

An H(5)⋯H(5) separation of 2.58 Å suggests that compounds of the type (CH₃)₂Sn(O₂CR)₂ with R different from H would not have the same structure as that described here for the formate.

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Structure of *trans*-Dichlorotetra(2-furaldehyde oxime)cobalt(II)

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Abstract. [CoCl₂(C₅H₅NO₂)₄], *M_r* = 574.24, triclinic, *P* $\bar{1}$, *a* = 6.9707 (8), *b* = 9.4963 (12), *c* = 10.7001 (11) Å, α = 77.691 (12), β = 70.739 (11), γ = 81.750 (11)°, *V* = 651.23 (10) Å³, *Z* = 1, *D_x* = 1.464 Mg m⁻³, λ (Mo *K* α) = 0.7107 Å, μ = 0.91 mm⁻¹, *F*(000) = 293, room temperature. The refinements converged to *R* = 0.036 for 2028 unique reflections with *I* > 3 σ (*I*). The Co atom is bonded to four N atoms from four furaldehyde oxime ligands in a square-planar geometry and to two Cl atoms in a *trans* position thus forming an octahedral complex. The compound consists of van der Waals packed molecules. Each Cl atom forms two internal hydrogen bonds to the OH group from the two different oxime ligands. Acceptor–donor distances observed are: Co–Cl = 2.4377 (8) and Co–N = 2.171 (2)–2.173 (2) Å.

Introduction. Oxime compounds contain the group C=N–OH and possess two potential donor sites, *i.e.* the N and the O atoms. Hence, they can act as ambidentate ligands in coordinating metal ions (Mehrotra, Rai, Singh & Bohra, 1975; Chakravorty, 1974; Chatterjee, 1978; Nakamura, Konishi & Otsuka, 1979; Singh, Gupta, Srivastava & Mehrotra, 1974). The various modes of possible metal–oxime bonding include monodentate as well as bidentate oxime ligands coordinating *via* the N and/or O atom.

In the second case the oximes preferably react as the conjugate base, *i.e.* the oximate anion. Polynuclear complexes could also be formed in which different metal atoms are bonded to the N atom and the O atom, respectively. Intra- or intermolecular hydrogen bonds are also important for the formation of discrete or polymeric coordination compounds.

The present investigation was performed to establish the donor behaviour of furaldehyde oxime towards cobalt(II). Moreover there seem to be only few earlier X-ray investigations of cobalt(II) oxime compounds (Bekaroglu, Sarisaban, Koray & Ziegler, 1977; Alcock, Atkins, Curzon, Golding & Sellars, 1980; Kubel & Strähle, 1981, 1982).

Experimental. The title compound was prepared by reacting CoCl₂·6H₂O (1 mmol) with furaldehyde oxime (FDH, C₅H₅NO₂, 4 mmol) in ethanol at 333 K. Cooling to room temperature and recrystallization from a mixture of methanol and ethanol gave single crystals. The intensity data set was collected at room temperature with the aid of a CAD-4 diffractometer. The intensities in one half of the reflection sphere (3 ≤ θ ≤ 28°) were measured with ω –2 θ scans. The ratio σ (*I*)/*I* requested in a scan was 0.028. Three standard reflections were measured at regular intervals. The intensities decreased linearly by 0.24% in one hour exposure time (total 34%). All the collected

reflections were corrected, by a least-squares fit, for this intensity decrease giving a random variation of the standard reflections within $\pm 2\%$. Unit-cell dimensions were obtained from least-squares calculations of 50 θ values determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$. The diffractometer with $\omega_{\bar{h}\bar{k}\bar{l}}$ measured at negative θ angle was used. Information on the collection and reduction of the data is given in Table 1. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects. The absorption correction was made according to the method by Walker & Stuart (1983). The corrections were in the ranges 0.87–1.12 for $A_{p,s}$ and 0.92–1.05 for A_{θ} (Ugozzoli, 1987). Reflections with $I < 3\sigma(I)$ were considered insignificantly different from the background and excluded from all subsequent calculations [$\sigma(I)$ is based on counting statistics]. Laue class $\bar{1}$ and the absence of systematic extinctions gave $P1$ and $P\bar{1}$ as possible space groups.

The structure was solved by Patterson and difference Fourier methods assuming the space group $P\bar{1}$. It was refined by full-matrix least-squares calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with empirical weights $w^{-1} = \sigma^2/[4|F_o|^2 + (0.010|F_o|)^2]$. Scattering factors with corrections for anomalous dispersion were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). Non-H atoms were refined with anisotropic thermal parameters. All H atoms could now be determined from a $\Delta\rho$ map. Both their positions and isotropic thermal parameters could be refined. Details of the refinements are given in Table 1 and the final atomic parameters in Table 2.* The centrosymmetric space group $P\bar{1}$ adopted in this study is supported by the results of the structural refinements. Computer programs used were those compiled and amended by Lundgren (1982).

