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The Crystal Structure of Tris(oxamide oxime)cobalt(III) Trichloride, Co(C₂H₆N₄O₂)₃Cl₃

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Monoclinic, $P2_1/c$, $a = 13.429$ (2), $b = 15.831$ (2), $c = 9.455$ (3) Å, $\beta = 115.63$ (2)°. There are four discrete formula units in the unit cell, forming a racemate. The Co^{III} atoms are octahedrally coordinated by the bidentate ligand. The structure was solved by Patterson and Fourier methods and refined by a least-squares procedure to $R = 0.037$ for 4990 independent reflections.

Introduction

The compound under investigation has been synthesized by dissolving bis(oxamide oximato)cobalt(II)–oxamide oxime, Co(C₂H₅N₄O₂)₂.C₂H₆N₄O₂ (I) (Bekaroglu, Sarisaban, Koray & Kiegler, 1977), in water and recrystallizing the brown precipitate which appeared after 2 h from hydrochloric acid (Sarisaban, 1976). The possibly chelating ligand oxamide oxime ('diaminoglyoxime') recently received new interest when the X-ray structure determinations of (I) and bis(oxamide oximato)nickel(II)–water–dimethylformamide, Ni(C₂H₅N₄O₂)₂.H₂O.C₃H₇O (II) (Endres, 1978), were reported. In the Co complex mentioned above the Co atom has a pseudooctahedral environment, being coordinated by four oxime N atoms of two chelating C₂H₅N₄O₂⁻ groups (OAOH) and one amino N of two adjacent complex molecules each. By this mechanism a chain polymer is formed. In contrast to the Co^{II} complex, there are no interactions between the Ni central atom and amino N atoms of adjacent molecules, there being discrete square-planar Ni(C₂H₅N₄O₂)₂ units with DMF acting solely as a 'space filler'. We now report the X-ray structure determination of tris(oxamide oxime)cobalt(III) trichloride, Co(C₂H₆N₄O₂)₃Cl₃ (III), in which the oxamide oxime ligands are bonded in

a different way from that which has been reported for the Ni and Co complexes discussed above and also from that known for diacetyldioxime complexes.

Rotating-crystal and Weissenberg photographs (Cu $K\alpha$ radiation) showed the crystal to be monoclinic and provided rough lattice constants. Exact lattice parameters could be calculated by the least-squares method (Berdesinski & Nuber, 1966) from diffractometrically determined exact θ values of 75 selected reflections. Intensity measurements were performed on a computer-controlled single-crystal diffractometer (AED-Siemens, Mo $K\alpha$, θ–2θ scans, five-value method) up to $2\theta = 69.98°$. Reflections with an intensity less than 2.58 times the standard deviation were not considered. A total of 4990 observed independent intensities remained for calculations. They

Table 1. *Crystal data*

Co₂H₆N₄O₂)₃Cl₃	
Space group $P2_1/c$	$Z = 4$
λ(Mo $K\alpha$) = 0.7107 Å	$V = 1812.30$ Å³
$a = 13.429$ (2) Å	$D_o = 1.87$ g cm⁻³
$b = 15.831$ (2)	$D_c = 1.881$
$c = 9.455$ (3)	$F(000) = 1060.00$
$\beta = 115.63$ (2)°	FW 516.56
Systematic $0k0$: $k = 2n + 1$	μ(Mo $K\alpha$) = 7.84 cm⁻¹
absences $h0l$: $l = 2n + 1$	$69.977 \geq 2\theta \geq 4.235°$
Crystal size: $0.4 \times 0.2 \times 0.2$ mm	Independent reflections: 4990

were corrected for Lorentz and polarization factors only. Crystal data are listed in Table 1.

The positions of all non-hydrogen atoms were determined from a Patterson synthesis. Refinement with anisotropic temperature factors resulted in $R = 0.054$, at which point a difference Fourier map enabled all the H atoms to be located. Their coordinates were refined independently with isotropic thermal parameters equivalent to that of H(1) ($B = 4.54$ Å^2); the final R was 0.037 and R_w was 0.039.*

All calculations were performed on Siemens 301 (Anorg. Chem. Institut, Heidelberg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) computers with local versions of the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964). Atomic coordinates of the non-hydrogen atoms are listed in Table 2, those of the H atoms in Table 3. The atom-numbering scheme is that in Fig. 1.

