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cis-[Adeninato-chloro-bis(ethylenediamine)cobalt(III)] Bromide Monohydrate*

BY THOMAS J. KISTENMACHER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218, *U.S.A.*

Abstract. [CoClC$_9$H$_{20}$N$_9$]Br.H$_2$O, monoclinic, $I2/a$: $a = 27\cdot342(14)$, $b = 7\cdot692(4)$, $c = 16\cdot073(9)$ Å, $\beta = 99\cdot32(4)°$, $V = 3335\cdot5$A^3, $Z = 8$, $D_m = 1\cdot77(1)$, $D_c = 1\cdot78$ g cm^{-3}. Crystals were obtained from aqueous solution. The octahedral coordination sphere about the cobalt(III) ion is composed of two ethylenediamine chelate ligands in *cis* positions, a chloride ion, and N(9) of the unidentate monoanion of adenine. The conformation of the complex is such that N(3) of the adenine base forms interligand hydrogen bonds with two of the ethylenediamine hydrogen atoms.

Introduction. The complex was prepared by previously published methods (Kistenmacher, Marzilli & Chang, 1973). The X-ray intensities and cell dimensions were

obtained from a crystal $0\cdot15 \times 0\cdot20 \times 0\cdot25$ mm (with the long dimension approximately parallel to the φ axis of the diffractometer) on a Syntex $P\bar{1}$ computer-controlled diffractometer (Mo $K\alpha$ graphite-monochromated radiation, $2\theta_{max} = 55°$). In total, 3838 independent intensities (*hkl* and *hkī*) were measured (3545 with intensities above zero). Three standard reflections were measured after every 100 data points; there was no indication of crystal decomposition during the course of the experiment. The space group is $I2/a$ [systematic absences: *hkl*, $h + k + l = 2n + 1$; *h0l*, $h(l) = 2n + 1$]. Each reflection was assigned an observational variance based on the equation $\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$, where S, B_1 and B_2 are the scan and background counts, T_S and T_B are the scan and individual background counting times ($T_B = \frac{1}{4}T_S$ for all reflections), and p was taken to be equal to $0\cdot03$ and represents the error proportional to the diffracted beam intensity (Busing & Levy, 1957). The intensities and their stan-

Table 1. *Final heavy-atom parameters and their estimated standard deviations* ($\times 10^4$)

The form of the anisotropic ellipsoid is exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	−1881 (0·2)	−954 (0·6)	3797 (0·3)	7 (0·1)	169 (1)	37 (0·2)	5 (0·2)	3 (0·1)	−9 (0·4)
Co	1499 (0·2)	−255 (0·7)	3006 (0·3)	4 (0·1)	85 (1)	26 (0·2)	−1 (0·2)	2 (0·1)	5 (0·4)
Cl	1881 (0·4)	−2794 (1)	3408 (0·8)	8 (0·1)	104 (2)	54 (0·6)	5 (0·4)	5 (0·2)	17 (0·9)
O	21 (1)	−3617 (6)	5777 (2)	25 (1)	255 (10)	54 (2)	−6 (2)	13 (1)	17 (4)
N(1)	−529 (1)	3 (5)	3152 (2)	6 (1)	120 (7)	36 (2)	−1 (1)	2 (1)	2 (3)
N(3)	255 (1)	560 (4)	2691 (2)	6 (1)	104 (7)	35 (2)	−0 (1)	1 (1)	6 (3)
N(6)	−613 (1)	−1662 (6)	4315 (2)	7 (1)	221 (9)	36 (2)	−1 (2)	6 (1)	10 (3)
N(7)	523 (1)	−2095 (5)	4540 (2)	8 (1)	201 (9)	31 (2)	1 (2)	4 (1)	25 (3)
N(9)	954 (1)	−795 (4)	3609 (2)	5 (1)	128 (7)	25 (1)	−1 (1)	1 (1)	14 (2)
N(10)	2015 (1)	157 (5)	2304 (2)	6 (1)	129 (7)	35 (2)	−1 (1)	4 (1)	8 (3)
N(11)	1124 (1)	−1295 (5)	1993 (2)	7 (1)	118 (7)	33 (1)	−3 (1)	2 (1)	−7 (3)
N(12)	1884 (1)	878 (5)	3990 (2)	6 (1)	143 (7)	28 (1)	−1 (1)	1 (1)	5 (3)
N(13)	1215 (1)	2051 (4)	2742 (2)	6 (1)	104 (6)	32 (1)	−1 (1)	2 (1)	11 (2)
C(2)	−235 (1)	656 (5)	2633 (3)	6 (1)	109 (8)	39 (2)	4 (1)	1 (1)	6 (3)
C(4)	463 (1)	−381 (5)	3381 (2)	6 (1)	103 (7)	26 (2)	−2 (2)	2 (1)	−4 (3)
C(5)	202 (1)	−1176 (5)	3945 (2)	6 (1)	123 (8)	26 (2)	−3 (2)	2 (1)	0 (3)
C(6)	−317 (1)	−928 (6)	3816 (3)	7 (1)	116 (8)	29 (2)	−5 (2)	4 (1)	−12 (3)
C(8)	960 (1)	−1810 (7)	4289 (3)	7 (1)	173 (10)	35 (2)	4 (2)	3 (1)	27 (4)
C(10)	1903 (2)	−869 (6)	1524 (3)	10 (1)	163 (10)	43 (2)	10 (2)	9 (1)	−5 (4)
C(11)	1346 (2)	−821 (7)	1258 (3)	10 (1)	217 (11)	30 (2)	−7 (2)	3 (1)	−22 (4)
C(12)	1819 (2)	2790 (6)	3941 (3)	11 (1)	115 (9)	42 (2)	−9 (2)	1 (1)	−5 (4)
C(13)	1295 (2)	3135 (6)	3508 (3)	10 (1)	106 (8)	40 (2)	−1 (2)	4 (1)	−6 (3)

