Acta Cryst. (1992). C48, 1122–1124

Structure of (Aniline)(chloro)bis(ethylenediamine)cobalt(III) Chloride Monohydrate*

By R. J. Butcher,† H. H. Hayden and M. M. D. Deyrup
Department of Chemistry, Howard University, Washington, DC 20059, *USA*

and C. B. Storm
*MDO, P*915, *Los Alamos National Laboratory, University of California, Los Alamos, NM* 87545, *USA*

(*Received* 15 *March* 1991; *accepted* 11 *October* 1991)

Abstract. $C_{10}H_{23}ClCoN_5^{2+}.2Cl^-.H_2O$, $M_r = 396.64$, triclinic, $P\bar{1}$, $a = 8.189$ (3), $b = 9.502$ (4), $c = 12.051$ (5) Å, $\alpha = 104.12$ (2), $\beta = 101.89$ (2), $\gamma = 100.68$ (2)°, $V = 862.0$ (1) Å^3, $Z = 2$, $D_x = 1.53$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 14.7$ cm^{-1}, $F(000) = 412$, room temperature, final $R = 0.054$ for 1893 observed reflections [$I > 3\sigma(I)$] out of 3540 independent reflections. The aniline and chloride are in *cis* positions. The aniline nitrogen is sp^3 hybridized; the aniline N—Co distance is 0.07 Å longer than the ethylenediamine N—Co bonds. The aniline ring tilts away from the ethylenediamine chelate rings in contrast to the situation found in aniline complexes of organometallic cobalt dimethylglyoxime derivatives. An extended network of hydrogen bonds is formed by the chlorides, water, and one of the ethylenediamine N atoms. The Co—N(aniline) bonds in Co^{III} aniline complexes fall into long (2.156 Å av.) and short (2.022 Å av.) groups. The long Co—N(aniline) bonds are *trans* to alkyl groups; the short bonds are *trans* to N, Cl$^-$ or I$^-$.

Experimental. Title compound prepared as reported previously (Meisenheimer & Kiderlen, 1924; Bailar & Clapp, 1945; Chawla, Lambert & Jones, 1967). Chromatography on Dowex 50-X8 (200–400) mesh, elution with 3 *M* HCl, crystals obtained by vapor diffusion of ethanol into an aqueous solution of the title compound.

Dark red crystals, 0.25 × 0.22 × 0.35 mm; Nicolet *P*3*m* diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; ω–2θ scan. Scan speed 4–15° (θ) min^{-1}. Indicated Laue symmetry 1. Correct space group $P\bar{1}$ confirmed by subsequent calculations. Cell parameters from setting angles of 15 reflections between 30 and 35°. Data corrected for Lorentz and polarization effects; no correction made for absorption due to regular shape of crystal and small absorption coefficient. Intensities of three standard reflections measured after every 97 reflections did not show any systematic variation during data collection; 3540 unique reflections measured between $4 < 2\theta < 55°$, 1893 with $I > 3\sigma(I)$ used in refinement. Structure solved by direct methods (Karle & Karle, 1966) as implemented in the *TEXRAY*234 (Molecular Structure Corporation, 1985) crystallographic computing package. Non-H atoms refined with anisotropic themal parameters, all H atoms, located from subsequent difference syntheses, refined isotropically. Structures refined to convergence using 281 parameters by full-matrix least-squares methods (Molecular Structure Corporation, 1985) on a PDP 11/73 minicomputer. $\sum w(|F_o| - |F_c|)^2$ was minimized. $w^{-1} = \sigma^2(|F_o|) + 0.04(|F_o|)^2$. Final $R = 0.054$, $wR = 0.057$, $S = 1.24$, $(\Delta/\sigma)_{\max} = 0.07$, $-0.24 < \Delta\rho < 0.31$ e Å^{-3}. Atomic scattering factors used were those from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Fig. 1 is a view of the molecular ion showing the numbering scheme. Table 1 lists the refined coordinates and equivalent isotropic thermal parameters for the heavy atoms in the molecule.‡ Table 2 lists the bond distances and angles in the molecular ion. The coordination sphere of the Co^{III} ion is completed by the four N atoms of the two ethylenediamine ligands, N from the aniline molecule, and the Cl$^-$ ion to form an octahedral structure. Fig. 1 shows that the conformation of the complex is such that the aniline ring tilts away from the chelate ring made up of N(11), C(7), C(8), and N(12), in contrast to the situation in the Co^{III} dimethylglyoxime (dmg) com-

---

* Work performed under the auspices of the US Department of Energy.

† Author to whom correspondence should be addressed.

