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The Structure and Absolute Configuration of $(+)_{589}$-Tris(biguanide)cobalt(III) Trichloride Monohydrate, $Co(C_2H_7N_5)_3Cl_3.H_2O$

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The crystal structure of $(+)_{589}[Co(biguanide)_3]Cl_3.H_2O$ has been determined from 2161 reflexions collected by counter methods. The red crystals are orthorhombic, space group $C222_1$, with $a = 18{\cdot}675$ (9), $b = 14{\cdot}086$ (7), and $c = 15{\cdot}004$ (7) Å. The measured density is 1·65 (2) g cm^{-3} which agrees with the calculated density of 1·637 for $Z = 8$. The absorption corrected data gave a conventional R value of 0·021 on full-matrix least-squares refinement which included the hydrogen atoms. Bonding to cobalt in the six-coordinate tris(bidentate chelate) complex is through the terminal NH functions of the ligand, the average Co–N distance is 1·912 (3) Å. The carbon-nitrogen bond distances and valence bond numbers are N(ligand)–C, 1·282 (2), 1·5; C–N(ring), 1·365 (5), 1·2; and C–N(terminal), 1·353 (4), 1·3. The chelate ring is only approximately planar with displacements near 0·1 Å of the cobalt, a ligand nitrogen and the ring nitrogen from the least-squares planes. The absolute configuration of the complex is Δ. This result shows that the exciton method of determining absolute configuration from the ultraviolet components of the circular dichroism spectrum is not generally applicable.

Introduction

Biguanide, NH_2–C(NH)–NH–C(NH)NH_2 (bgH), forms complexes with many transition metal ions, of which the cobalt(III) and chromium(III) species $[M(bgH)_3]^{3+}$ have been noted in terms of their circular dichroism (c.d.) spectra (Michelsen, 1965; Igi, Yasui, Hidaka & Shimura, 1971). The spectra present a puzzling problem since while they closely parallel each other in the visible region of the c.d. spectrum they display opposite signs in the ultraviolet spectral region. The signs of bands in the spectra are related to the absolute configurations of the cations. The absolute configuration of $(-)_{589}[Cr(bgH)_3]^{3+}$ has been found to be Λ by Brubaker & Webb (1969) who carried out an X-ray structure analysis of the *d*-10-camphorsulphonate salt, but have not reported any molecular geometry for the cation. The cobalt complex $(-)_{589}$-$[Co(bgH)_3]^{3+}$ has been variously assigned the same configuration (Brubaker & Webb, 1969) or the opposite absolute configuration (Igi *et al.*, 1971). We have undertaken the structure analysis of $(+)_{589}$-$[Co(bgH)_3]Cl_3\cdot H_2O$ to settle this question and obtain accurate molecular geometry for the cation.

Experimental

The complex $(+)[Co(bgH)_3]Cl_3\cdot H_2O$ was prepared and resolved by standard methods (Michelsen, 1965; Ray & Dutt, 1939) except that the resolving agent, *l*-bromocamphorsulphonate, was substituted for the *d*-antipode. Suitable crystals were grown by placing concentrated aqueous solutions in an evacuated desiccator over ethanol for a day. A sample prepared in this way gave $[\alpha]^{22}_{589} = +470°$ [literature values: $-434°$ (Michelsen, 1965) and $-450°$ (Igi *et al.*, 1971) for the *l*-antipode].

The red crystals grew as prismatic needles elongated along **c** and exhibited the forms {110} and {111} (racemic crystals grown in the same manner appeared as regular tetrahedra). Preliminary Weissenberg and precession photographs (Cu $K\alpha$ radiation) established the crystals to be orthorhombic with space group $C222_1$ (D_2^5 No. 20). The cell constants at 21 °C were obtained from the ω scans of $h00$, $0k0$ and $00l$ reflexions on a Stoe automatic Weissenberg diffractometer fitted with a graphite monochromator. For these reflexions $\theta = \omega + \omega_0$ and ω_0 is iteratively adjusted until each reflexion of the festoon yields the same value of the cell constant as closely as possible. Calibration with a gold crystal [$a = 4{\cdot}0786(2)$Å at 25°C] showed the accuracy of this method to be 0·05%. The crystal data are collected in Table 1.

