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Di-μ-bromo-bis[bromo(diphenylethanedione dioxime)copper(II)]

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Abstract. $[CuBr_2(C_{14}H_{12}N_2O_2)]_2$, $C_{28}H_{24}Br_4Cu_2N_4O_4$, $M_r = 927{\cdot}24$, monoclinic, $P2_1/c$, $a = 7{\cdot}830$ (2), $b = 16{\cdot}846$ (4), $c = 12{\cdot}311$ (3) Å, $\beta = 102{\cdot}19$ (2)°, $V = 1587{\cdot}3$ Å^3, $Z = 2$, $d_c = 1{\cdot}939$, $d_o = 1{\cdot}93$ Mg m^{-3}. Final weighted $R = 0{\cdot}036$ for 1690 reflections. The structure consists of discrete dimers in which the coordination around Cu is a distorted square pyramid; the base of the pyramid is defined by the two Br and the two oxime N atoms of a monomer, while a Br of the other monomer lies at the apex, the apical Cu—Br distance being 3·427 (1) Å. The bridging angle Cu—Br—Cu of 78·1° is unusually small. The Cu—Cu distance is 3·737 (1) Å.

Introduction. Magnetic exchange interactions in di-μ-halo-bridged binuclear adducts of Cu^{II} halides with α,β-dione dioximes have been shown to occur by the mechanism of *superexchange* (Kramers, 1934; Ginsberg, 1971), involving the valence wavefunctions of the bridging halides (Watkins, Dixon, van Crawford, McGregor & Hatfield, 1973; Mégnamisi-Bélombé, 1979*a*,*b*; Mégnamisi-Bélombé & Novotny, 1980). Because of the simple nature of the bridges (only single atoms connecting the two paramagnetic centres), this class of dimeric complex appears to be best suited for correlations of *intradimer* magnetic exchanges as required by the molecular-field-approximation theory (Van Vleck, 1932). For these correlations to be most reliable, however, an accurate knowledge of the crystal structure of the system is indispensable.

Unfortunately, reports on adducts of Cu^{II} halides with α,β-dione dioxime ligands are rather scarce, and only two such adducts, namely those of $CuCl_2$ and $CuBr_2$ with 2,3-butanedione dioxime, have so far been structurally characterized (Svedung, 1969; Endres, 1978). Hence, the observed divergence in the magnetic behaviour of these isomorphous dimers was mainly traced to the different nature of the halide bridges (Mégnamisi-Bélombé & Novotny, 1980).

Recently, efforts have been undertaken to study, in a systematic manner, magnetic superexchange interactions in this type of Cu^{II} dimer, the main interest lying on molecular and structural variations as the most determining parameters. Thus, convenient synthetic routes have been developed which have led to the isolation of a number of new di-μ-halo-bis[halo(α,β-dione dioxime)copper(II)] dimers (Mégnamisi-Bélombé, 1979*a*,*b*; Mégnamisi-Bélombé & Novotny, 1980).

In continuation of this research, we have now synthesized the new di-μ-bromo-bis[bromo(diphenylethanedione dioxime)copper(II)] {di-μ-bromo-bis-[bromo(diphenylglyoxime)copper(II)]} (Andoseh, Douglas, Egharevba & Mégnamisi-Bélombé, 1981). In the present contribution, we describe its crystal structure, with the aim of facilitating the understanding of magnetic studies in progress.

Single crystals were grown as follows: the compound (1·70 g) was dissolved at room temperature in 50 ml of a mixture of acetonitrile and ether (1:1 b/v) and filtered into a 250 ml conical flask. Anhydrous ether was dropped slowly into the filtrate over a period of *ca* 3 d. Black crystals formed; they were collected by filtration, washed with cold ether, and used for X-ray diffraction.

A block-like crystal mounted on top of a glass capillary was used for the investigation. Lattice parameters were derived from the setting angles of 25 machine-centred reflections (Syntex *R*3, monochromatic Mo $K\alpha$ radiation). Data collection (θ–2θ scans, background–peak–background, $2\theta < 70°$) yielded 1690 observed independent reflections with $I > 1{\cdot}5\sigma(I)$. Lorentz and polarization corrections as well as an empirical (ψ scans) absorption correction were applied.

