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Structure of Bis(aniline)bis(hexylmethylglyoximato)cobalt(III) Chloride and Bis(aniline)bis(methyloctylglyoximato)cobalt(III) Chloride

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Abstract. (I): $[Co(C_9H_{17}N_2O_2)_2(C_6H_7N)_2]Cl$, M_r = 651·1, triclinic, $P\bar{1}$, a = 8·972 (2), b = 15·097 (4), c = 6·390 (4) Å, α = 81·62 (3), β = 99·12 (3), γ = 103·18 (2)°, V = 826·7 (6) Å^3, Z = 1, D_m = 1·31, D_x = 1·31 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 6·39 cm^{-1}, F(000) = 172, T = 294 (1) K, R_F = 0·051 for 3473 observed unique reflections. (II): $[Co(C_{11}H_{21}N_2O_2)_2(C_6H_7N)_2]Cl$, M_r = 707·2, triclinic, $P\bar{1}$, a = 8·995 (2), b = 17·291 (3), c = 6·346 (1) Å, α = 100·01 (1), β = 98·49 (1), γ = 95·98 (2)°, V = 952·7 (3) Å^3, Z = 1, D_m = 1·21, D_x = 1·23 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 5·59 cm^{-1}, F(000) = 188, T = 294 (1) K, R_F = 0·050 for 2908 observed unique reflections. In both (I) and (II), a cobalt(II) ion is octahedrally coordinated by four N atoms from two glyoximato ligands [Co—N = 1·894 (3)(× 2) and 1·904 (3)(× 2) Å for (I), and 1·885 (3)(× 2) and 1·913 (3)(× 2) Å for (II)], and by two N atoms from two aniline molecules [Co—N = 2·011 (3)(× 2) Å for (I) and 2·016 (3)(× 2) Å for (II)]. A possible hydrogen bond is found between the chloride ion and an aniline N atom with a Cl···N distance of 3·172 (3) Å for (I) and 3·176 (3) Å for (II).

Introduction. Bis(dioximato)cobalt(III) complexes have been investigated extensively in the last decade, since they are regarded as models for biochemically important complexes and are useful in catalytic reactions and template syntheses (Bresciani-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985). The dynamic structural analysis of crystalline-state racemization has also been reported (Ohashi, 1988). We have studied the molecular structure and dynamic properties of several bis(dioximato)cobalt(III) complexes in the solid state and in solution with ^{1}H and ^{13}C NMR spectroscopy (Kinoshita & Masuda, 1985; Kinoshita, Wakita & Masuda, 1986). As part of these investigations, we have synthesized the title compounds (I) and (II). In the series of bis(aniline)bis(2,3-R-methylglyoximato)cobalt(III) (R = n-C_nH_{2n+1}) complexes, only $[Co(dmgH)_2(C_6H_5NH_2)_2]Cl$ (dmgH is the dimethyglyoximato monoanion) has been determined (Battaglia, Corradi, Palmieri, Nardelli & Tani, 1974). In the present paper the structures of the title compounds [(I) and (II)] are reported and compared with that of the previously reported $[Co(dmgH)_2(C_6H_5NH_2)_2]Cl$.

Experimental. Title compounds (I) and (II) were synthesized in the following manner. A hot ethanol solution (95%, 100 ml), in which $CoCl_2.6H_2O$ (2·38 g, 0·01 mol) had been dissolved, was added to aniline (3·73 g, 0·04 mol). A hot ethanol solution (95%, 300 ml) containing hexylmethylglyoxime (3·72 g, 0·02 mol) or methyloctylglyoxime (4·28 g, 0·02 mol) was then added to the solution. The compound formed was oxidized by bubbling air for several hours. The precipitated yellow crystals were filtered and then washed with acetone. Single crystals were obtained by slow evaporation of a solution of the complex in a mixture of methanol and ethanol. D_m was measured by flotation in chloroform/ethanol.