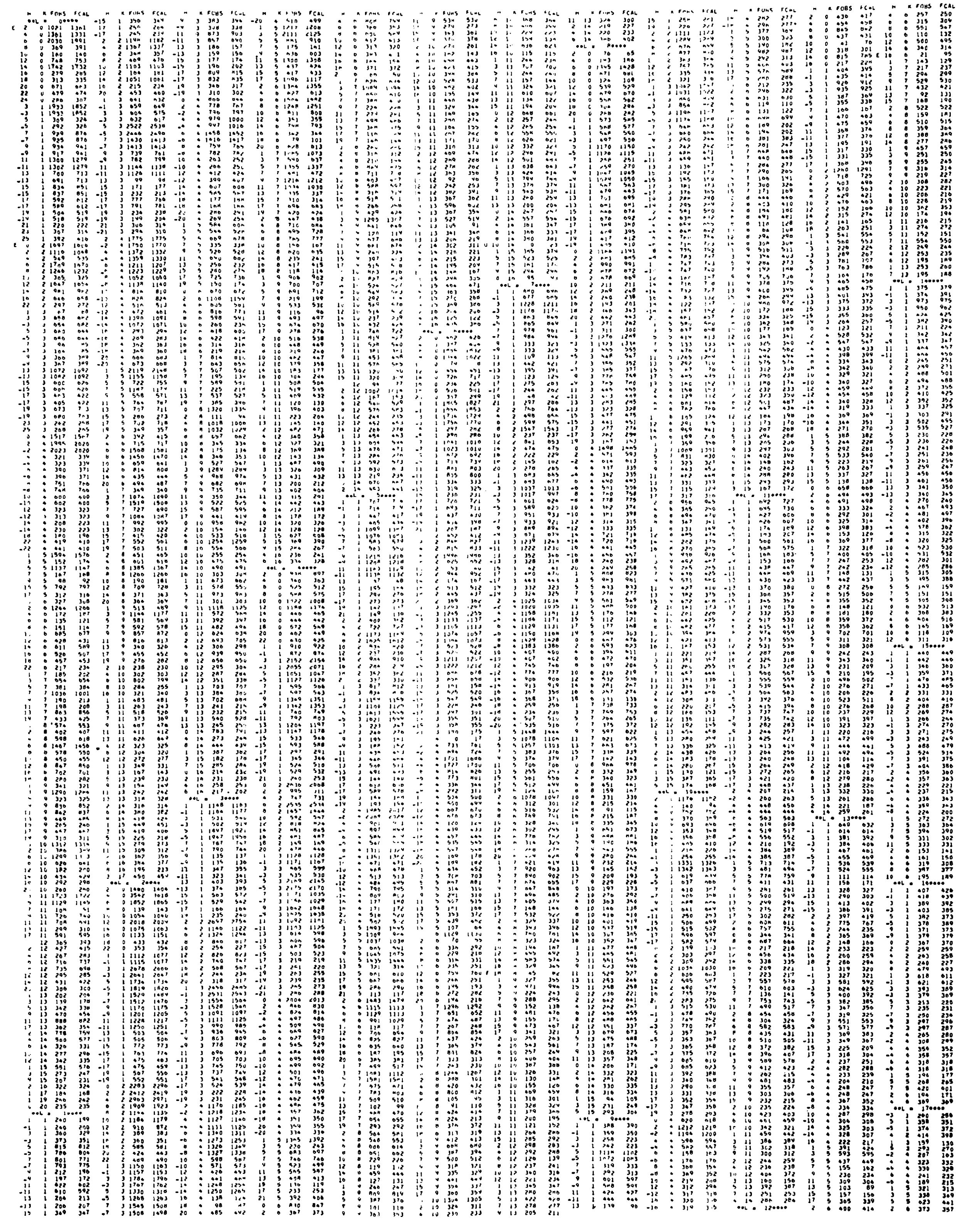
Table 1. *Crystal data*

$CoC_6H_{23}Cl_3N_{15}O$	F.W. 486·62
Orthorhombic	Space group $C222_1$
$a = 18{\cdot}675$ (9) Å	$F(000) = 2000$ e
$b = 14{\cdot}086$ (7)	$D_m = 1{\cdot}64$ (2) g cm^{-3}
$c = 15{\cdot}004$ (7)	$D_x = 1{\cdot}637$ g cm^{-3}
$Z = 8$	μMo $K\alpha = 8{\cdot}9$ cm^{-1}

(λMo $K\alpha = 0{\cdot}7107$ Å)

The mosaicity of the crystal was checked by low-angle ω scans; the average width of a number of such reflexions was 0·12°, which is acceptable (Furnas, 1957). The intensities were measured with Mo $K\alpha$ radiation by the ω scan technique at a take off angle of 4°. The Stoe supplied control program permits a preliminary observation of the peak count and either

Table 2. *Structure factor data for* $(+)_{589}$Co(bgH)$_3$ Cl$_3$.H$_2$O (e × 10)



inserts attenuators (over 4000 counts s^{-1}) or increases the measuring times in multiples of 2 up to a factor of 8 depending on the counts accumulated in the prescan. A basic step counting time of 0·5 s at each 0·01° of the scan range was used with 12·5 s for each background counting time. Reflexions with fewer than 8 counts s^{-1} are rejected as weak. For upper level reflexions the scan range ($\Delta\omega$) was varied according to a formula, $\Delta\omega = A + B[\sin\mu/\tan(\psi/2)]$, where μ is the equi-inclination angle and ψ is the detector angle. The formula allows for the angular range over which a crystal reflects in an upper level equi-inclinational setting (Phillips, 1954) and values of A and B near 0·7 and 0·8 were found satisfactory. Pairs of crossed aperture slits in the range 1 to 3mm were chosen for each layer to avoid the truncation of any reflexions.

