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Pseudo-Polymeric Chain Structure of Dibromo(1,2-cyclohexanedione dioxime)copper(II),* $CuBr_2(C_6H_{10}N_2O_2)$

BY MICHEL MÉGNAMISI-BÉLOMBÉ

Department of Chemistry, University of Ife, Ile-Ife, Nigeria

AND HELMUT ENDRES

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, *D*-6900 *Heidelberg* 1, *Federal Republic of Germany*

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Abstract. $M_r = 365{\cdot}51$, triclinic, $P\bar{1}$, $a = 7{\cdot}702\ (1)$, $b = 7{\cdot}942\ (2)$, $c = 10{\cdot}500\ (3)$ Å, $\alpha = 70{\cdot}05\ (2)$, $\beta = 68{\cdot}98\ (2)$, $\gamma = 63{\cdot}37\ (2)°$, $V = 523{\cdot}3$ Å^3, $Z = 2$, $D_x = 2{\cdot}32$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}63$ mm^{-1}, $F(000) = 350$, $T = 295 \pm 2$ K, $R_w(R) = 0{\cdot}039\ (0{\cdot}045)$ for 1659 observed independent reflections. Pseudo-polymeric columns occur where the Cu^{II} sites form infinite zig-zag chains along **b** with alternating Cu–Cu separations of 4·054 (4) and 4·453 (4) Å. The chains consist of dimers with bridging oxime O atoms and Cu–O distances of 3·240 (10) Å. Within a chain these dimers are linked by weak interdimer Cu–O contacts of 3·912 (10) Å.

Introduction. We recently reported the structure of di-μ-chloro-bis[chloro(1,2-cyclohexanedione dioxime)-copper(II)]† (Mégnamisi-Bélombé & Endres, 1983) which matches the dimeric structure type commonly found in adducts of Cu^{II} halides (CuX_2) with α, β-dione dioximes (α,β-dodoH). However, two examples of adducts of this kind were recently found to crystallize in a polymeric chain structure, notably the adducts of $CuCl_2$ with oxamide dioxime (Endres, Genç & Nöthe, 1983), and with diphenylethanedione dioxime (Mégnamisi-Bélombé, Singh, Bolster & Hatfield, 1983). Magnetic data analysis has revealed that the latter system represents the first ferromagnetic Heisenberg spin $-\frac{1}{2}$ linear chain based on an α,β-dodoH ligand. In the following we describe the preparation and structure of the adduct of $CuBr_2$ with 1,2-cyclohexanedione dioxime (nioxime, niox) which crystallizes in a pseudo-polymeric chain structure brought about by bridges of O atoms.

Experimental. 510 mg (2·3 mmol) of finely powdered $CuBr_2$ crystals were suspended at room temperature in a mixture of dry diethyl ether (50 ml) and reagent grade (98%) acetonitrile (5 ml). 350 mg (2·4 mmol) of fine-powder niox (EGA-Chemicals, 97%) was added in portions. The mixture turned green, and a dark-green precipitate formed instantaneously. Stirring was continued for 1 h, solid was separated by filtration, washed with dry Et_2O and dried at room temperature. Yield: 718 mg (86%) of dark-green microcrystals decomposing violently at 416–417 K. Material is readily soluble in H_2O (red-brown) and in acetone (green), but virtually insoluble in Et_2O. In many respects, it behaves like the $CuCl_2$(niox) adduct (Mégnamisi-Bélombé & Endres, 1983). Single crystals grown by dissolving the solid in a *ca* 313 K mixture of dry acetone and Et_2O (50:50 ml), and slowly adding dry Et_2O to the filtered solution over a period of 2 d. Rhombohedral crystal, 0·1 × 0·1 × 0·2 mm, lattice parameters from the setting angles of 25 reflections centered on a diffractometer (Syntex $R3$, monochromatic Mo $K\alpha$ radiation), θ–2θ scans, background–peak–background, $2\theta \leq 60°$, 1659 observed independent reflections with $I > 2{\cdot}5\sigma(I)$, index range h −9–+10, k −9–+11, l 0–+14, 1393 reflections

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* *catena*-Dibromo-μ-[(1,2-cyclohexanedione dioxime)-*N*,*N'*,μ-*O*,μ-*O'*]copper(II).