Table 2. *Final atomic fractional coordinates (for Co, Cl, × 10⁵, for O, N, C, × 10⁴) of the non-hydrogen atoms*

	x	y	z
Co	75330 (2)	49485 (2)	51301 (3)
Cl(1)	73909 (5)	43577 (5)	00348 (8)
Cl(2)	43553 (5)	25313 (4)	12527 (8)
Cl(3)	00476 (5)	29255 (5)	80780 (8)
O(1)	3898 (1)	1050 (1)	9032 (2)
O(2)	−0091 (1)	4717 (1)	7084 (2)
O(3)	8736 (1)	4052 (1)	3608 (2)
O(4)	6174 (1)	4096 (1)	6449 (2)
O(5)	5221 (1)	0352 (1)	7719 (2)
O(6)	0993 (1)	1208 (1)	0308 (2)
N(1)	2208 (2)	1524 (2)	6347 (3)
N(2)	0060 (2)	4112 (2)	0903 (3)
N(3)	8096 (2)	2457 (1)	9177 (3)
N(4)	6488 (2)	2403 (2)	0456 (3)
N(5)	4641 (2)	0856 (1)	4110 (2)
N(6)	2506 (2)	3317 (2)	8038 (3)
N(7)	2839 (2)	0772 (1)	8711 (2)
N(8)	1098 (1)	4991 (1)	3016 (2)
N(9)	7979 (2)	4020 (1)	4246 (2)
N(10)	6957 (2)	0974 (1)	0857 (2)
N(11)	3813 (2)	4879 (1)	6736 (2)
N(12)	1982 (2)	0775 (1)	0899 (2)
C(1)	2077 (2)	1006 (2)	7350 (3)
C(2)	0996 (2)	0617 (2)	7038 (3)
C(3)	7751 (2)	3260 (2)	4535 (3)
C(4)	7015 (2)	3277 (2)	5344 (3)
C(5)	3797 (2)	0673 (2)	2745 (3)
C(6)	2704 (2)	3914 (2)	7222 (3)

Table 3. *Final atomic fractional coordinates (× 10³) of the hydrogen atoms*

	x	y	z
H(1)	409 (3)	351 (3)	477 (4)
H(2)	999 (3)	094 (2)	246 (5)
H(3)	834 (3)	082 (3)	769 (5)
H(4)	655 (3)	075 (3)	237 (5)
H(5)	505 (3)	045 (2)	850 (4)
H(6)	050 (3)	421 (2)	487 (5)
H(11)	286 (3)	323 (3)	152 (5)
H(12)	166 (3)	338 (3)	039 (5)
H(21)	003 (3)	359 (3)	040 (4)
H(22)	939 (3)	434 (3)	085 (5)
H(31)	868 (3)	241 (3)	882 (4)
H(32)	794 (3)	202 (3)	450 (4)
H(41)	663 (3)	206 (3)	516 (4)
H(42)	588 (3)	234 (3)	076 (4)
H(51)	531 (3)	066 (3)	431 (5)
H(52)	455 (3)	122 (3)	478 (5)
H(61)	304 (3)	310 (3)	896 (4)
H(62)	178 (3)	193 (3)	264 (4)

Discussion

Fig. 1 shows a stereoscopic view of one of the four molecules in the unit cell. The interatomic distances and the bond angles of (III) are listed in Tables 4 and 5. There is one independent molecule in the unit cell, Z being 4. The Co atom has the oxidation number +3, octahedrally coordinated by three neutral oxamide oxime (OAOH₂) ligands. Because of this, the complex cation must exhibit optical activity. The space group $P2_1/c$ implies the presence of a racemate.

