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Crystal and Molecular Structure of Potassium Nitro(ethylenediaminetriacetato)cobaltate(III)-1.5-Water

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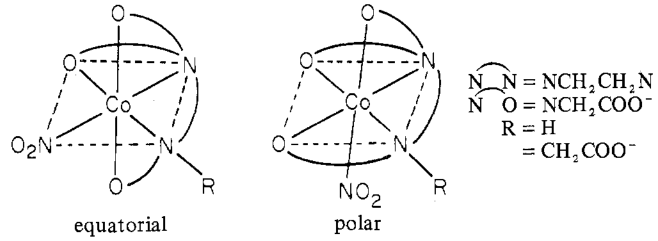
The structure of racemic potassium nitro(ethylenediaminetriacetato)cobaltate(III)-1.5-water, $KCo(C_8N_2O_6H_{11})(NO_2)\cdot 1.5H_2O$, has been determined from three-dimensional X-ray diffraction data collected with an automatic diffractometer. The complex crystallizes in space group $C2/c$ with eight molecules in the unit cell. The cell dimensions are $a = 17.29$ (1), $b = 15.70$ (1), $c = 13.78$ (1) Å, and $\beta = 129.7$ (1)°. The structure has been refined to convergence by full-matrix least-squares calculations to give a conventional R index (based on F) of 0.045 for 3872 observed reflections. When chelated to cobalt(III), the quinquedentate ethylenediamine-*N,N,N'*-triacetic acid ligand forms a coordination plane comprising one glycinate chelate ring, the ethylenediamine chelate ring, and the nitro group. The two remaining acetate groups coordinate the cobalt in positions axial to this plane. This geometric isomer, with the monodentate ligand in the plane of the ethylenediamine ring, is described as the equatorial isomer. The potassium ion is surrounded by seven oxygen atoms at distances of 2.67-2.88 Å. The orientation of the nitro group is stabilized by the involvement of one oxygen atom in a hydrogen bond with a water molecule. The geometric isomer found in this study confirms the results of a recent proton magnetic resonance study of nitro-substituted quinquedentate aminocarboxylate complexes of cobalt(III).

Introduction

When a quinquedentate ligand such as ethylenediaminetriacetic acid (ED3A), together with a monodentate ligand, such as the nitro group (NO_2^-), complexes cobalt(III), there are two possible geometric isomers which can result. They are described as equatorial or polar depending on the position that the monodentate ligand assumes relative to the coordination plane containing the ethylenediamine chelate ring (I).



I

A similar situation would exist in the EDTA (ethylenediaminetetraacetic acid)-Co(III) complex when one acetate group ($R^- = NCH_2COO^-$ in I) remains uncoordinated. The crystal structure of a nickel(II) complex of this type has been reported by Smith and Hoard.[1] Numerous studies of aminocarboxylate complexes[2-20] have indicated the existence of only one geometric isomer but have produced conflicting reports on which isomer is formed. In a recent proton magnetic resonance study, Blackmer and Sudmeier[20] found that the geminal coupling constants for glycinate AB splitting patterns, the results of a series of stereospecific acid- and base-catalyzed deuteration experiments, and chemical shift correlations could all be interpreted as evidence supporting the presence of the equatorial isomer alone. These results were in contrast with previous pmr and kinetic studies[17,19] which favored the existence of the polar isomer, based largely on the slow rate of base-catalyzed deuterium exchange.

The X-ray diffraction study reported here was undertaken to establish the correct structural isomer of the nitro(ethylenediaminetriacetato)cobaltate(III) complex. The structure is important because the ethylenediaminetriacetic acid ligand is a model for all quinquedentate aminopolycarboxylate acids, and the structure of this complex can therefore be used as the basis for structural assignment in a number of related complexes.