‡ Lists of structure factors, equivalent isotropic thermal parameters for C, N, O, Cl, Co, anisotropic thermal parameters, H-atom parameters, bond lengths involving H, and selected bond length and angle comparisons for thirteen Co^{III} aniline complexes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54747 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/92/061122-03$06.00

Table 1. *Final least-squares positional parameters for* C, N, Cl *and* Co (× 10^4)

	x	y	z	B_{eq} (Å^2)
Co	2067 (1)	3981 (1)	2655 (8)	3.97 (5)
Cl(1)	3518 (2)	2439 (2)	3354 (2)	6.16 (12)
Cl(2)	2376 (2)	4355 (2)	6310 (2)	5.24 (12)
Cl(3)	2481 (2)	6442 (2)	99 (2)	7.23 (12)
O(*W*)	193 (1)	957 (1)	125 (1)	16.8 (11)
N(1)	268 (7)	3427 (6)	3514 (4)	4.2 (3)
N(11)	951 (7)	5489 (6)	2197 (5)	4.7 (3)
N(12)	3405 (8)	5625 (7)	4074 (5)	5.2 (3)
N(21)	3793 (7)	4391 (7)	1788 (5)	5.7 (4)
N(22)	806 (7)	2392 (7)	1171 (5)	4.9 (4)
C(1)	−876 (9)	1950 (8)	3109 (6)	4.2 (4)
C(2)	−2438 (9)	1626 (8)	2246 (6)	5.5 (5)
C(3)	−3523 (11)	219 (10)	1869 (7)	6.6 (6)
C(4)	−3143 (12)	−870 (10)	2363 (8)	7.7 (7)
C(5)	−1626 (12)	−567 (9)	3217 (7)	8.5 (6)
C(6)	−474 (10)	831 (8)	3598 (6)	6.4 (5)
C(7)	1797 (13)	6975 (10)	3030 (8)	8.8 (7)
C(8)	2791 (17)	6969 (11)	4104 (11)	16.2 (10)
C(9)	3540 (10)	3058 (10)	765 (6)	7.1 (6)
C(10)	1631 (10)	2460 (10)	270 (6)	6.9 (6)

Table 2. *Bond distances* (Å) *and angles* (°) *in the cation*

Co—Cl(1)	2.259 (1)	Co—N(1)	2.031 (3)
Co—N(11)	1.964 (3)	Co—N(12)	1.963 (3)
Co—N(21)	1.960 (3)	Co—N(22)	1.972 (3)
N(11)—C(7)	1.463 (6)	C(7)—C(8)	1.382 (8)
C(8)—N(12)	1.452 (7)	N(21)—C(9)	1.484 (6)
C(9)—C(10)	1.507 (6)	C(10)—N(22)	1.486 (5)
C(1)—C(2)	1.402 (6)	C(2)—C(3)	1.371 (7)
C(3)—C(4)	1.367 (8)	C(4)—C(5)	1.371 (8)
C(5)—C(6)	1.388 (7)	C(6)—C(1)	3.92 (6)
C(1)—N(1)	1.441 (5)		

Cl(1)—Co—N(1)	88.88 (10)	Co—N(1)—C(1)	120.4 (2)
Cl(1)—Co—N(11)	174.01 (12)	N(1)—C(1)—C(2)	120.6 (4)
Cl(1)—Co—N(12)	88.88 (11)	N(1)—C(1)—C(6)	120.5 (4)
Cl(1)—Co—N(21)	88.93 (11)	C(2)—C(1)—C(6)	118.8 (4)
Cl(1)—Co—N(22)	92.34 (11)	C(1)—C(2)—C(3)	120.3 (4)
N(1)—Co—N(11)	91.17 (14)	C(2)—C(3)—C(4)	120.9 (5)
N(1)—Co—N(12)	90.32 (15)	C(3)—C(4)—C(5)	119.5 (5)
N(1)—Co—N(21)	176.69 (16)	C(4)—C(5)—C(6)	121.3 (5)
N(1)—Co—N(22)	93.15 (14)	C(1)—C(6)—C(5)	119.2 (4)
N(11)—Co—N(12)	85.13 (15)	Co—N(11)—C(7)	110.3 (3)
N(11)—Co—N(21)	91.27 (15)	N(11)—C(7)—C(8)	114.7 (5)
N(11)—Co—N(22)	93.64 (15)	C(7)—C(8)—N(12)	114.7 (5)
N(12)—Co—N(21)	92.13 (16)	Co—N(12)—N(8)	110.9 (3)
N(12)—Co—N(22)	176.4 (2)	Co—N(21)—C(9)	109.2 (3)
N(21)—Co—N(22)	84.45 (15)	N(21)—C(9)—C(10)	107.7 (4)
Co—N(22)—C(10)	112.0 (3)	C(9)—C(10)—N(22)	107.2 (4)

