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The Crystal and Molecular Structure of Bisanilinebis(dimethylglyoximato)cobalt(III) Chloride

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Crystals of the title compound, [Co(Hdmg)$_2$(aniline)$_2$]Cl (Hdmg is the dimethylglyoximato mono-anion), are monoclinic, space group $C2/c$ with $a=27·44$ (1), $b=6·32$ (1), $c=17·72$ (1) Å; $\beta=129·7$ (1)° and $Z=4$. The structure has been solved by Patterson and Fourier methods and refined by block-diagonal least squares (final $R=4·3$ %). The nitrogen atoms of two aniline molecules coordinate to cobalt in an octahedral axial position with respect to the plane of the chelate dimethylglyoximatocobalt(III) system. The approach distance of the aniline nitrogen to metal is significantly greater (2·001 Å) than those involving the dimethylglyoximato nitrogen atoms in the chelation plane (1·889, 1·885 Å). Packing is mainly due to the following hydrogen bonds O(1)···O(2) $(\bar{x},\bar{y},\bar{z})=2·49$ Å; N(1)···O(2) $(\bar{x},1-y,\bar{z})=2·92$ Å, N(1)···Cl = 3·19 Å.

Introduction

The crystal structure analysis of the title compound has been carried-out as part of a study of mixed ligand complexes formed by molecules containing nitrogen as donor atoms. In particular it was considered interesting to see how the aniline ligands influence the planar chelating system which the dimethylglyoxime forms in coordinating to cobalt.

Experimental

[Co(Hdmg)$_2$(aniline)$_2$]Cl, prepared following Masuda, Sakano & Shinra (1969), occurs as orange monoclinic crystals which show dichroic effects. When the crystals are examined with plane-polarized light, looking down the *a* and *c* axes, the colour ranges from orange to yellow when the electric vector vibrates perpendicular or parallel to the elongation, [010], respectively.

Crystal data, determined from rotation and Weissenberg photographs and from diffractometer measurements (Zr-filtered Mo $K\alpha$ radiation, $\lambda=0·71069$ Å), are as follows:

[Co(Hdmg)$_2$(C$_6$H$_5$NH$_2$)$_2$]Cl, $M=511$, $a=27·44$ (1), $b=6·32$ (1), $c=17·72$ (1) Å; $\beta=129·7$ (1)°; $V=2366$ Å^3; $Z=4$, $D_m=1·42$, $D_c=1·43$ g cm^{-3}; $F(000)=1064$, $\mu=9·1$ cm^{-1}. Space group: $C2/c$ (from systematic absences and structural analysis). Intensity data were collected on an on-line Siemens AED single-crystal diffractometer using the $\omega/2\theta$-scan technique and Mo $K\alpha$ radiation. 2844 independent reflexions were measured, of which only 1829 with $I>2\sigma(I)$ were used in the analysis. The sample was a small prism with a mean radius of 0·06 mm, so the μr value (0·05) was small enough to disregard any correction for absorption. After the usual data reduction, the intensities were put on absolute scale first by Wilson's (1942) method and later by correlation of observed and calculated values.

Structure analysis and refinement

The structure was solved by the heavy-atom technique, starting from a three-dimensional Patterson synthesis which showed that cobalt was on a symmetry centre and chlorine on a twofold axis. All the other non-hydrogen atoms were located in successive Fourier synthesis. At this point isotropic least-squares refinement was started, minimizing the function $\sum w|\Delta F|^2$ with unit weights, and the conventional R index decreased to 0·083; the subsequent anisotropic refinement improved it to 0·059. A final three-dimensional ΔF syntheses resolved all the hydrogen atoms, which were refined isotropically. The final R index is 0·043. The final atomic coordinates and thermal parameters are given in Tables 1 and 2. The atomic scattering factors used throughout all the calculations were those of Cromer & Mann (1968) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms.

All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, using programs written by Immirzi (1967).*

Description of the structure and discussion

The structure consists of bisanilinebis(dimethylglyoximato)Co(III) cations and chlorine anions which are not involved in coordination to metal. Fig. 1 shows a clinographic projection of the structure. Coordination around cobalt is octahedral and involves the nitrogen

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* Structure factor tables are available from the authors on request, and have also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30329 (13 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

atoms and two dimethylglyoximato ions which coordinate to metal in a plane and the nitrogen atoms of two aniline molecules in axial position with respect to the chelation plane.

