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, $Cu(C_2H_6N_4O_2)Cl_2$

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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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independent reflections with $I > 2{\cdot}5\sigma(I)$, h −9–8, k 0–8, l 0–11, Lorentz and polarization corrections, $w = 1/\sigma^2(F)$. As all the most prominent peaks in the Patterson map appeared in the planes $y = 0$ and $y = \frac{1}{2}$, consistent with atoms situated in the mirror plane ($y = \frac{1}{4}$) of the centrosymmetric space group $P2_1/m$, the choice of this space group seemed favored. Cu and Cl positions derived from Patterson map, Fourier synthesis revealed positions of the other non-H atoms, confined to a crystallographic mirror plane. As the strict planarity of the complex molecule thus implied caused some doubt, refinement was tried in the non-centrosymmetric space group $P2_1$ which gave a much worse result than the refinement in $P2_1/m$. Refinement in $P2_1/m$ by 'cascade matrix' least squares on F, anisotropic, $R_w(R) = 0{\cdot}049$ (0·057); difference Fourier map clearly showed all H positions; these did not refine reasonably, so were kept fixed in the final refinement cycles, $U = 0{\cdot}06$ Å^2, final refinement: $R_w(R) = 0{\cdot}046$ (0·054), all shifts $<0{\cdot}01\sigma$, largest features in a final difference Fourier map were +0·73 and −0·97 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 $\times 10^3$)

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

	x	y	z	U_{eq}
Cu	1415 (2)	2500	1355 (2)	28 (1)
Cl(1)	−1209 (4)	2500	−1136 (4)	39 (1)
Cl(2)	3489 (4)	2500	131 (4)	46 (2)
N(1)	35 (12)	2500	2876 (12)	30 (4)
N(2)	3435 (13)	2500	3664 (12)	27 (4)
O(1)	−1933 (10)	2500	2401 (10)	44 (4)
O(2)	5396 (10)	2500	4153 (10)	46 (4)
C(1)	971 (15)	2500	4549 (14)	23 (5)
C(2)	3060 (16)	2500	5022 (15)	28 (5)
N(3)	278 (13)	2500	5736 (12)	34 (5)
N(4)	4263 (14)	2500	6646 (13)	55 (6)

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

Cu–Cl(1)	2·253 (3)	Cu–Cl(2)	2·246 (4)
Cu–N(1)	1·981 (12)	Cu–N(2)	1·937 (8)
N(1)–O(1)	1·420 (12)	N(1)–C(1)	1·294 (13)
N(2)–O(2)	1·413 (13)	N(2)–C(2)	1·291 (19)
C(1)–C(2)	1·512 (17)	C(1)–N(3)	1·316 (18)
C(2)–N(4)	1·303 (13)		
Cl(1)–Cu–Cl(2)	97·2 (1)	Cl(1)–Cu–N(1)	94·2 (2)
Cl(2)–Cu–N(1)	168·6 (2)	Cl(1)–Cu–N(2)	171·9 (4)
Cl(2)–Cu–N(2)	90·9 (4)	N(1)–Cu–N(2)	77·7 (4)
Cu–N(1)–O(1)	129·0 (6)	Cu–N(1)–C(1)	119·3 (8)
O(1)–N(1)–C(1)	111·7 (11)	Cu–N(2)–O(2)	129·2 (8)
Cu–N(2)–C(2)	120·1 (8)	O(2)–N(2)–C(2)	110·6 (8)
N(1)–C(1)–C(2)	110·8 (12)	N(1)–C(1)–N(3)	127·0 (11)
C(2)–C(1)–N(3)	122·3 (9)	N(2)–C(2)–C(1)	112·2 (9)
N(2)–C(2)–N(4)	127·0 (12)	C(1)–C(2)–N(4)	120·9 (13)

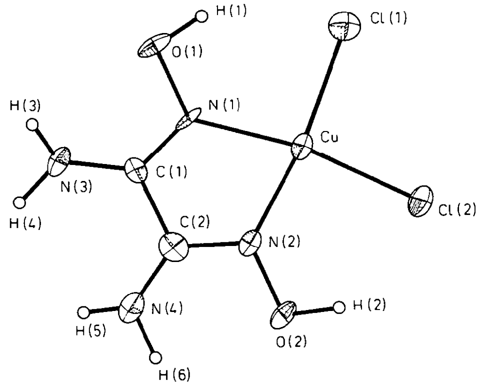

Fig. 1. The $CuCl_2(oaoH_2)$ complex molecule with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level, unrefined H atoms as small spheres.