Discussion. The compound is composed of discrete van der Waals packed complexes, $trans-[CoCl_2(FDH)_4]$ (Fig. 1). The numbering of the atoms in the furaldehyde oxime ligand is given in Fig. 2 and interatomic distances and angles of $[CoCl_2(FDH)_4]$ in Table 3.

The central Co^{II} atom is bonded to four N atoms from four furaldehyde oxime ligands in a square-planar geometry and to two Cl atoms in the *trans* position thus forming an octahedral coordination geometry. There are no hydrogen bonds between any of the four oxime ligands. However, each Cl atom forms two intramolecular hydrogen bonds to the

Table 1. Summary of the collection and reduction of intensity data and results of the least-squares refinements

Crystal size (mm)	0.25 × 0.35 × 0.20
Radiation (graphite monochromated)	Mo $K\alpha$
$[(\sin\theta)/\lambda]_{max}$ (\AA^{-1})	0.66
h, k, l range	0 → 9, -12 → 12, -14 → 14
ω - 2θ scan width, $\Delta\omega$ (°)	0.8 + 0.5tan θ
Maximum recording time (s)	240
Number of measured reflections	3369
Number of unique reflections	3077
R_{int}	0.015
Number of reflections used in the final refinement [$I > 3\sigma(I)$]	2028
Number of parameters refined	200
$(\Delta/\sigma)_{max}$ (non-H atoms)	0.02
$(\Delta\rho)_{max}$ ($e \text{\AA}^{-3}$)	0.44
$(\Delta\rho)_{min}$ ($e \text{\AA}^{-3}$)	-0.55
R	0.036
wR	0.045
S	1.89
δR plot, slope	0.58
δR plot, intercept	-0.02

Table 2. Atomic coordinates and equivalent isotropic temperature factor coefficients (calculated from the average of the anisotropic temperature factor over all directions) with e.s.d.'s in parentheses for $[CoCl_2(FDH)_4]$

	x	y	z	U_{eq}^* (\AA^2)
Co	0.00	0.00	0.00	0.0302 (2)
Cl	0.30856 (10)	0.12676 (7)	-0.06791 (7)	0.0392 (3)
O11	-0.0623 (4)	0.3094 (2)	0.0639 (2)	0.051 (1)
N1	-0.1686 (4)	0.1974 (2)	0.0616 (2)	0.036 (1)
C11	-0.3607 (5)	0.2262 (3)	0.1026 (3)	0.044 (1)
C12	-0.4727 (5)	0.3536 (3)	0.1491 (3)	0.045 (1)
C13	-0.4277 (7)	0.4801 (4)	0.1653 (4)	0.058 (2)
C14	-0.6139 (8)	0.5585 (4)	0.2164 (5)	0.080 (2)
C15	-0.7590 (8)	0.4802 (5)	0.2271 (5)	0.087 (2)
O12	-0.6810 (4)	0.3512 (3)	0.1863 (3)	0.078 (1)
H1	0.051 (8)	0.273 (5)	0.031 (4)	0.09 (2)
H11	-0.428 (5)	0.163 (3)	0.101 (3)	0.04 (1)
H13	-0.322 (6)	0.499 (4)	0.157 (4)	0.05 (1)
H14	-0.623 (8)	0.640 (5)	0.241 (4)	0.10 (2)
H15	-0.907 (8)	0.479 (5)	0.256 (4)	0.10 (2)
O21	0.1321 (5)	0.1591 (4)	-0.2946 (3)	0.078 (1)
N2	-0.0168 (4)	0.0761 (2)	-0.2028 (2)	0.038 (1)
C21	-0.1542 (5)	0.0605 (3)	-0.2513 (3)	0.040 (1)
C22	-0.1714 (5)	0.1182 (3)	-0.3828 (3)	0.044 (1)
C23	-0.0625 (7)	0.2010 (4)	-0.4955 (3)	0.061 (1)
C24	-0.1716 (8)	0.2198 (5)	-0.5890 (4)	0.072 (2)
C25	-0.3345 (8)	0.1501 (6)	-0.5304 (4)	0.085 (2)
O22	-0.3420 (4)	0.0838 (3)	-0.4022 (2)	0.074 (1)
H2	0.203 (8)	0.154 (5)	-0.254 (5)	0.09 (2)
H21	-0.257 (6)	0.000 (4)	-0.190 (4)	0.06 (1)
H23	0.072 (6)	0.233 (4)	-0.515 (3)	0.06 (1)
H24	-0.125 (8)	0.272 (5)	-0.681 (5)	0.11 (2)
H25	-0.446 (7)	0.125 (4)	-0.552 (4)	0.09 (1)

The H atoms were refined isotropically.

$$* U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

* Lists of distances, angles, least-squares planes, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53113 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hydroxy group from the two crystallographically independent oxime ligands. These bond to cobalt as neutral molecules, which have only been reported for oxime ligands in one earlier paper (Alcock *et al.*, 1980). In the closely related compound, $[CoCl_2-$

(FDH)₂], Sen & Pickerell (1973) conclude from electronic spectra, IR, magnetic measurements, conductivity and molecular-weight studies that furaldehyde oxime acts as a bidentate ligand, which is bonded to cobalt *via* the furan and oxime O atoms. An octahedral complex is completed with the two Cl atoms. Evidently the furaldehyde oxime molecules must have another conformation (*syn* isomer) in this compound than in the present one.