Data about two axes with separate crystals (c axis, hk0–13; b axis, $h0l$ to $h6l$) were gathered out to $2\theta = 50°$. A standard reflexion was monitored after every 30 reflexions on each layer and these showed no sensible change. Both crystals measured approximately 0·2 × 0·25 × 0·45mm and corrections for absorption were applied, though the range of transmission factor was small [0·78 to 0·82 (b axis), and 0·88 to 0·92 (c axis)]. Lorentz and polarization corrections (Whittaker, 1953) appropriate for use with a highly mosaic monochromator were applied and data from both axes were scaled together by a non-iterative least-squares

Table 3. *Positional and thermal parameters* ($\times 10^5$) *for* $(+)_{589}[\mathrm{Co(bgH)_3}]\mathrm{Cl_3 \cdot H_2O}$

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	17693 (2)	−4332 (3)	25881 (3)	130 (1)	262 (2)	233 (2)	−9 (1)	−4 (1)	−7 (2)
Cl(1)	27951 (6)	−26481 (8)	4347 (7)	319 (4)	568 (7)	290 (5)	−27 (4)	−12 (3)	15 (6)
Cl(2)	0 (0)	−43320 (9)	2500 (0)	173 (3)	290 (7)	860 (10)	0 (0)	22 (6)	0 (0)
Cl(3)	46509 (5)	−14155 (8)	42108 (9)	215 (3)	421 (6)	633 (7)	−12 (4)	56 (4)	53 (5)
Cl(4)	3328 (8)	0 (0)	0 (0)	362 (5)	448 (8)	297 (7)	0 (0)	0 (0)	3 (7)
O(1)	26833 (28)	0 (0)	0 (0)	416 (19)	2009 (70)	439 (25)	0 (0)	0 (0)	−8 (35)
O(2)	41982 (27)	0 (0)	0 (0)	333 (16)	1355 (55)	1277 (50)	0 (0)	0 (0)	724 (46)
N(1)	16160 (17)	−15131 (24)	33452 (20)	190 (9)	301 (17)	288 (15)	−20 (10)	−26 (9)	17 (13)
N(2)	11711 (16)	−10147 (23)	17211 (20)	202 (9)	346 (18)	242 (14)	−33 (11)	−55 (9)	45 (13)
N(3)	23745 (14)	1621 (22)	34559 (20)	166 (8)	382 (20)	281 (14)	−23 (10)	3 (9)	−77 (13)
N(4)	25870 (15)	−10309 (22)	20739 (20)	163 (8)	375 (18)	278 (14)	5 (10)	0 (9)	71 (13)
N(5)	9686 (14)	2018 (21)	31105 (21)	160 (8)	334 (20)	319 (15)	−12 (9)	51 (9)	48 (13)
N(6)	18869 (14)	6084 (22)	17869 (19)	188 (8)	327 (18)	272 (14)	−15 (10)	58 (8)	0 (13)
N(7)	13146 (23)	−3068 (31)	37200 (29)	371 (13)	430 (23)	517 (22)	−123 (14)	−150 (14)	182 (20)
N(8)	9993 (20)	−24818 (26)	23624 (27)	389 (12)	329 (17)	466 (19)	−127 (12)	−194 (13)	53 (18)
N(9)	4532 (24)	−2145 (31)	10381 (30)	447 (5)	505 (24)	446 (22)	−146 (15)	−228 (15)	21 (18)
N(10)	34372 (19)	7169 (28)	40820 (30)	242 (10)	555 (24)	536 (20)	−42 (13)	−145 (11)	−168 (19)
N(11)	34714 (15)	−3024 (25)	29033 (26)	130 (8)	494 (23)	725 (24)	5 (11)	−37 (11)	−222 (19)
N(12)	38004 (17)	−13253 (25)	17962 (26)	165 (9)	371 (19)	515 (21)	17 (11)	75 (11)	15 (16)
N(13)	3288 (19)	15013 (27)	36203 (27)	276 (11)	419 (21)	512 (21)	76 (13)	177 (13)	24 (17)
N(14)	11568 (15)	16882 (20)	25150 (26)	225 (8)	284 (16)	394 (16)	1 (10)	65 (12)	5 (16)
N(15)	17094 (21)	21429 (28)	12415 (28)	290 (11)	406 (21)	540 (20)	25 (13)	126 (13)	151 (16)
C(1)	13247 (19)	−23139 (27)	31690 (25)	186 (11)	351 (22)	338 (21)	−11 (12)	−37 (11)	66 (17)
C(2)	8904 (19)	−18397 (30)	17000 (27)	213 (11)	396 (24)	317 (19)	−18 (13)	−57 (12)	−12 (18)
C(3)	30630 (17)	1904 (25)	34890 (25)	191 (11)	284 (22)	373 (19)	−27 (11)	−34 (11)	25 (15)
C(4)	32540 (17)	−8840 (23)	22400 (21)	153 (9)	250 (17)	361 (18)	16 (12)	14 (11)	41 (14)
C(5)	8215 (18)	10897 (26)	30880 (26)	163 (10)	340 (21)	311 (19)	−14 (12)	14 (11)	−28 (17)
C(6)	15964 (17)	14325 (27)	18163 (23)	158 (11)	340 (20)	282 (18)	−49 (12)	9 (10)	48 (15)