Experimental Section

Small red crystals of $KCo(C_8N_2O_6H_{11})(NO_2)\cdot 1.5H_2O$, formula weight 402.16, were prepared by the method of Blackmer, *et al.*[18] The space group was deduced from extinctions observed in precession and Weissenberg photographs to be either $C2/c$ or Cc (hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$ ($h = 2n + 1$) absent). The cell parameters were determined from a least-squares refinement based on diffractometer-centered setting angles of 14 strong reflections, determined with Mo Kα radiation (wavelengths (Å): $K\alpha_1$, 0.70926; $K\alpha_2$, 0.71354; $K\bar{\alpha}$, 0.71069) in the range $36 < 2\theta < 48°$. The standard deviations derived from this calculation were considered unreasonably small and the values listed have therefore been estimated: $a = 17.29$ (1), $b = 15.70$ (1), $c = 13.78$ (1) Å, $\beta = 129.7$ (1)° at 21°. The crystal density is 1.86 (1) g cm^{-3}, measured by suspension in a chloroform-bromoform mixture. The calculated density is 1.85 g cm^{-3} for eight formula units per unit cell. The crystal used in data collection was bounded by nine faces, with approximate dimensions 0.227 × 0.151 × 0.222 mm, and was oriented so that the $10\bar{1}$

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Table I. Fractional Atomic Positional and Thermal[a] Parameters[b] for $KCo(C_8N_2O_6H_{11})(NO_2)\cdot 1.5H_2O$

Atom	10^5x	10^5y	10^5z	$10^5\beta_{1,1}$	$10^5\beta_{2,2}$	$10^5\beta_{3,3}$	$10^5\beta_{1,2}$	$10^5\beta_{1,3}$	$10^5\beta_{2,3}$
Co	27,661 (2)	20,179 (2)	31,664 (3)	210 (1)	122 (1)	325 (2)	12 (1)	175 (2)	10 (1)
K	34,902 (5)	5,362 (4)	10,642 (6)	360 (3)	189 (2)	552 (5)	−24 (2)	315 (4)	7 (3)
O(1)	35,502 (14)	14,404 (12)	28,677 (18)	321 (10)	200 (7)	442 (15)	71 (7)	271 (11)	39 (8)
O(2)	48,872 (17)	6,128 (14)	37,745 (23)	411 (12)	287 (9)	794 (22)	129 (9)	415 (15)	85 (11)
O(3)	17,702 (14)	22,005 (11)	13,825 (18)	272 (10)	181 (7)	391 (15)	5 (6)	187 (10)	33 (7)
O(4)	15,432 (19)	28,968 (14)	−1,878 (21)	526 (14)	296 (9)	483 (18)	46 (9)	308 (14)	103 (10)
O(5)	19,920 (14)	25,732 (11)	34,999 (19)	332 (10)	156 (6)	597 (18)	14 (6)	345 (12)	21 (8)
O(6)	14,805 (19)	38,480 (14)	35,768 (24)	619 (16)	211 (8)	979 (25)	93 (9)	660 (18)	58 (11)
O(7)	12,789 (19)	8,829 (18)	24,238 (32)	352 (14)	364 (12)	1402 (38)	−71 (10)	329 (19)	197 (17)
O(8)	27,307 (19)	3,482 (13)	37,944 (23)	540 (15)	190 (8)	720 (23)	33 (8)	316 (16)	97 (10)
O(9)	15,313 (23)	5,933 (20)	1,263 (32)	490 (17)	369 (12)	848 (30)	22 (11)	297 (19)	−131 (15)
O(10)	50,000[c]	47,852 (27)	25,000[c]	500 (24)	384 (17)	924 (41)	0[c]	417 (27)	0[c]
N(1)	39,443 (16)	19,557 (14)	49,540 (20)	250 (10)	207 (8)	345 (16)	11 (8)	189 (11)	10 (9)
N(2)	32,346 (16)	31,497 (13)	31,360 (21)	261 (11)	155 (7)	454 (18)	−19 (7)	249 (12)	−15 (8)
N(3)	21,990 (18)	9,541 (14)	31,319 (23)	356 (13)	160 (8)	506 (20)	−7 (8)	286 (14)	2 (10)
C(1)	43,717 (20)	10,961 (17)	38,498 (27)	276 (13)	180 (9)	544 (22)	22 (8)	283 (15)	45 (11)
C(2)	46,702 (21)	13,397 (19)	51,092 (26)	251 (13)	266 (11)	389 (21)	63 (10)	173 (14)	70 (12)
C(3)	43,719 (22)	28,318 (18)	53,595 (27)	300 (14)	239 (11)	420 (21)	−57 (9)	195 (15)	−84 (12)
C(4)	43,076 (22)	32,233 (19)	43,061 (29)	281 (14)	213 (10)	559 (24)	−66 (9)	236 (16)	−29 (12)
C(5)	30,530 (23)	31,709 (17)	19,239 (27)	381 (15)	186 (9)	530 (23)	−1 (9)	352 (17)	41 (11)
C(6)	20,454 (21)	27,396 (16)	9,370 (26)	342 (14)	155 (8)	459 (21)	54 (8)	280 (15)	30 (10)
C(7)	25,785 (22)	37,905 (16)	31,102 (29)	390 (16)	131 (8)	610 (25)	5 (9)	365 (18)	−4 (11)
C(8)	19,707 (20)	33,906 (16)	34,247 (25)	324 (14)	180 (9)	426 (21)	21 (9)	267 (15)	14 (11)