Experimental details are as follows. Values for (II) are the same as those for (I) unless given in parentheses. Yellow rectangular crystals; 0·10 × 0·15 × 0·20 mm (0·10 × 0·20 × 0·25 mm); Rigaku AFC-5R diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; ω–2θ scan. No systematic absences for (I) and (II) indicated the Laue symmetry $\bar{1}$ and the possible space group $P1$ or $P\bar{1}$. The correct space group $P\bar{1}$ was confirmed from subsequent calculations. Cell parameters from setting angles of 25 reflections with $8 \le 2\theta \le 30°$; data corrected for Lorentz and polarization effects, but no absorption correction was made. The intensities of three standard reflections did not show any systematic variation during the data collection; 9009 (4992) unique reflections were measured with $2 \le 2\theta \le 70°$ ($2 \le 2\theta \le 50°$); 3473 (2908) with $|F_o|/\sigma(|F|) > 3·0$ used in refinement. Data collected: $\pm h$, $\pm k$, l; h 0–14 (0–10), k 0–27 (0–20), l 0–10 (0–7). Structure solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Non-H atoms refined with anisotropic thermal parameters and all H atoms, located from subsequent difference syntheses, refined isotropically

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Table 1. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses, for* (I)

$\langle U^2\rangle = \frac{1}{3}(1/2\pi^2)\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	$\langle U^2\rangle \times 10^2$
Co	0·0000	0·0000	0·0000	2·23 (3)
Cl	0·5000	0·0000	0·0000	4·23 (6)
O(1)	0·1045 (3)	0·9410 (2)	0·4301 (3)	3·6 (1)
O(2)	0·1341 (3)	0·1574 (2)	0·7312 (3)	4·0 (1)
N(1)	0·1375 (3)	0·9324 (2)	0·8955 (4)	2·8 (1)
N(2)	0·1315 (3)	0·0047 (2)	0·2649 (4)	2·9 (1)
N(3)	0·1450 (3)	0·1086 (2)	0·9281 (4)	2·9 (1)
C(1)	0·1263 (4)	0·8359 (2)	0·9634 (5)	3·3 (1)
C(2)	0·2076 (5)	0·8090 (3)	0·1564 (6)	4·7 (1)
C(3)	0·1944 (6)	0·7161 (3)	0·2235 (8)	6·6 (3)
C(4)	0·1029 (6)	0·6515 (3)	0·1013 (10)	7·1 (3)
C(5)	0·0233 (6)	0·6791 (3)	0·9111 (10)	6·8 (3)
C(6)	0·0335 (4)	0·7714 (3)	0·8371 (7)	4·9 (2)
C(7)	0·2526 (3)	0·0712 (2)	0·2713 (5)	3·2 (1)
C(8)	0·3712 (4)	0·0818 (3)	0·4620 (6)	4·4 (2)
C(9)	0·2615 (4)	0·1324 (2)	0·0710 (5)	3·2 (2)
C(10)	0·3952 (4)	0·2105 (3)	0·0362 (6)	4·2 (2)
C(11)	0·4048 (5)	0·2906 (3)	0·1618 (8)	5·0 (2)
C(12)	0·5607 (5)	0·3574 (3)	0·1527 (9)	5·8 (2)
C(13)	0·5832 (5)	0·4354 (3)	0·2857 (9)	5·9 (3)
C(14)	0·7397 (7)	0·5005 (4)	0·2749 (12)	7·7 (3)
C(15)	0·7641 (10)	0·5786 (6)	0·4088 (15)	10·4 (5)

Table 2. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses, for* (II)