The heavy atoms were located by checking the peaks of an *E* map against a Patterson synthesis. Light atoms, and finally H atoms were found from Fourier

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* Correspondence about preparation and properties should be addressed to Dr M. Mégnamisi-Bélombé, about the structure to Dr H. Endres.

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Table 1. *Atomic coordinates* (×10⁴, H *coordinates* ×10³) *and isotropic temperature factors* (×10³)

U are the isotropic temperature factors before anisotropic refinement.

	x	*y*	*z*	*U* (Å²)
Cu	9504 (1)	545 (1)	1219 (1)	40·3 (6)
Br(1)	7518 (1)	−462 (1)	458 (1)	51·8 (6)
Br(2)	11182 (1)	−203 (1)	2673 (1)	62·5 (7)
O(1)	12532 (6)	1523 (3)	2357 (3)	80 (4)
O(2)	6720 (6)	1247 (3)	−568 (4)	47 (4)
N(1)	10999 (7)	1502 (3)	1586 (4)	39 (4)
N(2)	8340 (7)	1346 (3)	97 (4)	37 (4)
C(1)	10774 (8)	2090 (4)	885 (5)	29 (4)
C(2)	9104 (8)	2022 (4)	35 (5)	29 (4)
C(3)	12070 (8)	2718 (3)	880 (4)	32 (4)
C(4)	12595 (9)	3236 (4)	1769 (5)	47 (5)
C(5)	13829 (10)	3809 (4)	1732 (6)	51 (5)
C(6)	14589 (9)	3842 (4)	841 (6)	48 (5)
C(7)	14115 (9)	3354 (5)	−31 (5)	52 (6)
C(8)	12839 (9)	2784 (4)	−27 (5)	41 (5)
C(9)	8417 (7)	2678 (3)	−723 (5)	31 (4)
C(10)	8531 (8)	3463 (4)	−369 (5)	36 (4)
C(11)	7832 (10)	4060 (4)	−1094 (7)	61 (6)
C(12)	6994 (10)	3879 (5)	−2155 (7)	53 (6)
C(13)	6899 (9)	3120 (4)	−2523 (6)	50 (5)
C(14)	7588 (9)	2515 (4)	−1823 (5)	43 (5)
H(1)	1271 (7)	106 (3)	261 (4)	
H(2)	619 (7)	111 (3)	−41 (4)	
H(4)	1219 (7)	318 (3)	240 (4)	
H(5)	1404 (7)	405 (3)	233 (4)	
H(6)	1536 (7)	427 (3)	90 (4)	
H(7)	1471 (7)	335 (3)	−61 (4)	
H(8)	1261 (7)	250 (3)	−53 (4)	
H(10)	893 (7)	357 (3)	36 (4)	
H(11)	798 (7)	452 (3)	−79 (4)	
H(12)	670 (7)	426 (3)	−260 (4)	
H(13)	646 (7)	296 (3)	−328 (4)	
H(14)	760 (7)	208 (3)	−205 (4)	

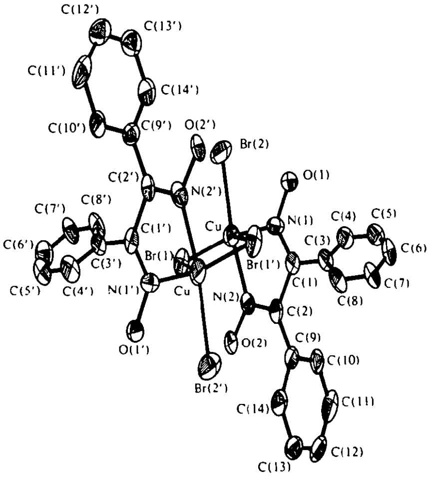

Fig. 1. Plot of the dimeric complex molecule.

and difference maps. Final refinement by a cascade-matrix procedure with anisotropic temperature factors for the non-H atoms, and with a fixed isotropic temperature factor, $U = 0{\cdot}06$ Å², for the H atoms, converged with a weighted $R = 0{\cdot}036$ (unweighted $R =$ 0·044).* The weighting scheme was $W = 1/\sigma^2(F)$. Calculations were carried out on a Nova 3 computer, plots were drawn on a Tektronix plotter. The program package was *SHELXTL* (Sheldrick, 1979).