Atom	10^3x	10^3y	10^3z	B, Å^2	Atom	10^3x	10^3y	10^3z	B, Å^2
H(1)	378 (3)	176 (2)	541 (3)	2.4 (7)	H(8)	361 (2)	286 (2)	208 (3)	1.5 (6)
H(2)	465 (3)	82 (2)	545 (3)	2.2 (7)	H(9)	306 (3)	378 (2)	168 (4)	2.9 (8)
H(3)	535 (3)	159 (3)	570 (4)	3.4 (9)	H(10)	217 (3)	404 (2)	229 (4)	2.6 (8)
H(4)	400 (3)	313 (2)	553 (3)	2.0 (7)	H(11)	300 (3)	430 (2)	371 (4)	2.6 (7)
H(5)	507 (3)	279 (2)	619 (3)	2.0 (7)	H(12)	99 (4)	55 (3)	−62 (5)	4.4 (11)
H(6)	474 (3)	289 (2)	421 (3)	2.1 (7)	H(13)	141 (5)	90 (5)	39 (7)	8.3 (21)
H(7)	450 (3)	382 (3)	449 (4)	2.9 (8)	H(14)	539 (3)	511 (3)	251 (5)	4.8 (11)

[a] The form of the anisotropic temperature parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the least significant figures are given in parentheses here and elsewhere in this paper. [c] Parameter fixed by crystallographic symmetry and not refined.

Table II. Interatomic Distances (Å)

Co–O(1)	1.882 (2)	N(3)–O(8)	1.230 (3)
Co–O(3)	1.919 (4)	K–O(2$^{\mathrm{i}}$)	2.672 (3)
Co–O(5)	1.884 (2)	K–O(2)	2.877 (5)
Co–N(1)	1.954 (4)	K–O(1)	2.806 (3)
Co–N(2)	1.965 (2)	K–O(4$^{\mathrm{ii}}$)	2.725 (3)
Co–N(3)	1.923 (3)	K–O(6$^{\mathrm{iii}}$)	2.692 (3)
O(1)–C(1)	1.299 (4)	K–O(8$^{\mathrm{iv}}$)	2.862 (4)
C(1)–O(2)	1.225 (3)	K–O(9)	2.751 (4)
C(1)–C(2)	1.510 (4)	N(1)–H(1)	0.89 (4)
C(2)–N(1)	1.488 (4)	C(2)–H(2)	0.96 (4)
N(1)–C(3)	1.492 (4)	C(2)–H(3)	0.99 (4)
C(3)–C(4)	1.514 (4)	C(3)–H(4)	0.94 (3)
C(4)–N(2)	1.495 (4)	C(3)–H(5)	1.01 (4)
N(2)–C(5)	1.490 (4)	C(4)–H(6)	0.98 (4)
C(5)–C(6)	1.523 (5)	C(4)–H(7)	0.98 (4)
C(6)–O(3)	1.301 (3)	C(5)–H(8)	0.98 (3)
C(6)–O(4)	1.224 (4)	C(5)–H(9)	1.01 (4)
N(2)–C(7)	1.500 (3)	C(7)–H(10)	0.95 (4)
C(7)–C(8)	1.506 (4)	C(7)–H(11)	1.05 (4)
C(8)–O(5)	1.287 (3)	O(9)–H(12)	0.84 (5)
C(8)–O(6)	1.227 (3)	O(9)–H(13)	0.70 (7)
N(3)–O(7)	1.232 (4)	O(10)–H(14)	0.84 (4)