The chelate ligands are bonded via the oxime N atoms. The interesting feature is that the ligands are bonded as neutral ligands. This is quite contrary to the situation in (I) (Bekaroglu, Sarisaban, Koray & Ziegler, 1977) and (II) (Endres, 1978), where the coordinating species are the anions OAOH⁻. The positive charge at the Co^{III} cation is equalized by the three Cl⁻ ions.

Co—N(oxime) bond distances in (III) are longer than those in the Co^{II} case, in accordance with the greater steric requirements in the former. The other distances
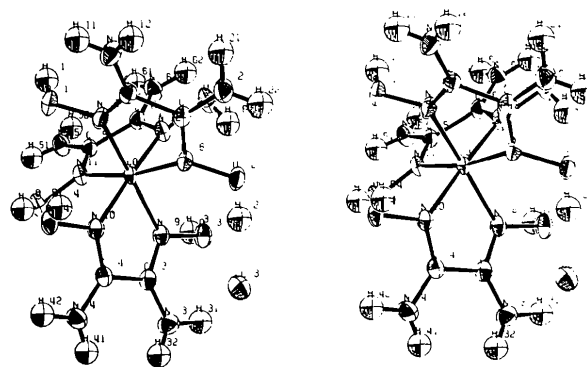
Fig. 1. Stereoview of $Co(C_2H_6N_4O_2)_3Cl_3$. 50% probability ellipsoids are displayed.

Table 4. *Bond lengths* (Å)

Co—N(7)	1·903 (2)	N(2)—H(21)	0·96 (5)
Co—N(8)	1·917 (2)	N(2)—H(22)	0·96 (5)
Co—N(9)	1·911 (2)	N(4)—H(41)	0·93 (6)
Co—N(10)	1·913 (2)	N(6)—H(61)	0·93 (4)
Co—N(11)	1·922 (2)	N(6)—H(62)	0·98 (4)
Co—N(12)	1·905 (2)	O(1)—O(4)	2·929 (2)
N(9)—C(3)	1·299 (3)	Cl(1)—O(3)	3·103 (2)
C(5)—N(5)	1·330 (3)	Cl(3)—O(2)	2·968 (2)
C(6)—N(6)	1·318 (4)	N(8)—O(2)	1·392 (3)
N(1)—H(11)	0·91 (5)	C(3)—C(4)	1·488 (4)
N(1)—H(12)	0·90 (4)	C(3)—N(9)	1·299 (3)
N(3)—H(31)	0·98 (6)	C(3)—N(3)	1·325 (4)
N(5)—H(51)	0·90 (5)	C(4)—N(4)	1·317 (4)
N(5)—H(52)	0·90 (5)	C(4)—N(10)	1·297 (3)
O(3)—O(6)	2·779 (2)	N(10)—O(4)	1·393 (3)
O(1)—O(5)	2·800 (3)	C(5)—N(11)	1·301 (3)
Cl(2)—O(1)	3·027 (2)	O(6)—N(12)	1·381 (3)
C(1)—C(2)	1·484 (4)	O(1)—H(1)	0·95 (4)
C(1)—N(1)	1·321 (4)	O(2)—H(2)	1·11 (4)
C(1)—N(7)	1·304 (3)	O(3)—H(3)	0·81 (4)
C(2)—N(2)	1·323 (3)	O(5)—H(5)	0·88 (5)
C(2)—N(8)	1·300 (3)	O(6)—H(6)	0·90 (4)
N(7)—O(1)	1·391 (3)	O(2)—O(3)	2·927 (3)
N(9)—O(3)	1·389 (3)	Cl(1)—O(4)	3·089 (2)
C(5)—C(6)	1·483 (3)		
C(6)—N(12)	1·303 (3)		

Table 5. *Bond angles* (°)