dard deviations were corrected for Lorentz and polarization effects, but no correction for absorption was applied ($\mu = 37.8$ cm^{-1}). The 293 intensities below zero were assigned F's and $w(F)$'s equal to zero.

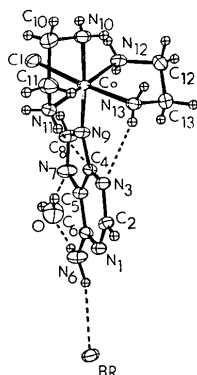The structure was solved by standard heavy-atom methods. Full-matrix least-squares refinement, mini-

Fig. 1. A perspective view of the cis-[adeninato-chloro-bis-(ethylenediamine)cobalt(III)]$^+$ ion. The dashed lines indicate hydrogen bonds. The thermal ellipsoids are drawn at the 40% probability level (ORTEP, Johnson, 1965).
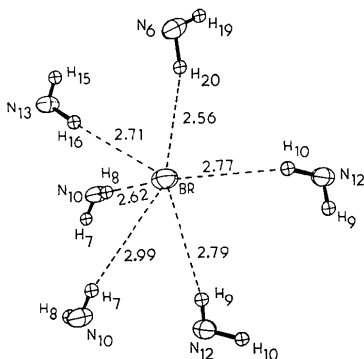

Fig. 2. Hydrogen-bonding environment about the bromide ion. The dashed lines indicate hydrogen bonds (H$\cdots$Br$^-$ distances given). The thermal ellipsoids are drawn at the 40% probability level (ORTEP, Johnson, 1965).
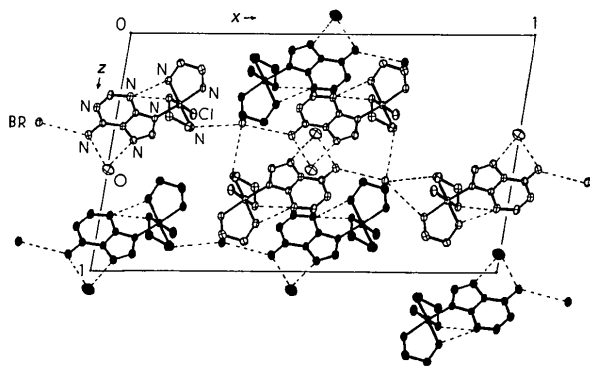

Fig. 3. A projection of the unit cell contents onto the ac plane. The shaded complexes have their centroids at about $y = \frac{1}{2}$ (ORTEP, Johnson, 1965).