Table III. Interatomic Angles (deg)[a]

O(1)–Co–O(3)	88.6 (1)	O(5)–C(8)–O(6)	123.9 (3)
O(1)–Co–O(5)	178.4 (1)	O(7)–N(3)–O(8)	119.6 (3)
O(1)–Co–N(1)	86.2 (1)	Co–O(1)–C(1)	115.7 (2)
O(1)–Co–N(2)	93.8 (1)	Co–O(3)–C(6)	113.7 (2)
O(1)–Co–N(3)	90.2 (1)	Co–O(5)–C(8)	115.5 (2)
O(3)–Co–O(5)	92.7 (1)	Co–N(1)–C(2)	108.6 (2)
O(3)–Co–N(1)	169.2 (1)	Co–N(1)–C(3)	107.1 (2)
O(3)–Co–N(2)	83.3 (1)	Co–N(2)–C(4)	107.0 (2)
O(3)–Co–N(3)	94.1 (1)	Co–N(2)–C(5)	104.4 (2)
O(5)–Co–N(1)	92.7 (1)	Co–N(3)–O(7)	118.7 (2)
O(5)–Co–N(2)	87.3 (1)	Co–N(3)–O(8)	121.7 (2)
O(5)–Co–N(3)	88.7 (1)	O(2$^{\mathrm{i}}$)–K–O(2)	85.6 (1)
N(1)–Co–N(2)	87.7 (1)	O(2$^{\mathrm{i}}$)–K–O(1)	117.4 (1)
N(1)–Co–N(3)	95.3 (1)	O(2$^{\mathrm{i}}$)–K–O(4$^{\mathrm{ii}}$)	73.8 (1)
N(2)–Co–N(3)	175.1 (1)	O(2$^{\mathrm{i}}$)–K–O(6$^{\mathrm{iii}}$)	97.7 (1)
O(2)–C(1)–C(2)	121.4 (3)	O(2$^{\mathrm{i}}$)–K–O(8$^{\mathrm{iv}}$)	80.7 (1)
O(1)–C(1)–C(2)	115.8 (2)	O(2$^{\mathrm{i}}$)–K–O(9)	161.9 (1)
O(1)–C(1)–O(2)	122.8 (3)	O(2)–K–O(1)	45.9 (1)
C(1)–C(2)–N(1)	111.2 (2)	O(2)–K–O(4$^{\mathrm{ii}}$)	107.5 (1)
C(2)–N(1)–C(3)	112.0 (2)	O(2)–K–O(6$^{\mathrm{iii}}$)	84.3 (1)
N(1)–C(3)–C(4)	107.5 (2)	O(2)–K–O(8$^{\mathrm{iv}}$)	149.1 (1)
C(3)–C(4)–N(2)	106.5 (2)	O(2)–K–O(9)	111.7 (1)
C(4)–N(2)–C(5)	115.8 (2)	O(1)–K–O(4$^{\mathrm{ii}}$)	85.1 (1)
N(2)–C(5)–C(6)	107.0 (2)	O(1)–K–O(6$^{\mathrm{iii}}$)	110.5 (1)
C(5)–C(6)–O(3)	115.0 (2)	O(1)–K–O(8$^{\mathrm{iv}}$)	160.9 (1)
C(5)–C(6)–O(4)	121.6 (3)	O(1)–K–O(9)	74.8 (1)
O(3)–C(6)–O(4)	123.4 (3)	O(4$^{\mathrm{ii}}$)–K–O(6$^{\mathrm{iii}}$)	164.5 (1)
C(4)–N(2)–C(7)	111.9 (2)	O(4$^{\mathrm{ii}}$)–K–O(8$^{\mathrm{iv}}$)	95.1 (1)
C(5)–N(2)–C(7)	110.1 (2)	O(4$^{\mathrm{ii}}$)–K–O(9)	95.2 (1)
N(2)–C(7)–C(8)	111.7 (2)	O(6$^{\mathrm{iii}}$)–K–O(8$^{\mathrm{iv}}$)	70.4 (1)
C(7)–C(8)–O(5)	116.7 (2)	O(6$^{\mathrm{iii}}$)–K–O(9)	89.5 (1)
C(7)–C(8)–O(6)	119.4 (2)	O(8$^{\mathrm{iv}}$)–K–O(9)	86.2 (1)

