2-diaminopropane: Helis, Goodman, Wilson, Morgan & Hodgson (1977). (*c*) 2-(2-Methylaminoethyl)pyridine: Wilson, Hatfield & Hodgson (1976). (*d*) *N*,*N*-Dimethylethylenediamine: Phelps, Goodman & Hodgson (1976). (*e*) *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine: Luukkonen & Pajunen (1973). (*f*) 2-Methylpyridine, Br: Singh, Jeter, Hatfield & Hodgson (1972), Cl: Duckworth & Stephenson (1969). (*g*) Pyridine, Br: Kupčik & Ďurovič (1960), Cl: Dunitz (1957). (*h*) 2,3-Butanedione dioxime, Br: this work, Cl: Svedung (1969).

* The analogous Cl compound forms infinite chains without the Cu_2Cl_2-motif: Bream, Estes & Hodgson (1975).

† Chains with distorted octahedral coordination around Cu.

‡ Trigonal bipyramidal.

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Antimony Trichloride 2:1 Complex with 1,3,5-Triacetylbenzene

BY WILLIAM A. BAKER AND DONALD E. WILLIAMS

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, *USA*

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Abstract. $2SbCl_3.C_{12}H_{12}O_3$, triclinic, $P\bar{1}$, $Z = 2$, $a = 8{\cdot}933$ (4), $b = 14{\cdot}045$ (4), $c = 8{\cdot}663$ (5) Å, $\alpha = 103{\cdot}70$ (5), $\beta = 104{\cdot}69$ (5), $\gamma = 95{\cdot}24$ (6)°, $D_m = 2{\cdot}06$, $D_c = 2{\cdot}07$ g cm^{-3}. Both Sb atoms have approximately octahedral configurations. Sb(1) is coordinated to three O atoms at 2·694, 3·023 and 3·040 Å. Sb(2) is coordinated to one O at 2·851 and two Cl atoms at 3·320 and 3·323 Å. The Sb(1) octahedra share an edge to form a bridged dimer with a nonbonded Sb···Sb distance of 3·777 Å.

Introduction. In a previous paper (Baker & Williams, 1978) the crystal structures of 1:1 adducts of antimony trichloride with terephthaldehyde and *p*-diacetylbenzene were described. The coordination about Sb in the terephthaldehyde adduct was found to be distorted pentagonal bipyramidal, described as AX_6E by valence-shell electron-pair repulsion (VSEPR) theory (Gillespie, 1967), with the lone pair axial. In the *p*-diacetylbenzene adduct the coordination about Sb was found to be distorted octahedral, described as AX_6 by VSEPR theory, with the lone pair not located. We have now examined the 2:1 complex with 1,3,5-triacetylbenzene in order to obtain more information about the nature of the coordination in antimony trichloride adducts with organic carbonyl compounds.

The 2:1 $SbCl_3$–triacetylbenzene adduct ($2SbCl_3.C_{12}H_{12}O_3$) was prepared (Park, 1969) by addition of 2·5 g of 1,3,5-triacetylbenzene (Eastman Chemical Co., m.p. 162–164 °C) to 100 ml of a solution of $CHCl_3$ containing 7·5 g of $SbCl_3$ (Baker Chemical Co., further purified by vacuum sublimation). The mixture was boiled and filtered. Light-yellow crystals were obtained on cooling and they were recrystallized from $CHCl_3$ (m.p. 122–124 °C). Elemental analysis for C, H, and Cl agreed with the above empirical formula.

X-ray intensity data were taken from a single crystal of approximate dimensions 0·2 × 0·2 × 0·3 mm sealed in a glass capillary tube. Lattice constants were obtained by a least-squares fit (Williams, 1964) using the Nelson & Riley (1945) extrapolation function to 27 high-angle reflections observed with Cr $K\alpha$ ($\lambda = 2{\cdot}28962$ Å) radiation. The conventional orientation for the reduced cell was obtained as described by Azaroff & Buerger (1958).

X-ray diffraction intensities for 2235 reflections were observed using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). A manually controlled $\theta/2\theta$ scan method was used with graphically estimated backgrounds. A scintillation counter detector was used. No significant decomposition of the crystal occurred during data collection, as indicated by the measurement of reference intensities