N(9)—Co—N(8)	94·60 (8)	C(3)—C(4)—N(10)	111·6 (2)
N(9)—Co—N(12)	93·63 (10)	Co—N(9)—O(3)	126·1 (2)
N(8)—Co—N(7)	79·99 (8)	Co—N(10)—O(4)	125·2 (2)
N(11)—Co—N(7)	93·12 (8)	N(5)—C(5)—N(11)	125·5 (2)
N(7)—Co—N(12)	93·25 (10)	N(6)—C(6)—N(12)	125·4 (2)
C(2)—C(1)—N(1)	122·5 (2)	Co—N(11)—C(5)	117·5 (2)
C(1)—C(2)—N(2)	122·0 (2)	Co—N(12)—C(6)	118·3 (2)
C(1)—N(7)—O(1)	114·6 (2)	N(8)—O(2)—H(2)	107 (3)
Co—N(8)—O(2)	124·4 (2)	N(9)—O(3)—H(3)	102 (4)
C(4)—C(3)—N(9)	111·2 (2)	N(9)—Co—N(11)	171·36 (10)
C(3)—C(4)—N(4)	121·8 (2)	N(8)—Co—N(11)	168·91 (14)
Co—N(9)—C(3)	118·2 (2)	N(8)—Co—N(10)	94·96 (8)
Co—N(10)—C(4)	117·7 (2)	N(11)—Co—N(10)	94·16 (9)
N(5)—C(5)—C(6)	122·2 (2)	N(12)—Co—N(10)	171·00 (8)
N(6)—C(6)—C(5)	122·8 (2)	N(1)—C(1)—N(7)	126·4 (2)
Co—N(11)—O(5)	128·3 (2)	N(2)—C(2)—N(8)	126·0 (2)
Co—N(12)—O(6)	128·0 (2)	O(1)—N(7)—Co	126·1 (1)
N(7)—O(1)—H(1)	109 (3)	O(2)—N(8)—C(2)	113·4 (2)
N(11)—O(5)—H(5)	110 (3)	N(9)—C(3)—N(3)	126·8 (3)
N(9)—Co—N(11)	93·21 (9)	N(4)—C(4)—N(10)	126·6 (3)
N(9)—Co—N(10)	79·76 (10)	C(3)—N(9)—O(3)	114·1 (2)
N(8)—Co—N(12)	91·63 (9)	C(4)—N(10)—O(4)	113·6 (2)
N(11)—Co—N(12)	80·02 (8)	C(6)—C(5)—N(11)	112·3 (2)
N(7)—Co—N(10)	93·92 (10)	C(5)—C(6)—N(12)	111·8 (2)
C(2)—C(1)—N(7)	111·1 (2)	O(5)—N(11)—C(5)	113·5 (2)
C(1)—C(2)—N(8)	111·9 (2)	O(6)—N(12)—C(6)	112·7 (2)
C(1)—N(7)—Co	118·3 (2)	N(12)—O(6)—H(6)	101 (3)
Co—N(8)—C(2)	116·8 (2)	N(10)—O(4)—H(4)	102 (4)
C(4)—C(3)—N(3)	122·0 (2)		

within the chelate rings of (III) are in agreement with those in (II). The C—N(amino) bond distances in (III) are distinctly shorter than in (II). This could be partly explained by the interaction of two of the amino N atoms with the Co atoms of the adjacent molecules causing a chain-like structure in (II). In any case the delocalization seems to be stronger in (III) than in (II). The three five-membered rings are planar, the amino N atoms being in the planes, within the standard deviations. Two of the angles between the plane normals of the three chelate rings are close to 90° but one deviates considerably, being only 80°. This might be because of intramolecular hydrogen bonding, this view being supported by some O–O distances [Table 4; O(3)–O(6), O(1)–O(4), O(2)–O(3) and O(1)–O(5)]. They fit well within the range given in the literature (Wells, 1975) for O—H—O interactions (2·40–2·90 Å).

Unsymmetric hydrogen bridges to the Cl⁻ anions are also indicated by some relatively short O–Cl distances [Table 4; Cl(1)–O(3), Cl(1)–O(4), Cl(2)–O(1) and Cl(3)–O(2)]; the range for O–H–Cl interactions has been found to be within 2·92–3·04 Å (Wells, 1975).

The amino N atoms are certainly sp^2 hybridized; this is established by the sum of the bond angles at these N atoms, ranging from 356–360°.

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