[a] Symmetry transformations are indicated by superscripts: (i) $1 - x, y, 0.5 - z$; (ii) $0.5 - x, 0.5 - y, -z$; (iii) $0.5 - x, -0.5 + y, 0.5 - z$; (iv) $x, -y, -0.5 + z$; (v) $0.5 - x, 0.5 - y, 1 - z$; (vi) $-0.5 + x, -0.5 + y, z$.

reciprocal lattice vector was approximately 3.5° from the diffractometer ϕ axis.

Reflection data were collected on a Syntex four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Intensities were measured in the range $2.2 < 2\theta < 70°$, with a θ-2θ scan, and a scan range in 2θ from $-1.15°$ from the Kα_1 peak to $+1.2°$ from the Kα_2 peak. The scan speed for each reflection was calculated from a preliminary stationary-crystal, stationary-counter inspection of the intensity and varied between 1.0 and 24.0°/min in such a way as to maintain satisfactory counting statistics even for reflections of only moderate intensity, while minimizing the total time required for data collection. Background counts were measured at each end of the scan, the summed counting times being equal to half the scan time. When the count rate from any $^1/_{96}$th of the scan range of a

Table IV. Least-Squares Planes

(a) Equations of Planes: $lx' + my' + nz' + p = 0^a$

Plane no.	Atoms included in plane	l	m	n	p
1	O(1), O(2), N(1), C(1), C(2)	0.635	0.770	0.057	−4.215
2	O(3), O(4), N(2), C(5), C(6)	0.686	−0.724	0.071	1.216
3	O(5), O(6), N(2), C(7), C(8)	0.162	0.074	0.984	−4.037
4	N(1), N(2), C(3), C(4)	−0.849	0.501	0.169	−0.489
5	N(3), O(7), O(8)	−0.602	0.325	0.729	−2.279

(b) Distances of Atoms from Planes, Å

Plane no.	Atoms and distances
1	O(1), −0.004; C(2), 0.012; N(1), 0.012; C(1), −0.007; C(2), −0.013; Co, −0.315
2	O(3), 0.084; O(4), −0.147; N(2), −0.186; C(5), 0.216; C(6), 0.033; Co, 0.529
3	O(5), −0.027; O(6), 0.047; N(2), 0.059; C(7), −0.073; C(8), −0.006; Co, −0.176
4	N(1), −0.150; N(2), 0.148; C(3), 0.288; C(4), −0.285; Co, −0.028
5	Co, −0.002

[a] x', y', z' are orthogonalized coordinates (in Å) parallel to the a, b, and c^* axes.

Table V. Distances (Å) and Angles (deg) of Atoms Involved in Hydrogen Bonding

O(3)---O(9)	2.937 (4)	O(3)---H(13)	2.32 (7)
O(6)---N(1^{v})	2.851 (3)	O(6)---H(1^{v})	1.97 (4)
O(7)---O(10^{vi})	2.857 (4)	O(7)---H(14^{vi})	2.02 (4)
O(10)---O(9^{ii})	2.868 (6)	O(10)---H(12^{ii})	2.07 (5)

O(3)---H(13)---O(9)	148 (7)	O(7)---H(14^{vi})---O(10^{vi})	177 (5)
O(6)---H(1^{v})---N(1^{v})	170 (3)	O(10)---H(12^{ii})---O(9^{ii})	159 (4)

Table VI. Conformations of Chelate Rings

Chelate ring	Conformn[a]	$\vert\alpha\vert$	β
O(1), C(1), C(2), N(1)	λ	6.7 (1)	−1.0 (3)
N(1), C(3), C(4), N(2)	δ	28.5 (2)	54.0 (3)
N(2), C(5), C(6), O(3)	λ	19.8 (1)	−24.5 (3)
N(2), C(7), C(8), O(5)	λ	6.8 (1)	−8.8 (4)

[a] Conformations are those for the molecule illustrated in Figure 1.