Table 2. *Bond distances* (Å) *and angles* (°)

Cu–Br(1)	2·358 (1)	C(5)–C(6)	1·355 (11)
Br(2)	2·351 (1)	H(5)	0·82 (5)
N(1)	1·987 (5)	C(4)–C(5)–C(6)	119·2 (6)
N(2)	2·007 (5)	H(5)	109 (4)
Br(1′)	3·427 (1)	C(6)–C(5)–H(5)	132 (4)
Cu′	3·737 (2)	C(6)–C(7)	1·341 (10)
Br(1)–Cu–Br(2)	97·6 (0)	H(6)	0·93 (5)
N(1)	168·9 (1)	C(5)–C(6)–C(7)	121·9 (7)
N(2)	92·6 (1)	H(6)	111 (3)
Br(1′)	101·9 (0)	C(7)–C(6)–H(6)	127 (3)
Br(2)–Cu–N(1)	93·1 (1)	C(7)–C(8)	1·387 (10)
N(2)	169·8 (1)	H(7)	0·93 (6)
Br(1′)	95·5 (0)	C(6)–C(7)–C(8)	120·0 (7)
N(1)–Cu–N(2)	76·8 (2)	H(7)	122 (3)
Br(1′)	74·2 (2)	C(8)–C(7)–H(7)	118 (3)
N(2)–Cu–Br(1′)	83·2 (2)	C(8)–H(8)	0·77 (5)
O(1)–N(1)	1·365 (6)	C(3)–C(8)–C(7)	119·8 (6)
H(1)	0·84 (5)	H(8)	122 (4)
N(1)–O(1)–H(1)	106 (3)	C(7)–C(8)–H(8)	118 (4)
O(2)–N(2)	1·367 (6)	C(9)–C(10)	1·389 (8)
H(2)	0·54 (6)	C(14)	1·400 (8)
N(2)–O(2)–H(2)	121 (5)	C(2)–C(9)–C(10)	121·7 (5)
N(1)–C(1)	1·301 (8)	C(14)	119·9 (5)
Cu–N(1)–O(1)	124·7 (4)	C(10)–C(9)–C(14)	118·4 (5)
C(1)	118·4 (4)	C(10)–C(11)	1·379 (9)
O(1)–N(1)–C(1)	114·7 (5)	H(10)	0·91 (5)
N(2)–C(2)	1·296 (8)	C(9)–C(10)–C(11)	120·1 (6)
Cu–N(2)–O(2)	124·0 (4)	H(10)	119 (3)
C(2)	118·9 (4)	C(11)–C(10)–H(10)	120 (3)
O(2)–N(2)–C(2)	117·0 (5)	C(11)–C(12)	1·367 (11)
C(1)–C(2)	1·496 (8)	H(11)	0·86 (5)
C(3)	1·467 (9)	C(10)–C(11)–C(12)	120·0 (6)
N(1)–C(1)–C(2)	112·5 (5)	H(11)	112 (3)
C(3)	123·7 (5)	C(12)–C(11)–H(11)	128 (3)
C(2)–C(1)–C(3)	123·7 (5)	C(12)–C(13)	1·353 (11)
C(2)–C(9)	1·473 (8)	H(12)	0·84 (5)
N(2)–C(2)–C(1)	111·8 (5)	C(11)–C(12)–C(13)	120·8 (7)
C(9)	125·8 (5)	H(12)	118 (3)
C(1)–C(2)–C(9)	122·3 (5)	C(13)–C(12)–H(12)	121 (3)
C(3)–C(4)	1·393 (8)	C(13)–C(14)	1·369 (9)
C(8)	1·380 (9)	H(13)	0·97 (5)
C(1)–C(3)–C(4)	122·6 (6)	C(12)–C(13)–C(14)	120·4 (6)
C(8)	118·8 (5)	H(13)	125 (3)
C(4)–C(3)–C(8)	118·6 (6)	C(14)–C(13)–H(13)	114 (3)
C(4)–C(5)	1·373 (10)	C(14)–H(14)	0·78 (5)
H(4)	0·90 (6)	C(9)–C(14)–C(13)	120·2 (6)
C(3)–C(4)–C(5)	120·5 (6)	H(14)	120 (3)
H(4)	121 (3)	C(13)–C(14)–H(14)	120 (4)
C(5)–C(4)–H(4)	118 (3)		