Selected intermolecular distances		Symmetry operation
Cl(1)—O(*W*)	3.078 (7)	$x, y-1, z$
Cl(3)—O(*W*)	3.119 (7)	x, y, z
N(22)—O(*W*)	3.00 (7)	$x, y-1, z$

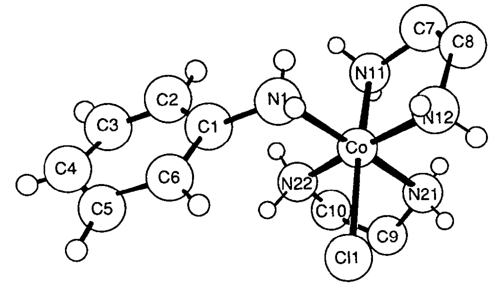

Fig. 1. View of the complex cation with the atomic numbering scheme.

plexes where the aniline ring projects over one of the five-membered chelate rings. The Co—N(aniline) bond lengths fall into long (2.156 Å av.) and short (2.022 Å av.) groups. The long Co—N(aniline) bonds are *trans* to alkyl anions. The short bonds are *trans* to N, Cl^-, or I^-. A table of comparison of key metrical parameters for thirteen Co—aniline complexes has been deposited. The C(1)—N(1) distance at 1.441 (5) Å is lengthened by 0.06 Å from that found in the free aniline molecule (Fukuyo, Hirotsu & Higuchi, 1982).

Related literature. There are twelve structures of Co^{III} aniline complexes reported. Battaglia, Corradi, Palmieri, Nardelli & Tani (1974), bis(aniline)-bis(dimethylglyoximato)cobalt chloride, Co—N(aniline) 2.001 Å; Botoshanskii, Simonov, Malinovskii, Avblov & Bologa (1975), (aniline)-bis(dimethylglyoximato)(chloro)cobalt, Co—N(aniline) 2.019 Å; Marzilli, Bayo, Summers, Thomas, Zangrando, Bresciano-Pahor, Mari & Randaccio (1987), (aniline)bis(dimethylglyoximato)-(*R*)cobalt, $R = CH_2CH_3$, CH_2OCH_3, $CH(CH_3)_2$, Co—N(aniline) 2.147, 2.169, 2.177 Å; Parker, Zangrando, Bresciano-Pahor, Randaccio & Marzilli (1986), (aniline)(*N*2,*N*2′-propanediyl)bis(2,3-butanedione 2-imine 3-oxime)(*R*)cobalt hexafluorophosphate, $R = CH_3$, $CH_2CO_2CH_3$, Co—N(aniline) 2.147, 2.126 Å; Simonov, Botoshanskii, Malinovskii, Ablov & Nemchinova (1978), (aniline)bis(dimethylglyoximato)(iodo)cobalt, Co—N(aniline) 2.053 Å; Yanase, Yoshimura, Kinoshita, Yamaguchi & Wakita (1990), bis(aniline)bis(hexylmethylglyoximato)cobalt chloride, bis(aniline)bis(methyloctylglyoximato)cobalt chloride, Co—N(aniline) 2.011, 2.106 Å; Zangrando, Parker & Mezzetti (1987), (aniline)[3,3′-(1,3-propanediyldinitrilo)di(2-butanone oximato)(1 −)](*R*)cobalt hexafluorophosphate, $R = CH_2CH_3$, CH_2CF_3, Co—N(aniline) 2.174, 2.130 Å.

References

Bailar, J. C. Jr & Clapp, L. B. (1945). *J. Am. Chem. Soc.* **67**, 171–175.

Battaglia, L. P., Corradi, A. B., Palmieri, C. G., Nardelli, M. & Tani, M. E. V. (1974). *Acta Cryst.* **B30**, 1114–1116.

Botoshanskii, M. M., Simonov, Yu. A., Malinovskii, T. I., Ablov, A. V. & Bologa, O. A. (1975). *Dokl. Akad. Nauk SSSR*, **225**, 625–627. [English edition.]

Chawla, N. K., Lambert, D. G. & Jones, M. M. (1967). *J. Am. Chem. Soc.* **89**, 557–560.

Fukuyo, M., Hirotsu, K. & Higuchi, T. (1982). *Acta Cryst.* **B38**, 640–643.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

MARZILLI, L. G., BAYO, F., SUMMERS, M. F., THOMAS, L. B., ZANGRANDO, E., BRESCIANO-PAHOR, N., MARI, M. & RANDACCIO, L. (1987). *J. Am. Chem. Soc.* **109**, 6045–6052.