Bond distances and angles are given in Table 3. The distance of the aniline nitrogen to metal (2·001 Å) is significantly greater than those involving the dimethylglyoximato nitrogens in the chelation plane (1·885, 1·889 Å). These last distances which agree with those found in other planar cobalt(III) complexes {*e.g.* 1·881 and 1·889 Å in benzoylacetonato-[*N*,*N*′-ethylenebis(salycilideneiminato)]Co(III). 1·5H_2O (Bailey, Higson & McKenzie, 1972); 1·89 and 1·90 Å in [*N*,*N*′-ethylenebis(salycilideneiminato)]acetylacetonatocobalt(III). 0·7 H_2O (Calligaris, Manzini, Nardin & Randaccio, 1972); 1·88 and 1·87 Å in *N*,*N*′-ethylenebis(acetylacetoneiminato)methylcobalt(III) (Brückner, Calligaris, Nardin & Randaccio, 1969)} can be explained by some π-delocalization along the metal and the chelate system. No effect of this kind is of course present in the axial direction and the distance Co–N(aniline) is consequently longer. The dimethylglyoxime molecule is planar; the largest displacement from the mean plane O(1)N(2)C(7)C(8)C(9)C(10)N(3)O(2) being −0·02 Å for N(3) and C(10). The Co–N(aniline) bond is a little tilted (86·8°) with respect to the chelation plane and the orientation of the aniline molecule is determined by the tetrahedral character of N(1) and by the hydrogen bonds this atom forms with Cl [N(1)–H(1)···Cl = 3·19 ± 0·01 Å; N(1)H(1)Cl = 169°] and O(2^{ii})* [N(1)–H(2)

Table 2. *Final fractional coordinates* (× 10^3) *and thermal parameters* (× 10 $Å^2$) *for hydrogen atoms, with estimated standard deviations in parentheses*

	x/a	*y/b*	*z/c*	*B*
H(1)	26 (2)	116 (8)	161 (4)	22 (11)
H(2)	42 (2)	283 (9)	117 (4)	26 (12)
H(3)	145 (3)	364 (10)	165 (4)	39 (14)
H(4)	253 (3)	306 (11)	289 (5)	45 (16)
H(5)	281 (3)	16 (11)	389 (4)	42 (14)
H(6)	216 (3)	−203 (10)	391 (4)	40 (15)
H(7)	110 (3)	−111 (10)	262 (4)	36 (14)
H(8)	74 (3)	−301 (10)	90 (4)	45 (15)
H(9)	138 (3)	−75 (10)	−51 (4)	42 (15)
H(10)	168 (3)	104 (11)	−8 (5)	48 (16)
H(11)	176 (3)	−50 (10)	37 (4)	40 (15)
H(12)	99 (3)	473 (11)	−76 (4)	46 (15)
H(13)	64 (3)	338 (10)	−156 (4)	41 (15)
H(14)	25 (2)	484 (11)	−154 (4)	37 (13)

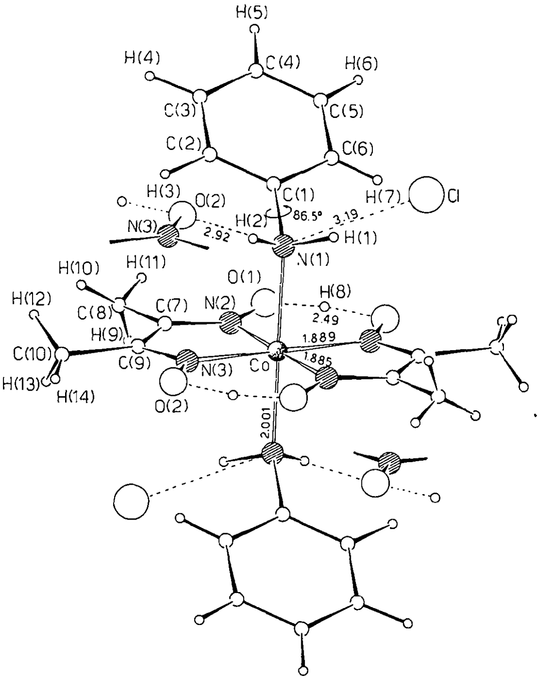

Fig. 1. Clinographic projection of the structure.

Table 1. *Final fractional coordinates* (× 10^4) *and thermal parameters* (× $10^2Å^2$) *for non-hydrogen atoms, with estimated standard deviations in parentheses*

The anisotropic temperature factors are expressed in the form:

$$\exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*\cos\gamma^*+2B_{13}hla^*c^*\cos\beta^*+2B_{23}klb^*c\cos\alpha^*)\right].$$