Discussion. Atomic coordinates are listed in Table 1, bond distances and angles in the di-μ-bromo-bridged dimer in Table 2. Fig. 1 gives a view of the dimeric molecule, the centre of which (midway on the line joining the two Cu atoms) coincides with a crystallographic inversion centre. Fig. 2 is an enlarged sketch of the nearest surroundings of the Cu atoms. The

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35764 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Angles* (°) *between selected planes* (*e.s.d.'s* 0·5–1·0°)

		Angles (°) to planes			
Plane	Defined by	1	2	3	4
1	Cu, Br(1), Br(2)				
2	Cu, N(1), N(2)	3·1			
3	Cu, N(1), N(2), O(1), O(2), C(1), C(2)	8·5	5·8		
4	C(3) through C(8)	66·8	67·9	67·0	
5	C(9) through C(14)	30·6	33·6	39·0	65·7

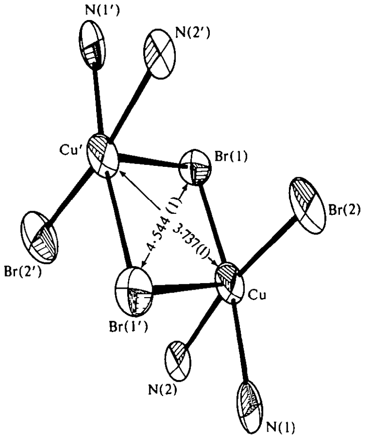

Fig. 2. Enlarged view of the coordination around Cu.

ligand-field geometry around Cu is a distorted, elongated square pyramid, the equatorial plane of which is defined by the two N atoms of the bidentate diphenylethanedione dioxime ligand [Cu—N 1·987 (5) and 2·007 (5) Å], and by the two Br atoms [Cu—Br 2·358 (1) and 2·351 (1) Å]. Br(2) is bonded to one Cu atom only, whereas Br(1) acts as a bridge between the two Cu atoms and forms the apex of the coordination pyramid of the adjacent Cu' [Cu'—Br(1) 3·427 (1) Å]. The Cu—Cu' distance is 3·737 (1) Å. Table 3 contains information about the angles between selected planes of a monomer and reveals, in particular, the large tilt of the phenyl groups with respect to the mean plane through Cu and the chelating part of the organic ligand.

Compared with the previously studied analogous di-μ-bromo-bis[bromo(2,3-butanedione dioxime)copper(II)] dimer (Endres, 1978), the apical Cu—Br distance of 3·427 Å in the present dimer (*vs* 2·883 Å in the former) and the Cu—Cu contact of 3·737 Å (*vs* 3·599 Å) are considerably longer. The equatorial Cu—Br separations, by contrast, are substantially shorter here, 2·358 and 2·351 Å *vs* 2·387 and 2·372 Å. Also, the Cu—Br—Cu bridge angle of only 78·1° is considerably smaller than in the former dimer (85·59°). The oxime H atoms do not form H bridges between dimers, as in the 2,3-butanedione dioxime compound (Endres, 1978), nor do such bridges contribute to link the two halves of a dimer.

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Structure of Methylammonium Hexabromoindate(III) Monobromide

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Abstract. $4[NH_3(CH_3)]^+.[InBr_6]^{3-}.Br^-$, M_r = 802·4, monoclinic, $P2_1/c$, a = 16·838 (6), b = 7·722 (2), c = 20·864 (6) Å, β = 128·67 (2)°, V = 2118 (1) Å^3, ρ = 2·516 Mg m^{-3}, Z = 4, Mo $K\bar{\alpha}$ radiation, λ = 0·71069 Å, μ = 15·08 mm^{-1}; R = 0·038 for 1558 unique reflections. The crystal structure is isomorphous with that of $(CH_3NH_3)_4InCl_7$, consisting of $CH_3NH_3^+$ cations, and Br^- and octahedral $InBr_6^{3-}$

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