	x	y	z	$\langle U^2\rangle \times 10^2$
Co	0·0000	0·0000	0·0000	2·71 (4)
Cl	0·5000	0·0000	0·0000	4·78 (8)
O(1)	0·1139 (3)	−0·0502 (2)	0·3878 (4)	4·2 (1)
O(2)	0·1104 (3)	0·1363 (2)	−0·1599 (4)	4·9 (2)
N(1)	−0·1478 (3)	0·0583 (2)	0·1544 (4)	3·1 (2)
N(2)	0·1324 (3)	0·0058 (2)	0·2691 (4)	3·3 (2)
N(3)	0·1286 (3)	0·0937 (2)	0·0033 (4)	3·4 (2)
C(1)	−0·1477 (4)	0·1416 (2)	0·1582 (6)	3·9 (2)
C(2)	−0·2311 (6)	0·1663 (3)	−0·0150 (8)	5·5 (3)
C(3)	−0·2298 (8)	0·2462 (4)	−0·0110 (10)	8·1 (4)
C(4)	−0·1490 (8)	0·3022 (3)	0·1610 (12)	8·5 (4)
C(5)	−0·0687 (8)	0·2761 (4)	0·3299 (12)	7·8 (4)
C(6)	−0·0670 (6)	0·1971 (3)	0·3309 (8)	5·2 (3)
C(7)	0·2421 (4)	0·0620 (2)	0·3192 (5)	3·4 (2)
C(8)	0·3619 (5)	0·0716 (3)	0·5164 (7)	5·1 (3)
C(9)	0·2428 (4)	0·1161 (2)	0·1618 (6)	3·7 (2)
C(10)	0·3624 (6)	0·1837 (3)	0·1820 (8)	5·0 (3)
C(11)	0·3603 (6)	0·2525 (3)	0·3680 (10)	6·5 (3)
C(12)	0·5056 (7)	0·3105 (4)	0·4089 (11)	7·4 (4)
C(13)	0·5179 (7)	0·3765 (4)	0·6041 (11)	7·6 (4)
C(14)	0·6633 (8)	0·4334 (4)	0·6444 (12)	8·9 (4)
C(15)	0·6793 (9)	0·4983 (4)	0·8458 (12)	9·5 (5)
C(16)	0·8173 (10)	0·5565 (5)	0·8810 (14)	11·2 (6)
C(17)	0·8309 (14)	0·6205 (7)	1·0850 (16)	16·2 (8)

(*LINEX*; Tanaka, 1978). $\sum w(|F_o| - |F_c|)^2$ was minimized. $w^{-1} = \sigma^2(|F_o|) + (0{\cdot}005|F_o|)^2$. Final $R = 0{\cdot}051$ (0·050), $wR = 0{\cdot}054$ (0·055), $S = 0{\cdot}859$ (0·966), $(\Delta/\sigma)_{\max} = 0{\cdot}28$ (0·28), $-0{\cdot}18$ $(-0{\cdot}57) < \Delta\rho < 0{\cdot}27$ (0·58) e Å^{-3}. Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Program package *RASA-5P* (Rigaku, 1984) was used on a PANAFACOM U-1500II computer, *LINEX* and *ORTEP*II (Johnson, 1976) on a FACOM M-780/10S computer of this university.

Final atomic parameters for non-H atoms are given in Tables 1 and 2[*] for compounds (I) and (II), respectively.

Discussion. Stereoscopic views of the Co-containing moiety in (I) and (II), with atomic labels, are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are given in Tables 3 and 4.

A cobalt(III) ion is surrounded by four N atoms from two glyoximato ligands and two N atoms from two aniline molecules in axial sites to form an octahedral structure. The Co—N bond lengths and N—Co—N angles in the present complexes are not significantly different from those in $[Co(dmgH)_2(C_6H_5NH_2)_2]Cl$ (Battaglia, Corradi, Palmieri, Nardelli & Tani, 1974). Thus, the coordination geometry of a glyoximato ligand around a Co^{III} ion is not affected by the length of alkyl substituents of the ligand. A similar bis(glyoximato)cobalt(III) moiety has also been found for $[Co(dmgH)_2(NH_3)_2]NO_3$ (Elder, Nerone & Barrick, 1980) and $[Co(dmgH)_2$(4-cyanopyridine)$Cl].\frac{1}{3}H_2O$ (López, Alvarez, Solans & Font-Altaba, 1986).

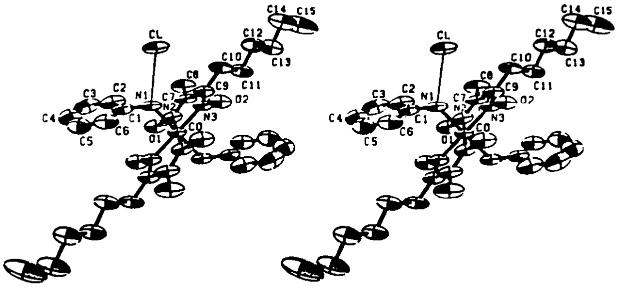

Fig. 1. Stereoscopic view (*ORTEP*II; Johnson, 1976) of the structure of (I).