† Henceforth $CuCl_2$(niox).

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classified as unobserved, empirical absorption correction (ψ scans) (minimum transmission factor 0·74, maximum transmission taken as unity), $R_{\text{int}} = 0{\cdot}05$; Cu and Br positions from Patterson map, Fourier syntheses revealed the other non-H atoms, refinement by 'cascade-matrix' least squares on F, anisotropic, $R_w(R) = 0{\cdot}049$ (0·043); difference Fourier map clearly showed H atoms, which were kept fixed with $U_{\text{iso}} = 0{\cdot}06$ Å^2, final refinement: $R_w(R) = 0{\cdot}039$ (0·045), all shifts $<0{\cdot}01\sigma$, $w = 1/\sigma^2(F)$, largest features in final difference map +1·14 and −0·61 e Å^{-3}, calculations performed on a Nova 3 computer, plots drawn on a Tektronix plotter; *SHELXTL* (Sheldrick, 1981), which uses scattering factors from *International Tables for X-ray Crystallography* (1974) and takes anomalous dispersion into account, was used.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

$U_{\text{eq}} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$, $\tilde{\mathbf{U}}$ signifying the diagonalized U matrix.

	x	y	z	U_{eq}
Cu	−191 (2)	7360 (1)	5793 (1)	35 (1)
Br(1)	−3530 (1)	7620 (1)	6801 (1)	48 (1)
Br(2)	553 (2)	7369 (2)	7774 (1)	53 (1)
N(1)	2467 (10)	7377 (9)	4574 (6)	36 (4)
N(2)	−319 (10)	7350 (10)	3926 (7)	41 (4)
O(1)	3998 (9)	7337 (9)	4987 (6)	52 (4)
O(2)	−1885 (9)	7305 (11)	3609 (6)	67 (4)
C(1)	2852 (11)	7419 (11)	3270 (8)	34 (4)
C(2)	4737 (12)	7498 (13)	2188 (8)	43 (5)
C(3)	4892 (14)	7125 (15)	810 (9)	59 (6)
C(4)	2994 (14)	8187 (15)	371 (8)	61 (6)
C(5)	1289 (13)	7574 (14)	1383 (8)	48 (5)
C(6)	1168 (12)	7448 (11)	2880 (8)	38 (4)

Table 2. *Bond distances* (Å) *and angles* (°) *for the non*-H *atoms*

Cu–Br(1)	2·345 (1)	Cu–Br(2)	2·351 (2)
Cu–N(1)	1·990 (7)	Cu–N(2)	2·000 (8)
N(1)–O(1)	1·380 (12)	N(1)–C(1)	1·284 (11)
N(2)–O(2)	1·379 (13)	N(2)–C(6)	1·282 (9)
C(1)–C(2)	1·501 (11)	C(1)–C(6)	1·483 (15)
C(2)–C(3)	1·527 (15)	C(3)–C(4)	1·475 (14)
C(4)–C(5)	1·520 (14)	C(5)–C(6)	1·512 (13)
Br(1)–Cu–Br(2)	98·1 (1)	Br(1)–Cu–N(1)	168·3 (2)
Br(2)–Cu–N(1)	92·5 (3)	Br(1)–Cu–N(2)	92·3 (2)
Br(2)–Cu–N(2)	169·5 (2)	N(1)–Cu–N(2)	77·0 (3)
Cu–N(1)–O(1)	126·4 (5)	Cu–N(1)–C(1)	118·7 (7)
O(1)–N(1)–C(1)	114·8 (7)	Cu–N(2)–O(2)	127·1 (4)
Cu–N(2)–C(6)	118·3 (8)	O(2)–N(2)–C(6)	114·6 (8)
N(1)–C(1)–C(2)	126·3 (10)	N(1)–C(1)–C(6)	112·8 (7)
C(2)–C(1)–C(6)	120·8 (8)	C(1)–C(2)–C(3)	112·9 (10)
C(2)–C(3)–C(4)	112·2 (7)	C(3)–C(4)–C(5)	113·2 (7)
C(4)–C(5)–C(6)	111·7 (10)	N(2)–C(6)–C(1)	113·1 (8)
N(2)–C(6)–C(5)	125·8 (10)	C(1)–C(6)–C(5)	121·1 (7)