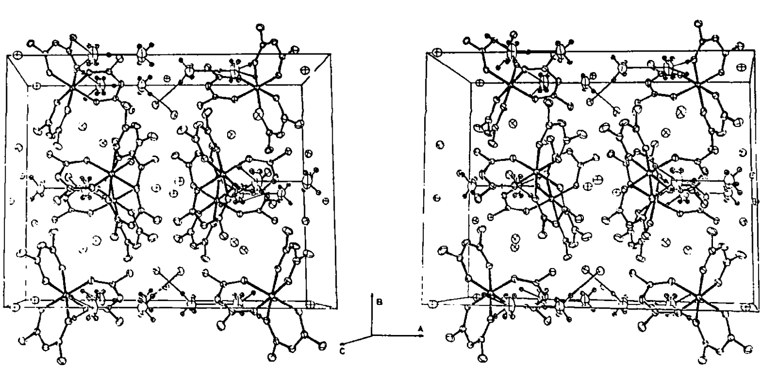


Fig. 1. A stereoscopic view of the unit cell of the $\mathrm{Co(biguanide)_3Cl_3 . H_2O}$ structure. The view is approximately along **c**. Hydrogen bonding with the disordered water molecules is shown; other hydrogen atoms are omitted for clarity. The atoms other than hydrogen are drawn with 25% probability ellipsoids.

method (Rae, 1965). In all, 2161 reflexions were obtained including 360 non-equivalent Friedel pairs.

Solution and refinement of structure

The Patterson synthesis gave the four heavy-atom positions. These atoms were refined by least-squares calculations, with mimimization of the function $\sum w(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weights, w, were unity. This refinement of the scale factor, positional parameters, and individual isotropic temperature factors led to a conventional R index $(R_1=\sum||F_o|-|F_c||/\sum|F_o|)$ of 0·35. A subsequent difference map located the carbon and nitrogen positions and suggested sites for two half-water molecules. Further refinement cycles eventually incorporating anisotropic thermal parameters for all atoms converged with $R=0{\cdot}045$. During this process the absolute configuration was determined by incorporating the effects of the imaginary component of scattering by Co and Cl. The inequalities among the observed and calculated Friedel pairs showed that the wrong absolute configuration had been initially chosen and refinement was continued with the correct absolute configuration using the anomalous scattering components. Difference maps calculated in the ligand planes were used to locate the hydrogen atoms. Owing to computer storage restrictions refinement was continued in blocks comprising the coordinates of all atoms in one cycle and the anisotropic temperature factors of all non-hydrogen atoms in the next cycle. The scale factor was included in all cycles. A difference map computed in the region of the water molecules showed the hydrogen atom disorder illustrated in Fig. 1. These hydrogen positions were included in the final cycles of the refinement, but were not refined. At convergence R_1 was 0·021 and R_2, 0·025 $\{R_2=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}\}$. The error in an observation of unit weight is 0·44 from the final coordinate refinement block. The unit weighting scheme was checked by plotting $\sum \omega(|F_o|-|F_c|)^2$ averaged in ranges of $|F_o|$ *versus* $|F_c|$. It was evident that the very weak and very strong reflexions had received weights that were relatively too large; the range of averaged $\sum w(|F_o|-|F_o|)^2$ values was 1·5 to 3·2 for all except the two terminal ranges. A similar analysis *versus* $\sin\theta/\lambda$ showed an average value of 4·3 for this quantity in the low-angle range and other values varied non-systematically between 1·4 and 1·7. These results are satisfactory. The final difference map shows no peaks of height greater than 0·2 e Å^{-3} which is approximately 40% of the height of a typical hydrogen peak in the earlier difference maps.

The scattering factors used for Co^{2+}* and Cl^- were those of Doyle & Turner (1968); for O, N and C the values from *International Tables for X-ray Crystallography* (1962) were used; for H the values were those of Stewart, Davidson & Simpson (1965). The values of the components $\Delta f'$ and $\Delta f''$ for Co(0·299, 0·973) and Cl(0·132, 0·159) were obtained from Cromer & Liberman (1970).

Programs used for solution, refinement and geometry calculations were local modifications of the following: Busing & Levy's *ORFLS* and *ORFFE*, Zalkin's *FORDAP*, Johnson's *ORTEP* and *ORTEP* II and Blount's *PLANE* and *BLANDA*.

The final least-squares parameters of the non-hydrogen atoms and their standard deviations are given in Table 3. The refined positional and fixed thermal parameters of the hydrogen atoms appear in Table 4. Table 2 contains the observed and calculated structure factors (×10). Table 5 presents the r.m.s. amplitudes of vibration and the geometry of the $[Co(bgH)_3]^{3+}$ cation is given in Table 6.