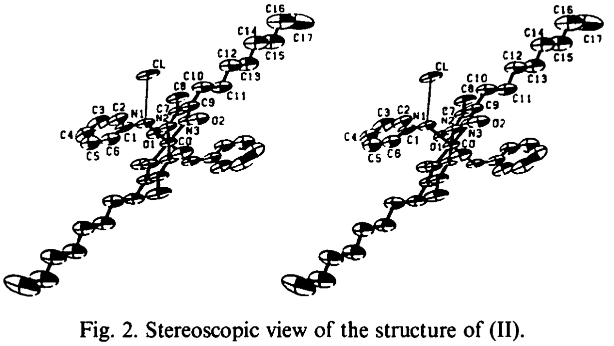

Fig. 2. Stereoscopic view of the structure of (II).

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52189 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond lengths* (Å) *and angles* (°) *for* (I)

(*a*) Coordination polyhedron			
Co—N(1)	2·011 (3)	N(1)—Co—N(2)	89·4 (1)
Co—N(2)	1·904 (3)	N(1)—Co—N(3)	86·8 (1)
Co—N(3)	1·894 (3)	N(2)—Co—N(3)	81·3 (1)
(*b*) Aniline molecule			
N(1)—C(1)	1·444 (4)	Co—N(1)—C(1)	119·8 (2)
C(1)—C(2)	1·386 (5)	N(1)—C(1)—C(2)	119·0 (3)
C(2)—C(3)	1·388 (6)	N(1)—C(1)—C(6)	120·0 (3)
C(3)—C(4)	1·375 (7)	C(2)—C(1)—C(6)	121·0 (3)
C(4)—C(5)	1·368 (8)	C(1)—C(2)—C(3)	118·9 (4)
C(5)—C(6)	1·392 (6)	C(2)—C(3)—C(4)	120·9 (5)
C(6)—C(1)	1·392 (5)	C(3)—C(4)—C(5)	119·5 (5)
		C(4)—C(5)—C(6)	121·6 (5)
		C(1)—C(6)—C(5)	118·1 (4)
(*c*) Hexylmethylglyoxime molecule			
N(2)—O(1)	1·333 (3)	Co—N(2)—O(1)	121·8 (2)
N(2)—C(7)	1·300 (4)	Co—N(2)—C(7)	115·9 (2)
C(7)—C(8)	1·488 (5)	O(1)—N(2)—C(7)	122·2 (3)
C(7)—C(9)	1·467 (4)	N(2)—C(7)—C(8)	122·7 (3)
C(9)—N(3)	1·296 (4)	N(2)—C(7)—C(9)	113·3 (3)
N(3)—O(2)	1·364 (3)	C(8)—C(7)—C(9)	124·0 (3)
C(9)—C(10)	1·497 (5)	C(7)—C(9)—C(10)	122·9 (3)
C(10)—C(11)	1·526 (6)	C(7)—C(9)—N(3)	112·4 (3)
C(11)—C(12)	1·530 (6)	C(10)—C(9)—N(3)	124·7 (3)
C(12)—C(13)	1·510 (7)	C(9)—N(3)—O(2)	120·6 (3)
C(13)—C(14)	1·525 (8)	O(2)—N(3)—Co	122·3 (2)
C(14)—C(15)	1·513 (11)	C(9)—N(3)—Co	117·0 (2)
		C(9)—C(10)—C(11)	114·5 (3)
		C(10)—C(11)—C(12)	110·5 (4)
		C(11)—C(12)—C(13)	113·7 (4)
		C(12)—C(13)—C(14)	112·6 (4)
		C(13)—C(14)—C(15)	113·0 (6)

Table 4. *Selected bond lengths* (Å) *and angles* (°) *for* (II)