	x/a	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0 (0)	0 (0)	0 (0)	148 (3)	117 (3)	147 (3)	16 (4)	93 (2)	15 (4)
Cl(1)	0 (0)	830 (4)	2500 (0)	350 (9)	302 (8)	280 (8)	–	235 (7)	–
O(1)	1089 (2)	−2447 (6)	685 (3)	282 (16)	237 (16)	310 (18)	99 (13)	189 (15)	68 (14)
O(2)	−402 (2)	3873 (6)	−1029 (3)	275 (16)	157 (15)	296 (17)	48 (12)	182 (14)	58 (13)
N(1)	473 (2)	1546 (7)	1276 (3)	206 (16)	162 (16)	181 (16)	12 (13)	115 (14)	1 (14)
N(2)	746 (2)	−681 (7)	206 (3)	210 (16)	177 (16)	180 (16)	20 (13)	107 (14)	2 (13)
N(3)	40 (2)	2367 (7)	−609 (3)	209 (16)	159 (15)	169 (16)	8 (13)	110 (14)	13 (14)
C(1)	1148 (2)	1192 (8)	2032 (4)	219 (20)	224 (22)	189 (20)	−9 (16)	129 (17)	−30 (17)
C(2)	1579 (3)	2477 (10)	2097 (4)	264 (23)	277 (24)	280 (24)	−27 (20)	152 (20)	−4 (21)
C(3)	2224 (3)	2096 (12)	2823 (5)	273 (25)	445 (34)	366 (30)	−81 (24)	170 (23)	−43 (27)
C(4)	2427 (3)	467 (12)	3463 (5)	256 (23)	478 (40)	303 (26)	37 (23)	119 (21)	4 (25)
C(5)	1997 (3)	−808 (11)	3394 (5)	301 (26)	436 (32)	284 (26)	89 (24)	158 (22)	88 (25)
C(6)	1352 (3)	−458 (9)	2672 (4)	273 (22)	285 (28)	254 (23)	32 (18)	152 (19)	41 (19)
C(7)	927 (2)	590 (8)	−139 (4)	220 (20)	219 (21)	195 (20)	−16 (15)	130 (17)	15 (16)
C(8)	1493 (3)	279 (11)	−61 (5)	271 (22)	384 (33)	418 (29)	30 (23)	244 (22)	42 (26)
C(9)	505 (3)	2413 (8)	−632 (4)	241 (20)	181 (20)	193 (20)	−44 (16)	134 (17)	34 (16)
C(10)	599 (3)	4083 (10)	−1110 (5)	393 (28)	276 (25)	335 (27)	−59 (22)	268 (24)	10 (22)

Table 3. *Bond distances and angles*

(*a*) Coordination polyhedron

Co—N(1)	2·001 (5) Å	N(1)—Co—N(2)	93·0 (0·5)°
Co—N(2)	1·885 (6)	N(1)—Co—N(3)	91·5 (0·4)
Co—N(3)	1·889 (5)	N(2)—Co—N(3)	80·8 (0·3)

(*b*) Aniline molecule

N(1)–C(1)	1·451 (7) Å	Co—N(1)–C(1)	119·5 (0·7)°
C(1)–C(2)	1·377 (11)	N(1)—C(1)–C(2)	120·5 (1·1)
C(2)–C(3)	1·392 (8)	N(1)—C(1)–C(6)	119·2 (0·9)
C(3)–C(4)	1·360 (11)	C(2)—C(1)–C(6)	120·3 (1·3)
C(4)–C(5)	1·368 (12)	C(1)—C(2)–C(3)	119·5 (1·3)
C(5)–C(6)	1·388 (8)	C(2)—C(3)–C(4)	120·2 (1·2)
C(6)–C(1)	1·370 (8)	C(3)—C(4)–C(5)	120·1 (1·6)
		C(4)—C(5)–C(6)	120·5 (1·4)
		C(1)—C(6)–C(5)	119·4 (1·1)

(*c*) Dimethylglyoxime molecule

O(1)–N(2)	1·353 (6) Å	O(1)—N(2)–Co	122·9 (0·7)°
N(2)–C(7)	1·286 (10)	O(1)—N(2)–C(7)	119·2 (1·0)
C(7)–C(8)	1·482 (12)	C(7)—N(2)–Co	117·8 (0·9)
C(7)–C(9)	1·463 (7)	N(2)—C(7)–C(8)	125·0 (1·6)
C(9)–C(10)	1·476 (11)	N(2)—C(7)–C(9)	112·2 (0·9)
C(9)–N(3)	1·303 (10)	C(8)—C(7)–C(9)	122·9 (1·3)
N(3)–O(2)	1·333 (6)	C(7)—C(9)–C(10)	123·0 (1·2)
		C(7)—C(9)–N(3)	112·4 (1·0)
		C(10)–C(9)–N(3)	124·6 (1·6)
		C(9)—N(3)–O(2)	121·8 (1·2)
		O(2)—N(3)–Co	121·4 (0·6)
		C(9)—N(3)–Co	116·8 (0·9)