MEISENHEIMER, J. & KIDERLEN, E. (1924). *Annalen (Leipzig)*, **438**, 217–278.

Molecular Structure Corporation (1985). *TEXRAY*-234. Crystallographic computing system implemented on a PDP 11/73 supplied by Molecular Structure Corporation, Houston, TX, USA.

PARKER, W. O. JR., ZANGRANDO, E., BRESCIANO-PAHOR, N., RANDACCIO, L. & MARZILLI, L. G. (1986). *Inorg. Chem.* **25**, 3489–3497.

SIMONOV, YU. A., BOTOSHANSKII, M. M., MALINOVSKII, T. I., ABLOV, A. V. & NEMCHINOVA, L. A. (1978). *Koord. Khim.* **4**, 830–833. [English edition.]

YANASE, Y., YOSHIMURA, H., KINOSHITA, S., YAMAGUCHI, T. & WAKITA, H. (1990). *Acta Cryst.* **C46**, 36–38.

ZANGRANDO, E., PARKER, W. O. & MEZZETTI, A. (1987). *Acta Cryst.* **C43**, 2277–2280.

Acta Cryst. (1992). **C48**, 1124–1125

Structure of the Methyl Ester of Everninic Acid (Methyl 2-Hydroxy-4-methoxy-6-methylbenzoate)

BY DENIS BLASER AND HELEN STOECKLI-EVANS*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, *CH*-2000 *Neuchâtel, Switzerland*

(*Received* 21 *August* 1991; *accepted* 24 *October* 1991)

Abstract. $C_{10}H_{12}O_4$, $M_r = 196.2$, monoclinic, $P2_1/n$, $a = 11.418$ (2), $b = 7.989$ (1), $c = 11.231$ (2) Å, $\beta = 106.36$ (1)°, $V = 983.0$ Å^3, $Z = 4$, D_m (flotation in KI/H$_2$O) = 1.30, $D_x = 1.326$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.10$ mm^{-1}, $F(000) = 416$, room temperature, $R = 0.045$, $wR = 0.078$ for 1107 observed reflections. The molecule is essentially planar with a strong intramolecular hydrogen bond involving the adjacent hydroxyl and carboxylate groups.

Experimental. The synthesis of the title compound (1) has been described previously (Nicollier, Rebetez, Tabacchi, Gerlach & Thalmann, 1978). Transparent block-like crystals of a synthetic sample of (1) were grown by slow evaporation of a concentrated solution in 1,2-dimethoxyethane. A crystal of dimensions 0.38 × 0.36 × 0.30 mm was used for data collection using a Stoe AED2 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. When mounted on a glass fiber the crystal melted in the X-ray beam (melting point 339–340 K). Hence the crystal was sealed in a Lindemann-glass capillary and suffered no thermal damage during data collection. $< 2\%$ intensity variation for 5 standard reflections measured every hour. Accurate cell parameters from $\pm\omega$ values of 25 reflections and their equivalents in the range $25 < 2\theta < 40°$. 3922 reflections were measured by the $\omega/2\theta$ scan mode with $\theta_{max} = 25°$, and index limits h −13 to 13, k −9 to 9, l 0 to 13. The systematic absences were consistent with space group $P2_1/n$. 1737 unique reflections, $R_{int} = 0.034$; 1107 [$I > 3.5\sigma(I)$] were considered observed and used for all further calculations. Structure solved using a combination of *SHELXS*86 (Sheldrick, 1986) and *PATSEE* (Egert, 1985). Refinement and all further calculations were carried out using the NRCVAX system (Gabe, Le Page, Charland & Lee, 1989). H atoms located from difference maps and refined isotropically. Weighted full-matrix least-squares refinement for 1107 reflections gave $R = 0.045$ and $wR = 0.078$; function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma^2(F_o) + 0.002(F_o^2)$. In the final cycle of refinement the maximum shift/σ ratio was 0.022. Residual density limits in final difference map +0.16 and −0.20 e Å^{-3}. Neutral complex-atom scattering factors in *NRCVAX* from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final positional† and equivalent isotropic thermal parameters are given in Table 1 and interatomic distances and angles in Table 2. The numbering scheme use is illustrated in Fig. 1.

Related literature. Simple monoaryl compounds are commonly found in mushrooms but are relatively rare in lichens (Culberson, 1969; Tabacchi &

---

* Author for correspondence.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54806 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0507]

0108-2701/92/061124-02$06.00