(*a*) Coordination polyhedron			
Co—N(1)	2·016 (3)	N(1)—Co—N(2)	88·9 (1)
Co—N(2)	1·913 (3)	N(1)—Co—N(3)	86·6 (1)
Co—N(3)	1·885 (3)	N(2)—Co—N(3)	80·6 (1)
(*b*) Aniline molecule			
N(1)—C(1)	1·437 (5)	Co—N(1)—C(1)	119·5 (2)
C(1)—C(2)	1·393 (6)	N(1)—C(1)—C(2)	119·2 (4)
C(2)—C(3)	1·375 (8)	N(1)—C(1)—C(6)	121·0 (4)
C(3)—C(4)	1·382 (9)	C(2)—C(1)—C(6)	119·8 (4)
C(4)—C(5)	1·371 (10)	C(1)—C(2)—C(3)	119·0 (5)
C(5)—C(6)	1·369 (8)	C(2)—C(3)—C(4)	121·6 (6)
C(6)—C(1)	1·380 (6)	C(3)—C(4)—C(5)	118·2 (6)
		C(4)—C(5)—C(6)	121·8 (6)
		C(1)—C(6)—C(5)	119·7 (5)
(*c*) Methyloctylglyoxime molecule			
N(2)—O(1)	1·339 (4)	Co—N(2)—O(1)	120·4 (2)
N(2)—C(7)	1·272 (5)	Co—N(2)—C(7)	116·5 (3)
C(7)—C(8)	1·499 (6)	O(1)—N(2)—C(7)	122·9 (3)
C(7)—C(9)	1·482 (5)	N(2)—C(7)—C(8)	123·2 (4)
C(9)—N(3)	1·302 (5)	N(2)—C(7)—C(9)	113·8 (3)
N(3)—O(2)	1·372 (4)	C(8)—C(7)—C(9)	123·0 (4)
C(9)—C(10)	1·479 (6)	C(7)—C(9)—C(10)	123·4 (3)
C(10)—C(11)	1·527 (8)	C(7)—C(9)—N(3)	110·7 (3)
C(11)—C(12)	1·522 (8)	C(10)—C(9)—N(3)	125·8 (4)
C(12)—C(13)	1·515 (9)	C(9)—N(3)—O(2)	119·3 (3)
C(13)—C(14)	1·513 (10)	O(2)—N(3)—Co	122·4 (2)
C(14)—C(15)	1·525 (10)	C(9)—N(3)—Co	118·2 (3)
		C(9)—C(10)—C(11)	114·5 (4)
		C(10)—C(11)—C(12)	110·8 (5)
		C(11)—C(12)—C(13)	113·9 (5)
		C(12)—C(13)—C(14)	113·5 (6)
		C(13)—C(14)—C(15)	113·8 (6)

The Co—N(aniline) distances (2·011, 2·016 Å) found in (I) and (II) are considerably longer than the Co—N(NH_3) length (1·951 Å) in $[Co(dmgH)_2(NH_3)_2]NO_3$ and the Co—N(4-cyanopyridine) distance (1·95–1·97 Å) in $[Co(dmgH)_2$(4-cyanopyridine)Cl].$\frac{1}{3}H_2O$. This lengthening of the Co—N distance may reflect the basicity of the N atom of the ligands in the axial positions (the acid dissociation constant, pK_a, is 9·24 for NH_4^+ and 4·65 for aniline); the small electron donating power of the N atom of the axial ligand leads to the weak Co—N bond, resulting in the long Co—N bond length. The N(1)—C(1) distance within the coordinated aniline molecules lengthens by 0·06 Å from the mean N—C value (1·382 Å) in a free aniline molecule (Fukuyo, Hirotsu & Higuchi, 1982).

As seen in Tables 1 and 2, the isotropic thermal parameters of the C atoms in the hexyl and octyl groups of the glyoximato ligand increased with increasing distance of each C atom from the C(9) atom of the glyoximato ligand. This suggests a segmental motion of the alkyl substituent around the C(9) atom.

A hydrogen bond possibly forms between a Cl atom and the N(1) atom of an aniline molecule with the Cl—N(1) distance 3·172 (3) Å for (I) and 3·176 (3) Å for (II) (see Figs. 1 and 2). Such a hydrogen bond has been found in $[Co(dmgH)_2(C_6H_5NH_2)_2]Cl$ (3·19 Å).

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