(*d*) Involving the hydrogen atoms

N(1)—H(1)	1·09 Å	C(1)—N(1)—H(1)	106 (7)°
N(1)—H(2)	0·82	C(1)—N(1)—H(2)	108 (6)
C(2)—H(3)	0·97	C(1)—C(2)—H(3)	122 (10)
C(3)—H(4)	0·98	C(3)—C(2)—H(3)	119 (7)
C(4)—H(5)	0·98	C(2)—C(3)—H(4)	119 (10)
C(5)—H(6)	1·06	C(4)—C(3)—H(4)	121 (11)
C(6)—H(7)	1·02	C(3)—C(4)—H(5)	126 (8)
C(8)—H(9)	0·91	C(5)—C(4)—H(5)	113 (7)
C(8)—H(10)	0·89	C(4)—C(5)—H(6)	120 (9)
C(8)—H(11)	0·80	C(6)—C(5)—H(6)	120 (7)
C(10)–H(12)	0·92	C(5)—C(6)—H(7)	119 (10)
C(10)–H(13)	0·98	C(1)—C(6)—H(7)	121 (11)
C(10)–H(14)	0·89	C(7)—C(8)—H(9)	104 (9)
		H(10)–C(8)—H(9)	116 (15)
		H(9)—C(8)—H(11)	90 (11)
		H(10)–C(8)—H(11)	110 (16)
		C(7)—C(8)—H(10)	118 (11)
		C(7)—C(8)—H(11)	114 (9)
		C(9)—C(10)–H(12)	119 (9)
		C(9)—C(10)–H(13)	107 (9)
		C(9)—C(10)–H(14)	113 (9)
		H(12)–C(10)–H(13)	93 (10)

···O(2$^{\mathrm{ii}}$) = 2·91 ± 0·06 Å; N(1)H(2)O(2$^{\mathrm{ii}}$) = 167°]. The internal rotation angle around N(1)–C(1), *i.e.* the dihedral angle C(1)C(2)C(3)C(4)C(6)$\wedge$C(1)N(1)Co is 86·5°. The structural function of the chlorine ions is to connect adjacent cations through hydrogen bonds involving the aniline nitrogen. The structure of the chelate system is similar to that found in other glyoxime complexes with a short hydrogen bond [O(1)···H(8)···O(2$^{\mathrm{i}}$)* = 2·491 ± 0·008 Å] in which the hydrogen atom is in the middle of the line joining the two oxygens (Chiesi Villa, Gaetani Manfredotti & Guastini, 1973; Bowers, Banks & Jacobson, 1972; Murmann & Schlemper, 1967; Calleri, Ferraris & Viterbo, 1967; Godycki & Rundle, 1953).

Packing is determined by the previously mentioned hydrogen bonds and by the van der Waals contacts listed in Table 4.

Table 4. *The most significant van der Waals contacts*

N(1)–O(1$^{\mathrm{i}}$)	3·43 (1)
N(1)–N(2$^{\mathrm{i}}$)	2·68 (1)
N(1)–N(3)	2·79 (1)
O(1)–N(3$^{\mathrm{i}}$)	3·01 (1)
O(2)–O(2$^{\mathrm{ii}}$)	3·15 (1)
N(3)–O(2$^{\mathrm{ii}}$)	3·37 (7)

(i)	$\bar{x}$	$\bar{y}$	$\bar{z}$
(ii)	$\bar{x}$	$1-y$	$\bar{z}$

Bond distances and angles involving hydrogen atoms are in the range usually found.

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* (i) $\bar{x},\bar{y},\bar{z}$. (ii) $\bar{x},1-y,\bar{z}$.

References

Bailey, N. A., Higson, B. M. & McKenzie, E. D. (1972). *J. Chem. Soc. Dalton*, pp. 503–508.

Bowers, R. H., Banks, C. V. & Jacobson, R. A. (1972). *Acta Cryst.* B**28**, 2318–2322.

Brückner, S., Calligaris, M., Nardin, G. & Randaccio, L. (1970). *J. Chem. Soc.* pp. 152–153.

Calleri, M., Ferraris, G. & Viterbo, D. (1967). *Acta Cryst.* **22**, 468–475.

Calligaris, M., Manzini, G., Nardin, G. & Randaccio, L. (1972). *J. Chem. Soc. Dalton*, pp. 543–547.

Chiesi Villa, A., Gaetani Manfredotti, A. & Guastini, C. (1973). *Cryst. Struct. Commun.* **2**, 129–132.

Cromer, D. T. & Mann, G. B. (1968). *Acta Cryst.* A**24**, 321–324.

Godycki, L. E. & Rundle, R. E. (1953). *Acta Cryst.* **6**, 487–495.

Immirzi, A. (1967). *Ric. Sci.* **34**, 743–749.

Masuda, J., Sakano, M. & Shinra, K. (1969). *Bull. Chem. Soc. Japan*, **42**, 2296–2300.

Murmann, R. K. & Schlemper, E. O. (1967). *Acta Cryst.* **23**, 667–669.

Stewart, R. I., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.