mizing $\sum w(|F_o| - |F_c|)^2$ and weights equal to $1/\sigma^2(F)$, has led to final R values of 0.063 (excluding zeros) and 0.072 (including zeros). The final weighted R value and goodness-of-fit for the 3545 non-zero reflections and 287 variables (heavy atoms anisotropic and hydrogen atoms isotropic) were 0.049 and 1.6, respectively. Initial atomic coordinates for the hydrogen atoms were obtained by difference Fourier techniques. The scattering factors for Br, Co, Cl, C, N, and O were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The scattering curve for H was that

Table 2. Interatomic distances (Å) and angles (°)

Estimated standard deviations: this study: Co–Cl 0.001, Co–N 0.003, N–C 0.005 Å, angles 0.3°; adenosine: N–C 0.003 Å, angles 0.2°.

(a) Primary coordination sphere about the cobalt atom

Co–Cl	2.259 Å		Co–N(11)	1.950 Å	
Co–N(9)	1.949		Co–N(12)	1.957	
Co–N(10)	1.970		Co–N(13)	1.955	
Cl——Co——N(9)		91.6°	N(9)—Co——N(12)		92.8°
Cl——Co——N(10)		87.8	N(9)—Co——N(13)		89.6
Cl——Co——N(11)		92.3	N(10)-Co——N(11)		85.2
Cl——Co——N(12)		89.4	N(10)-Co——N(12)		92.8
Cl——Co——N(13)		174.4	N(10)-Co——N(13)		91.5
N(9)—Co——N(13)		174.4	N(11)-Co——N(12)		177.2
N(9)—Co——N(11)		89.2	N(11)-Co——N(13)		93.1

N(12)–Co–N(13) 85.1°

(b) Ethylenediamine chelate rings

N(10)–C(10)	1.471 Å		N(12)–C(12)	1.482 Å
C(10)–C(11)	1.515		C(12)–C(13)	1.511
C(11)–N(11)	1.468		C(13)–N(13)	1.474
Co——N(10)–C(10)	109.4°		Co——N(12)–C(12)	110.8°
N(10)–C(10)–C(11)	107.1		N(12)–C(12)–C(13)	107.2
C(10)–C(11)–N(11)	106.8		C(12)–C(13)–N(13)	106.7
C(11)–N(11)–Co	110.2		C(13)–N(13)–Co	109.4

(c) Comparison of bond lengths and angles in the coordinated adenine anion (K) and adenosine (Lai & Marsh, 1972: LM)

	K	LM		K	LM
N(1)–C(2)	1.344 Å	1.340 Å	N(7)–C(5)	1.383 Å	1.385 Å
N(1)–C(6)	1.377	1.351	N(7)–C(8)	1.340	1.308
N(3)–C(2)	1.333	1.330	N(9)–C(4)	1.371	1.374
N(3)–C(4)	1.369	1.349	N(9)–C(8)	1.341	1.362
N(6)–C(6)	1.352	1.332	C(4)–C(5)	1.384	1.381
C(5)–C(6)	1.414	1.415			

	K	LM
C(2)–N(1)–C(6)	118.1°	119.3°
C(2)–N(3)–C(4)	111.6	110.4
C(5)–N(7)–C(8)	101.8	103.5
C(4)–N(9)–C(8)	103.6	105.7
Co*–N(9)–C(4)	127.7	124.3
Co*–N(9)–C(8)	128.3	130.0
N(1)–C(2)–N(3)	129.1	128.9
N(3)–C(4)–N(9)	126.9	126.7
N(3)–C(4)–C(5)	125.0	127.6
N(9)–C(4)–C(5)	108.0	105.7
N(7)–C(5)–C(4)	110.0	110.8
N(7)–C(5)–C(6)	132.9	132.8
C(4)–C(5)–C(6)	117.1	116.4
N(1)–C(6)–N(6)	118.3	118.1
N(1)–C(6)–C(5)	119.0	117.4
N(6)–C(6)–C(5)	122.7	124.5
N(7)–C(8)–N(9)	116.6	114.3

* C(1') of the ribose ring in adenosine.