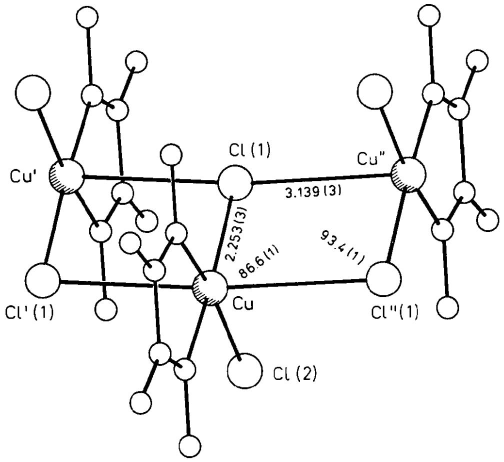

Fig. 2. Section of the polymeric chain structure. All atoms lie on crystallographic mirror planes. Cu' and Cu'' are related by a unit translation **b**, Cu and Cu'' by an inversion center. The Cu–Cu'' distance is 3·972 (2) Å.

Discussion. Fig. 1 shows the $CuCl_2(oaoH_2)$ complex molecule. Atomic coordinates are listed in Table 1, bond distances and angles in Table 2. All atoms lie on a crystallographic mirror plane, and hence the molecule is strictly planar. As indicated in Fig. 2, the molecules form chains parallel to **b**, held together by bridging Cl atoms. The Cu–Cl(1)–Cu''–Cl(1'') parallelogram corresponds to the core usually found in the dimeric $[CuX_2(\alpha,\beta\text{-dodoH})]_2$ complexes (Mégnamisi-Bélombé & Endres, 1983*a*). The outstanding feature is that these

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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 38620 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parallelograms form ribbons by sharing common Cu—Cl(1) edges, which lie in crystallographic mirror planes. The dihedral angle between two adjacent parallelograms is insignificantly different from zero, 0·6 (5)°. Alternatively, the structure may be regarded as containing nearly linear Cu—Cl—Cu chains with a Cu′—Cl(1)—Cu″ angle of 173·1 (1)° and equal Cu—Cl separations, 3·139 (3) Å. The Cl(1′)—Cu—Cl(1″) angle is also 173·1 (1)°. Further geometrical information is included in Fig. 2.

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Structure of (*tert*-Butyl isocyanide)carbonyl(chloro)bis[dimethyl(phenyl)phosphine]phenylruthenium(II), $[Ru(C_6H_5)(C_5H_9N)(C_8H_{11}P)_2(CO)Cl]$

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Abstract. $M_r = 601{\cdot}15$, orthorhombic, *Pnma*, $a = 22{\cdot}250\,(7)$, $b = 13{\cdot}706\,(4)$, $c = 9{\cdot}963\,(3)$ Å, $V = 3038{\cdot}3$ Å^3, $F(000) = 1239{\cdot}5$, $T = 290 \pm 1$ K, $Z = 4$, $D_x = 1{\cdot}31$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu(\mathrm{Cu}\,K\alpha) = 62{\cdot}6$ cm^{-1}, $R = 0{\cdot}047$ for 1613 observed reflections. The complex consists of discrete monomeric units, with octahedral coordination for the Ru atom. The chloride, carbonyl, phenyl and isocyanide ligands lie on a crystallographic mirror plane. The mutually *trans* chloride and carbonyl ligands are disordered. The Ru—P distance is 2·366 (2) Å. The isocyanide and phenyl ligands lie *trans* to one another with Ru—C distances of 2·013 (9) and 2·141 (9) Å respectively. The isocyanide is slightly non-linear [C—N—CMe$_3$ 169·7 (9)°].

Introduction. Complexes $[Ru(CO)_2RCl(PMe_2Ph)_2]$ ($R = C_6H_5$, p-MeC_6H_4, p-$MeOC_6H_4$, *etc.*) react with the isocyanide Me_3CNC in two quite different ways. One mode of reaction involves substitution of a carbonyl ligand and formation of $[Ru(CO)RCl(CNCMe_3)(PMe_2Ph)_2]$, while the other yields benzoyl complexes $[Ru(CO)(COR)(CNCMe_3)_2(PMe_2Ph)_2]^+$. The relative yields of the two types of product are markedly affected by the nature of the group R and by the conditions used for the reactions.

Beyond establishing that the two PMe_2Ph ligands were mutually *trans*, it was not possible to use spectroscopic methods to determine the ligand arrangement in substitution products $[Ru(CO)RCl(CNCMe_3)(PMe_2Ph)_2]$. In addition, the exact orientation of the aryl ligand and the lengths of the various Ru—C bonds were of particular interest following the recent determination of the structure of the complex $[Ru(CO)(COPh)Ph(CNCMe_3)(PMe_2Ph)_2]$ (Chawdhury, Dauter, Mawby, Reynolds, Saunders & Stephenson, 1983). For these reasons, the crystal structure of $[Ru(CO)PhCl(CNCMe_3)(PMe_2Ph)_2]$ was determined.

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