Table 4. *Parameters for the hydrogen atoms*

	10^3x	10^3y	10^3z	B(Å^2)
N(1)H	172 (2)	−144 (3)	368 (3)	4·3
N(2)H	110 (2)	−67 (3)	136 (3)	4·3
N(3)H	215 (2)	50 (3)	381 (3)	4·3
N(4)H	248 (2)	−139 (3)	172 (3)	4·3
N(5)H	80 (2)	−4 (3)	341 (3)	4·3
N(6)H	209 (2)	46 (3)	137 (3)	4·3
N(7)H(1)	100 (2)	−348 (4)	363 (4)	5·9
N(7)H(2)	140 (2)	−295 (4)	425 (4)	5·9
N(8)H	81 (2)	−294 (3)	226 (3)	4·9
N(9)H(1)	47 (2)	−181 (4)	55 (4)	5·9
N(9)H(2)	37 (2)	−277 (4)	96 (3)	5·9
N(10)H(1)	391 (2)	55 (3)	419 (3)	5·9
N(10)H(2)	327 (3)	110 (3)	444 (3)	5·9
N(11)H	392 (2)	−27 (3)	302 (3)	4·9
N(12)H(1)	371 (2)	−161 (4)	134 (4)	5·9
N(12)H(2)	422 (3)	−108 (4)	177 (4)	5·9
N(13)H(1)	24 (2)	211 (3)	357 (3)	5·9
N(13)H(2)	12 (3)	117 (3)	398 (3)	5·9
N(14)H	111 (2)	227 (3)	255 (3)	4·9
N(15)H(1)	193 (2)	201 (4)	80 (3)	5·9
N(15)H(2)	144 (2)	270 (4)	123 (3)	5·9
O(1)H(1)*	319	0	0	7·0
O(1)H(2)	255	−40	12	8·0
O(1)H(3)	280	−40	28	8·0
O(2)H(1)	413	30	30	8·0
O(2)H(2)	450	−45	30	8·0

* Hydrogen atoms of the water molecules were not refined. Their multipliers in the refinement were 0·25, 0·375, 0·375, 0·55. and 0·45 respectively.

Results and discussion

Description of the structure

A stereoview of the unit cell of the structure is shown in Fig. 1. The tris(biguanide)cobalt(III) cation has an approximate threefold axis which is aligned almost parallel to the c axis. The angle between the threefold axis of the CoN_6 set of atoms and the c axis is 11·7°. The threefold axis was defined as the normal to the plane through the metal atom corresponding to the average of the planes through the two

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* The Co^{2+} curve was used for the Co(III) atom to allow for the increased electron density found experimentally (Kobayashi, Marumo & Saito, 1972).

Table 5. *Root-mean-square amplitudes of vibration* × 10^3 (Å)

	Min.	Intermed.	Max.
Co	150 (1)	162 (1)	166 (1)
Cl(1)	182 (2)	231 (2)	246 (2)
Cl(2)	171 (2)	174 (2)	314 (2)
Cl(3)	186 (2)	207 (2)	274 (2)
Cl(4)	185 (2)	212 (2)	253 (2)
O(1)	224 (7)	271 (7)	449 (8)
O(2)	243 (6)	251 (6)	468 (7)
N(1)	170 (4)	173 (4)	200 (4)
N(2)	150 (4)	176 (4)	211 (4)
N(3)	161 (4)	172 (5)	211 (4)
N(4)	163 (4)	170 (4)	207 (4)
N(5)	150 (4)	183 (4)	206 (5)
N(6)	154 (4)	181 (4)	202 (4)
N(7)	172 (5)	204 (4)	309 (5)
N(8)	157 (5)	191 (5)	307 (5)
N(9)	161 (6)	221 (6)	325 (5)
N(10)	150 (4)	236 (5)	286 (4)
N(11)	149 (4)	194 (5)	310 (5)
N(12)	160 (4)	193 (3)	250 (4)
N(13)	160 (5)	207 (5)	285 (5)
N(14)	169 (4)	181 (4)	228 (4)
N(15)	172 (5)	207 (5)	284 (5)
C(1)	168 (5)	180 (5)	215 (5)
C(2)	168 (5)	200 (5)	212 (6)
C(3)	163 (5)	180 (5)	214 (5)
C(4)	153 (4)	166 (4)	207 (5)
C(5)	168 (5)	179 (5)	197 (5)
C(6)	150 (5)	179 (5)	201 (5)

Table 6. *Geometry of the* Co(bgH)$_3^{3+}$ *ion*

Distances (Å)