Table 3. *Distances and angles in the hydrogen bonds,* D–$H \cdots A$

D	H	A	D–H	$D \cdots A$	$H \cdots A$	$\angle D$–$H \cdots A$
(*a*) Interligand						
N(11)	H(2)	N(3)	0·72 (5) Å	3·131 (5) Å	2·55 (5) Å	139 (4)°
N(13)	H(15)	N(3)	0·67 (5)	2·853 (5)	2·32 (5)	139 (4)
(*b*) Others						
O	H(21)	N(7)	0·87 (5)	2·845 (4)	1·99 (5)	168 (4)
N(6)	H(19)	O	0·78 (5)	3·077 (4)	2·31 (5)	168 (4)
N(6)	H(20)	Br	0·95 (5)	3·475 (2)	2·56 (4)	162 (2)
N(10)	H(8)	Br	0·86 (5)	3·464 (2)	2·62 (4)	167 (2)
N(13)	H(16)	Br	0·94 (5)	3·640 (2)	2·71 (4)	171 (2)
N(12)	H(10)	Br	0·89 (5)	3·561 (2)	2·77 (4)	149 (2)
N(12)	H(9)	Br	0·79 (5)	3·438 (2)	2·79 (4)	142 (2)
N(10)	H(7)	Br	0·69 (5)	3·592 (2)	2·99 (4)	147 (2)

of Stewart, Davidson & Simpson (1965). The real part of the scattering curves for Br, Co and Cl were corrected for anomalous dispersion effects (Cromer, 1965). Final heavy-atom positional and thermal parameters are given in Table 1. The hydrogen positional and thermal parameters, as well as a complete list of calculated and observed structure factors, are available.*

Discussion. This crystal structure determination provides detailed information relating to interligand hydrogen bonding in transition-metal complexes containing purines as coordinated ligands (Kistenmacher, Marzilli & Chang, 1973; Marzilli, Kistenmacher & Chang, 1973). Fig. 1 shows the conformation of the cis-$[Co(en)_2Cl(C_5N_5H_4)]^+$ cation and, in particular, the interligand hydrogen bonding between N(3) of the adenine base and two of the ethylenediamine hydrogen atoms. These interligand hydrogen bonds surely play an important role in determining the conformation of the complex. The two hydrogen bonds are different, N(3)$\cdots$N(11) 3·13 Å with a N$\cdots$N–H angle of 34°; N(3)–N(13) 2·85 Å with a N$\cdots$N–H angle of 32°. This difference appears to be a result of the attractive interaction between the hydrogen atom on C(8) and the coordinated chloride ion [H$\cdots$Cl, 2·79 Å, Cl$\cdots$C(8)–H angle of 58°]. The hydrogen bonding between N(7) and N(6) and the water of crystallization and the bromide anion are also shown in Fig. 1. Table 2 gives the heavy-atom interatomic distances and angles and a comparison with the structural parameters in the coordinated adenine anion and adenosine (Lai & Marsh, 1972). The substitution of the Co–N(9) coordination bond in the complex for the C(1')–N(9) glycosidic bond in adenosine has produced small (0·02–0·04 Å) differences in some bond lengths, notably N(7)–C(8) 1·340 Å in the complex and 1·308 Å in adenosine. The bond angles at N(9) and C(4) of the

base have also been significantly disturbed. As expected, the principal differences occur in the imidazole ring of the adenine system. Sundaralingam & Carrabine (1971) have noted similar effects, albeit in the opposite direction, in a comparison of guanine, protonated guanine, and guanine which is both protonated and coordinated. The nine atoms of the adenine framework are approximately coplanar with maximum deviations at C(2), 0·03 Å, and C(4), −0·03 Å. The exocyclic amine nitrogen, N(6), the cobalt, and the hydrogen-bonded bromide anion and water oxygen lie 0·03, 0·14, 0·14, and −0·09 Å, respectively, out of the mean plane of the adenine ring system. The deviation of the latter three atoms, and the interaction between the C(8) hydrogen and the coordinated chloride anion, probably account for much of the non-planarity of the adenine moiety.

The bromide anion acts as an acceptor in six hydrogen bonds (H$\cdots$Br$^-$ distance less than 3·0 Å; Fig. 2) which serve to interconnect the complex cations in a three-dimensional network (Fig. 3). The parameters in these hydrogen bonds, as well as those noted above, are given in Table 3.

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