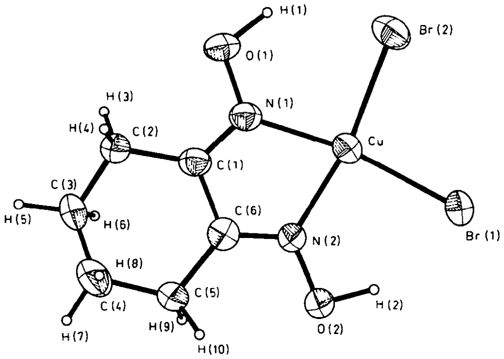

Fig. 1. View of the molecule with the numbering scheme. Thermal ellipsoids are drawn at 50% probability level, unrefined H positions from a difference Fourier map as small spheres with arbitrary radius.

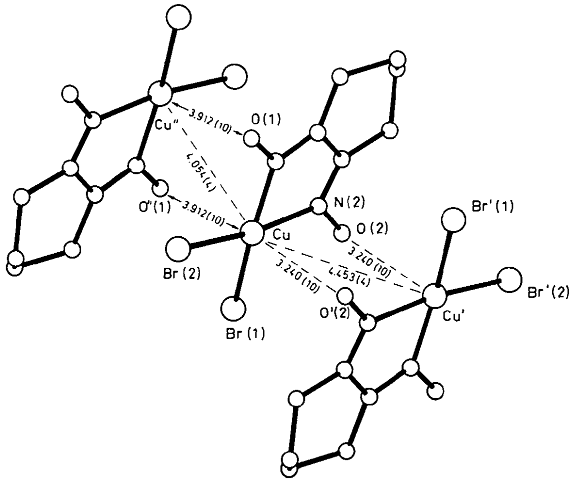

Fig. 2. View of a section of the pseudo-polymeric stack along **b** with the important intermolecular distances. Cu′ and Cu″ are related by a unit-cell translation along **b**, and these molecules are generated from the unprimed one by inversion centers midway between them. Angles of possible relevance are: Cu′–Cu–Cu″ 138·0 (4); O′(2)–Cu–O″(1) 163 (1)°.

Discussion. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2. Fig. 1 shows the monomer which makes up the asymmetric unit. Its structure corresponds to that of $CuCl_2$(niox) (Mégnamisi-Bélombé & Endres, 1983), yet the crystal structures of these two compounds differ markedly. Whereas $CuCl_2$(niox) forms discrete dimers with chloro bridges, a pseudo-polymeric chain structure is found for $CuBr_2$(niox) (Fig. 2). Dimerization is realized by Cu–O contacts of 3·24 (1) Å between two monomers, a feature reminiscent of the dimeric structure of bis(2,3-butanedione dioximato)copper(II) (Frasson, Bardi & Bezzi, 1959). The dimers are linked into infinite chains along **b** by weak interdimer Cu–O interactions, 3·91 (1) Å. It is interesting to note that the intradimer Cu–Cu separation, 4·453 (4) Å, is longer than the

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* Lists of structure factors, anisotropic thermal parameters and unrefined H coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38621 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

interdimer one, 4·054 (4) Å. The relevant distances which may be important for the interpretation of possible magnetic exchange interactions are summarized in Fig. 2. The Cu–O(2′) vector forms an angle of 6 (1)° with the normal of the plane defined by Cu, Br(1), Br(2), N(1) and N(2). Whereas equal Cu–Cu separations occur in the polymeric CuX_2(α,β-dodoH) complexes quoted above, the present structure contains two alternating Cu–Cu spacings along a chain.