Co—N(1)	1·922 (3)	C(1)–N(8)	1·377 (5)
Co—N(2)	1·902 (3)	C(2)–N(8)	1·361 (5)
Co—N(3)	1·920 (3)	C(3)–N(11)	1·356 (5)
Co—N(4)	1·908 (3)	C(4)–N(11)	1·354 (4)
Co—N(5)	1·911 (3)	C(5)–N(14)	1·359 (5)
Co—N(6)	1·911 (3)	C(6)–N(14)	1·382 (5)
C(1)–N(1)	1·280 (5)	C(1)–N(7)	1·347 (5)
C(2)–N(2)	1·275 (5)	C(2)–N(9)	1·357 (5)
C(3)–N(3)	1·287 (4)	C(3)–N(10)	1·354 (5)
C(4)–N(4)	1·287 (4)	C(4)–N(12)	1·368 (4)
C(5)–N(5)	1·281 (5)	C(5)–N(13)	1·351 (5)
C(6)–N(8)	1·282 (5)	C(6)–N(15)	1·339 (5)
N(1)–N(2)	2·674 (4)		
N(3)–N(4)	2·702 (4)		
N(5)–N(6)	2·689 (4)		

Angles (°)

Co—N(1)–C(1)	129·7 (3)	N(1)—Co—N(2)	88·7 (2)
Co—N(2)–C(2)	130·6 (3)	N(3)—Co—N(4)	89·8 (2)
Co—N(3)–C(3)	128·9 (3)	N(5)—Co—N(6)	89·4 (2)
Co—N(4)–C(4)	128·7 (3)	C(1)—N(8)—C(2)	126·7 (3)
Co—N(5)–C(5)	127·9 (3)	C(3)—N(11)–C(4)	128·3 (3)
Co—N(6)–C(6)	128·7 (3)	C(5)—N(14)–C(6)	126·5 (3)
N(1)–C(1)–N(8)	121·4 (3)	N(7)—C(1)—N(8)	113·6 (4)
N(2)–C(2)–N(8)	121·7 (3)	N(8)—C(2)—N(9)	114·6 (4)
N(3)–C(3)–N(11)	121·4 (3)	N(10)–C(3)—N(11)	114·7 (3)
N(4)–C(4)–N(11)	122·0 (3)	N(11)–C(4)—N(12)	114·2 (3)
N(5)–C(5)–N(14)	121·6 (3)	N(13)–C(5)—N(14)	115·1 (3)
N(6)–C(6)–N(14)	120·9 (3)	N(14)–C(6)—N(15)	113·0 (3)
N(1)–C(1)–N(7)	125·0 (4)		
N(2)–C(2)–N(9)	123·7 (4)		
N(3)–C(3)–N(10)	123·9 (4)		
N(4)–C(4)–N(12)	123·7 (3)		
N(5)–C(5)–N(13)	123·3 (4)		
N(6)–C(6)–N(15)	126·0 (3)		

opposing sets of three non-linked ligator atoms. The cations are linked together by hydrogen bonds with the chloride anions. Table 7 shows that each chloride ion has at least four such interactions with N–H groups having Cl···N distances less than 3·4 Å. [Cl(2) and Cl(4) lie on twofold axes and only the unique contacts are listed in Table 7]. The range of N···Cl contacts (down to 3·21 Å) and N–H···Cl angles 126° to 180° found here lie well within the ranges (3·15 to 3·51 Å and 122° to 180°) established by neutron diffraction for NH to Cl hydrogen bonds (Hamilton & Ibers, 1968). The two disordered water molecules lie on a twofold axis and are hydrogen bonded by the hydrogen atom O(1)H(1) whose site is only half occupied (multiplier assigned on the basis of difference map peak height, 0·25). The water···water distance 2·83(1) Å, is at the upper end of the range, 2·69 to 2·81 Å, of water···water hydrogen bonds established in metal salts by neutron diffraction. Symmetry equivalent pairs of hydrogen bonds are formed by O(2)H(2) with Cl(3) and by O(1) with N(6)H.

Table 7. *Hydrogen bonds*

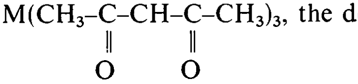
	A···*B*(Å)	*A*···H···*B*(°)
O(1)—O(2)	2·829 (8)	180 (0)
O(1)—N(6)	3·189 (4)	178 (4)
N(12)–N(14)	2·985 (4)	158 (5)
Cl(1) –N(4)	3·379 (3)	153 (4)
Cl(1) –N(12)	3·345 (4)	147 (4)
Cl(1) –N(10^{iii})	3·336 (4)	141 (4)
Cl(1) –N(7^{v})	3·230 (4)	153 (4)
Cl(2) –N(8)	3·212 (4)	158 (5)
Cl(2) –N(11^{ii})	3·223 (4)	142 (4)
Cl(3) –N(11)	3·343 (4)	126 (4)
Cl(3) –N(15^{iii})	3·323 (4)	178 (4)
Cl(3) –N(13^{iv})	3·317 (4)	159 (4)
Cl(3) –O(2^{vi})	3·163 (5)	165 (4)
Cl(3) –N12^{vii})	3·267 (4)	137 (4)
Cl(4) –N(2)	3·346 (3)	153 (4)
Cl(4) –N(9)	3·409 (5)	140 (4)
Cl(4) –N(13^{i})	3·210 (4)	163 (4)

I $-x,y,\frac{1}{2}-z$; II $\frac{1}{2}+x,\frac{1}{2}+y,z$; III $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; IV $\frac{1}{2}+x,y-\frac{1}{2},z$; V $\frac{1}{2}-x,-\frac{1}{2}-y,\frac{1}{2}+z$; VI $1-x,-y,\frac{1}{2}+z$; VII $1-x,y,\frac{1}{2}-z$.