The two Co^{II}—N distances in the present compound, 2.171 (2) and 2.173 (2) Å, are not significantly different and there is a good agreement with the Co^{II}—N distances in bis(trifluoroacetoxy)bis(dimethylglyoxime)cobalt(II), 2.13–2.15 Å (Alcock *et al.*, 1980), where two dimethylglyoxime molecules are coordinated to Co^{II} as bidentate, neutral ligands. When these types of ligands are deprotonated, as in bis(diaminoglyoximate)(diaminoglyoxime)cobalt(II) (Bekaroglu *et al.*, 1977), bis(dimethylglyoximate)(4,4'-bipyridine)cobalt(II) (Kubel & Strähle, 1982), and bis(dimethylglyoximate)(pyrazine)cobalt(II) (Kubel & Strähle, 1981), the Co^{II}—N distances are drastically shortened, 1.873 (4)–1.904 (4) Å.

The geometry of the furaldehyde oxime ligands (Table 3) in the present compound is in close agreement with the results of Jensen & Jerslev (1967). Both furaldehyde oxime molecules are planar within ±0.018 Å (excluding H atoms) and the Cl atom is close to these planes, 0.26 Å from ligand 1 and 0.25 Å from ligand 2. The angle between the two ligand planes is 89.3 (3)°.

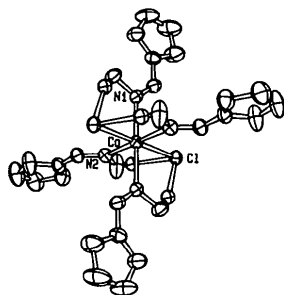


Fig. 1. View of the coordination around Co in [CoCl₂(FDH)₄].

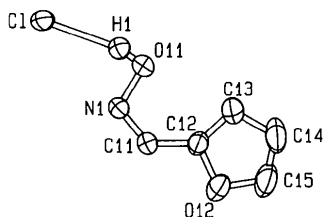


Fig. 2. The hydrogen bond between the Cl atom and the O atom in the oxime group in the furaldehyde oxime ligand. The numbering of the atoms in ligand 1 is also shown.

Table 3. Selected interatomic distances (Å) and angles (°), with *e.s.d.*'s in parentheses

Coordination geometry around the Co atom			
Co—Cl	2.4377 (8)	Co—N2	2.173 (2)
Co—N1	2.171 (2)		
Cl—Co—N1	87.27 (7)	N1—Co—N2	90.50 (8)
Cl—Co—N2	87.64 (7)		
Bond angles around the donor atoms N1, N2 and Cl			
Co—N1—O11	119.2 (2)	Co—N2—C21	128.8 (2)
Co—N1—C11	128.6 (2)	Co—Cl...H1	73 (1)
Co—N2—O21	119.1 (2)	Co—Cl...H2	73 (2)
Geometry of the furaldehyde oxime molecules			
H1—O11	0.81 (5)	H2—O21	0.75 (5)
O11—N1	1.390 (3)	O21—N2	1.377 (4)
N1—C11	1.272 (4)	N2—C21	1.269 (4)
C11—C12	1.432 (4)	C21—C22	1.435 (4)
C12—C13	1.344 (5)	C22—C23	1.346 (5)
C13—C14	1.402 (7)	C23—C24	1.415 (6)
C14—C15	1.301 (7)	C24—C25	1.300 (7)
C15—O12	1.366 (5)	C25—O22	1.370 (5)
O12—C12	1.375 (4)	O22—C22	1.366 (4)
H1—O11—N1	97 (3)	H2—O21—N2	100 (4)
O11—N1—C11	112.2 (2)	O21—N2—C21	112.0 (2)
N1—C11—C12	128.8 (3)	N2—C21—C22	128.7 (3)
C11—C12—C13	136.4 (3)	C21—C22—C23	136.5 (3)
C12—C13—C14	106.7 (4)	C22—C23—C24	106.5 (4)
C13—C14—C15	107.6 (4)	C23—C24—C25	107.2 (4)
C14—C15—O12	111.0 (4)	C24—C25—O22	111.1 (4)
C15—O12—C12	105.6 (3)	C25—O22—C22	105.8 (3)
O12—C12—C11	114.5 (3)	O22—C22—C21	114.1 (3)
O12—C12—C13	109.1 (3)	O22—C22—C23	109.4 (3)
Geometry of the hydrogen bonds			
O11...Cl	3.005 (3)	H1...Cl	2.22 (5)
O21...Cl	3.006 (3)	H2...Cl	2.29 (4)
O11—H1...Cl	163 (4)	O21—H2...Cl	159 (5)

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