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An Unusual Chloro Bridge in the Polymeric Chain Structure of Dichloro(oxamide dioxime)copper(II)* Phase II, $Cu(C_2H_6N_4O_2)Cl_2$

BY HELMUT ENDRES

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, *D*-6900 *Heidelberg* 1, *Federal Republic of Germany*

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Abstract. $M_r = 252·55$, monoclinic, $P2_1/m$, $a = 7·804$ (7), $b = 6·267$ (3), $c = 8·414$ (7) Å, $\beta = 114·14$ (3)°, $V = 375·52$ Å^3, $Z = 2$, $D_x = 2·23$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 3·59$ mm^{-1}, $F(000) = 250$, $T = 295 \pm 2$ K, $R_w(R) = 0·046$ (0·054) for 554 observed independent reflections. A polymeric chain structure is formed where a Cl atom bridges three Cu atoms. This leads simultanously to bent and to nearly linear Cu—Cl—Cu chains, and to zig-zag chains of Cu atoms. The coordination around Cu has the shape of an elongated square bipyramid.

Introduction. The title compound is a member of the CuX_2(α,β-dodoH) family, where *X* is Cl or Br, and α,β-dodoH is a chelating α,β-dione dioxime ligand. Usually these complexes form halide-bridged dimers with square pyramidal coordination of Cu (Mégnamisi-Bélombé & Endres, 1983*a*). Yet in some cases polymeric chains have been found, as in phase I of $CuCl_2(oaoH_2)$, $oaoH_2$ = oxamide dioxime (Endres, Genc & Nöthe, 1983), $CuCl_2$(diphenylethanedione dioxime) (Mégnamisi-Bélombé, Singh, Bolster & Hatfield, 1983), and in the pseudo-polymeric chain structure of $CuBr_2$(1,2-cyclohexanedione dioxime) (Mégnamisi-Bélombé & Endres, 1983*b*). Structural investigations of compounds of this type have as their main purpose to yield data for a correlation of magnetic properties and structural features, as discussed, for example, by Marsh, Hatfield & Hodgson (1982). The static magnetic properties of first-row transition-metal compounds with chain structures have been summarized recently (Hatfield, Estes, Marsh, Pickens, ter Haar & Weller, 1982); the magnetic properties of dinuclear Cu^{II} complexes have been reviewed earlier (Hatfield, 1974).

Experimental. Phase II of $CuCl_2(oaoH_2)$ was obtained as a by-product in the preparation of phase I and of $CuCl(oaoH)(oaoH_2)$ (Endres *et al.*, 1983). A sintered glass filtration funnel was placed upside down in a beaker containing methanol, $CuCl_2$ was dissolved in the beaker, and solid oxamide dioxime (Ephraim, 1889) was put onto the filter plate. After standing for a week at room temperature, the $oaoH_2$ crystals above the filter plate had disappeared, and dark-green crystals of $CuCl(oaoH)(oaoH_2)$ had formed instead. A green precipitate beneath the filter plate was collected by filtration: it consisted of large dark-green crystals of phase I $CuCl_2(oaoH_2)$, contaminated with small light-green crystals of phase II. Another crop of this mixture was obtained by slow evaporation of the mother liquor. Flake-like crystal, 0·1 × 0·1 × 0·05 mm, lattice parameters derived from the setting angles of 34 reflections centered on a diffractometer (Siemens AED, Zr-filtered Mo $K\alpha$ radiation), θ–2θ scans, 'five-value' method, $2\theta \le 50°$, 554 observed (out of 672 measured)

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* *catena*-μ_3-Chloro-chloro(oxamide dioxime-*N*,*N*′)copper(II).

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