The tris(*biguanide*)*cobalt*(III) *cation*

Fig. 2 shows the labelling scheme and the averaged molecular geometry of the cation. Standard deviations in the mean values are given in parentheses. The average cobalt–nitrogen distance, 1·912 Å, is in the range of cobalt(III)–trigonal nitrogen distances, 1·89–1·93 Å, found in Schiff-base complexes (Cesari, Neri, Perego, Perrotti & Zaggetta, 1970; Calligaris, Nardin & Randacci, 1970.)

The ligand geometry very closely resembles that found in ethylenebis(biguanidine)nickel(II) dichloride monohydrate by Holian & Marsh (1970). The two structures have comparable errors, and differences between their averaged geometries are only several standard deviations at most, and this result is also generally true for geometry involving the hydrogens. The conclusions of Holian & Marsh (1970) for the bond number of the ligand bonds and their resonance description of the bonding in terms of three principal canonical structures would also apply to the cobalt complex. The valence bond numbers are thus for N(ligand)–C, 1·5; for C–N(ring),1·2; and for N(terminal)–C, 1·3. It is probable, however, that there is little real difference between the last two bonds. Thermal corrections to the C–N(terminal) bonds with a mean value of +0·02 Å were computed with the assumption that N(terminal) rides on C. Any corrections to the ring bonds are most likely to be smaller and lead to near equality of the corrected C–N(ring) and C–N(terminal) bonds. Holian & Marsh (1970) observed that the N-H distances increased in the order N(ligand) < N(ring) < N(terminal). Fig. 2 shows the average values found in this study follow the same trend which Holian & Marsh have related to the formal charge on the various nitrogen atoms. The only noteworthy differences concern the angles metal–N–H and planarity of the ligand rings. In the nickel complex, the overall complex is planar and the hydrogen atoms of the Ni–N–H angles point towards each other and their mutual repulsion opens up this angle to 120° (*cf.* 111·6(8)° for the tris cobalt complex where this in-plane interaction is absent).

The guanidine residues $-NH-C(NH_2)-NH$ are only slightly non-planar; the average deviation of the carbon atom from the plane of the three nitrogen atoms is 0·013 Å, and the largest deviation [C(6)] is 0·03 Å. The angles between guanidine residues of the same ligand vary between 2° and 13°. Each chelate ring is significantly non-planar (Table 8) and shows the same mode of distortion. Each ligand has the cobalt, one ligand nitrogen and the ring nitrogen significantly out of the chelate ring plane. The ligand nitrogen atoms most displaced [N(1), N(3), and N(5)] are all at one end of the pseudo-threefold axis of the complex ion. This suggests that the distortions may be concerted and depend to some degree on intermolecular repulsions. In comparable unsaturated six-membered chelate ring systems such as those formed by acetylacetone,  $M(CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3)_3$, the degree of metal ion displacement from the ligand plane varies widely (Morosin & Montgomery, 1969) and the precise details of any ring distortion depend on its environment.

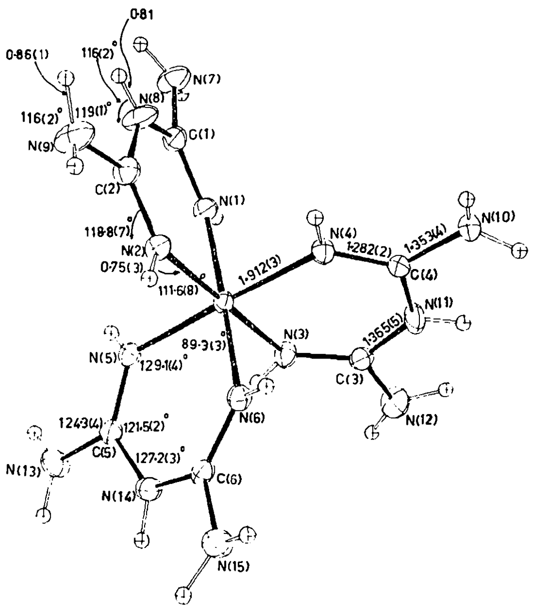


Fig. 2. Labelling scheme and average geometry of the Co(biguanide)$_3^{3+}$ cation.

Table 8. *Ligand planes and atomic deviations* (Å)

Plane 1		Plane 2		Plane 3	
Co	0·054	Co	0·064	Co	0·113
N(1)	−0·102	N(3)	−0·066	N(5)	−0·185
N(2)	0·001	N(4)	−0·040	N(6)	−0·016
C(1)	−0·014	C(3)	−0·016	C(5)	−0·007
C(2)	0·018	C(4)	0·012	C(6)	−0·010
N(7)	0·012	N(10)	0·023	N(13)	0·016
N(8)	0·096	N(11)	0·032	N(14)	0·171
N(9)	−0·066	N(12)	−0·008	N(15)	−0·082
N(2)H*	−0·06	N(3)H	−0·05	N(5)H	−0·23
N(1)H	−0·20	N(4)H(1)	−0·09	N(6)H	−0·21
N(9)H(1)	0·10	N(12)H(1)	0·11	N(15)H(1)	−0·26
N(9)H(2)	0·19	N(12)H(2)	0·31	N(15)H(2)	−0·20
N(8)H	0·11	N(11)H	−0·01	N(14)H	0·40
N(7)H(1)	−0·20 (5)	N(10)H(1)	−0·22	N(13)H(1)	−0·12
N(7)H(2)	−0·26	N(10)H(2)	0·09	N(13)H(2)	−0·06

Plane equations. Coordinate standard deviations are for Co, 4×10^{-4} for C and N, 4×10^{-3} and for H, 0·05 Å. Each plane is represented by $lx'+my'+nz'+p=0$ with respect to orthogonal axes, where x', y' and z' are coordinates in Å.

	Plane 1	Plane 2	Plane 3
l	0·82238	0·03940	−0·71573
m	−0·37384	0·77457	−0·31601
n	−0·42907	−0·63125	−0·62279
p	−1·22100	2·86362	4·48320

Angles between planes: 1 and 2, 89·2°; 1 and 3, 101·7°; 2 and 3; 83·1°.

* Hydrogen atoms were not included in the least-squares determination of the plane. Other atoms were equally weighted.

Recently there has been considerable interest in the geometry of trigonal metal complexes from the viewpoint of their reaction mechanism (Larsen, LaMar, Wagner, Parks & Holm, 1972) and their circular dichroism spectra (Butler & Snow, 1972). In 32 (D_3) symmetry the geometry of the metal and ligand atom core (here CoN_6) can be represented by the metal–ligand distance and two of three interrelated angles. These are the chelate bite angle N–Co–N, the angle that the N–Co bond makes with the threefold axis (θ) and the angle N–Co–N projected on to the plane perpendicular to the threefold axis (ω). The mean values and ranges of values of θ and ω are 54·58° (53·55° to 55·79°) and 58·42° (57·01° to 59·59°) respectively. The CoN_6 core therefore has a close approach to 32 symmetry which is not evident in the complete complex (see Table 8 where the angles between the ligand planes vary widely).

Absolute configuration

The $(+)_{589}[Co(bgH)_3]^{+3}$ ion has absolute configuration Δ. The structure of $(-)_{589}[Cr(bgH)_3]^{3+}$(*d*-10-camphorsulphonate)$_3$ by Brubaker & Webb (1969) shows that the $(+)_{589}[Cr(bgH)_3]^{3+}$ ion would have the same absolute configuration. According to Michelsen (1965) these enantiomorphs have the least soluble *l*-bromocamphorsulphonate diastereoisomers as well as similar c.d. spectra in the visible region of the spectrum (580 to 300 nm). Brubaker & Webb (1969) have incorrectly assigned the absolute configuration of $(-)_{589}[Co(bgH)_3]^{3+}$ as Δ on the basis of the effect of PO_4^{3-} on the solution rotatory strengths in the visible region of the c.d. spectrum. Igi, Yasui, Hidaka & Shimura (1971) have shown that the hydroxide ion has the same effect and generates the neutral, deprotonated $[Co(bg)_3]$ complex. These authors also confirm the validity of the visible ultraviolet c.d. spectrum for $(-)_{589}[Co(bgH)_3]^{3+}$ reported by Michelsen (1965), and suggested correctly that the absolute configuration of this species is Λ.

In the ultraviolet region of the c.d. spectrum Michelsen (1965) reports very intense bands for the cobalt and (chromium) complexes (same absolute configuration) at 247(242) and 218(222nm). The corresponding cobalt and chromium bands have opposite signs. It has been suggested (Igi *et al.*, 1971) that these bands arise from π–π^* transitions of the coordinated biguanide ligand. Split bands of this type have been interpreted as exciton splitting by several groups of workers (Mason, 1968; Bosnich, 1968, 1969; Ferguson, Hawkins, Kane-Maguire & Lip, 1969) in other systems where absolute configurations have been assigned using models for the exciton splitting.

Professor S.F. Mason (private communication) has also measured the circular dichroism spectrum of the $(-)_{589}[Co(bgH)_3]^{3+}$ complex and has extended it to lower wavelengths. He assigns the negative 247nm band to a charge transfer process, not an internal ligand transition, and reports a new negative band at 197nm. In the absence of a detailed analysis and confident assignment of this region of the c.d. the exciton method of assigning absolute configuration must therefore remain equivocal. Conversely, knowledge of the absolute configurations of both the Co and Cr complexes does add support to the assignment of the 247nm c.d. band of the Co species to a transition not localized on the ligand.

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