reflection exceeded the maximum linear count rate, the true count for that fraction of the scan was calculated from the observed value using a parabolic approximation to the Schiff formula.[21] The intensities of three standard reflections were measured at 80 reflection intervals and remained essentially constant. The values of $\sigma(I)$ were calculated in a manner similar to that of Corfield, *et al.*,[22] from $\sigma^2(I) = \sigma_c^2 + (0.04I)^2$, where σ_c is the standard deviation of the intensity I, derived from counting statistics. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects using the expression[23] $Lp^{-1} = \sin 2\theta + \cos^2 2\theta_m$, where $2\theta_m$ is the monochromator angle. The linear absorption coefficient for Mo Kα radiation is 15.8 cm^{-1}, and from a calculation of transmission coefficients for selected reflections it was concluded that absorption corrections were unnecessary.

Solution and Refinement of the Structure

The coordinates of the cobalt and potassium atoms were determined from a three-dimensional Patterson synthesis. The space group was assumed to be centrosymmetric *C*2/*c*, rather than *Cc*. The positions of the nonhydrogen atoms, with the exception of a water oxygen atom, were obtained from a heavy-atom Fourier synthesis. The scattering curves used were those of Cromer and Waber[24] with the exception of the hydrogen curve, which was that derived by Stewart, *et al.*[25] The effects of anomalous dispersion were included in calculations, with the values of $\Delta f'$ and $\Delta f''$ given by Cromer.[26] Three least-squares refinement calculations with isotropic temperature parameters reduced the discrepancy factors $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ to 0.12 and 0.15, respectively, for 5758 reflections. In these and subsequent calculations 1135 reflections for which $I < 1.95\sigma_B$ (where σ_B is the standard deviation of the background measurement of a reflection with intensity I) were considered unobservably weak and excluded from the refinement. Also excluded was the reflection 200 whose intensity was too large to permit a satisfactory coincidence correction. The weights, $w(F)$, were assigned as $1/\sigma^2(F)$.

Based on a subsequent structure factor calculation, a difference Fourier synthesis revealed a water molecule oxygen atom lying on a twofold axis and peaks close to the expected positions of all except two of the hydrogen atoms. In two subsequent least-squares calculations all hydrogen atoms were included in calculated positions (C–H = 1.05 Å, N–H = 0.95 Å), with isotropic temperature factors of 3.5 Å^2, but were not refined. The nonhydrogen atoms were refined with anisotropic temperature parameters. In three additional least-squares calculations all position and temperature parameters were optimized. An analysis of the function minimized, $\Sigma w(F_o - F_c)^2$, indicated no dependence on $|F_o|$ or $\sin\theta$, with the exception of a group comprising the 751 smallest structure amplitudes. Further examination revealed that these reflections should have been treated as unobservably weak, and they were excluded from two final cycles of refinement.

The final values of R_1 and R_2 were 0.0450 and 0.0487 for the 3872 observed data, and 0.0832 and 0.0526 for all data. In the last refinement cycle the positional parameter shifts were less than 0.3 times and the thermal parameter shifts less than their respective standard deviations. The estimated standard deviation of an observation of unit weight was 1.53. The final atomic parameters are listed in Table I. A difference Fourier synthesis using the structure factors calculated from these parameters showed no significant maxima. No evidence was found to indicate disorder in the positions of the nitro group oxygen atoms. The final values of $2|F_o|$ and $2F_c$ in electrons are given in Table VII.[27] For the unobserved reflections, which are not listed in this table, no structure factor exceeded the minimum structure amplitude of the observed data by more than $3\sigma(F)$. No evidence of secondary extinction was found.

Description of the Structure

The crystal structure consists of nitro(ethylenediaminetriacetato)cobaltate(III) complexes, packed so as to provide five carboxyl oxygen atoms able to make contacts with the potassium ions. Figure 1 shows a stereoscopic view of the complex, which this study has established to be the equatorial isomer as postulated earlier.[20] The bond lengths and potassium–oxygen contacts are listed in Table II, with the

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(21) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," Wiley, New York, N. Y., 1949.

(22) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(23) The term $(1 + \cos^2 2\theta_m)$ which normally appears in the numerator was a constant for all data and was therefore not included.

(24) D. T. Cromer and J. A. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(25) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(26) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(27) Table VII will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-836.

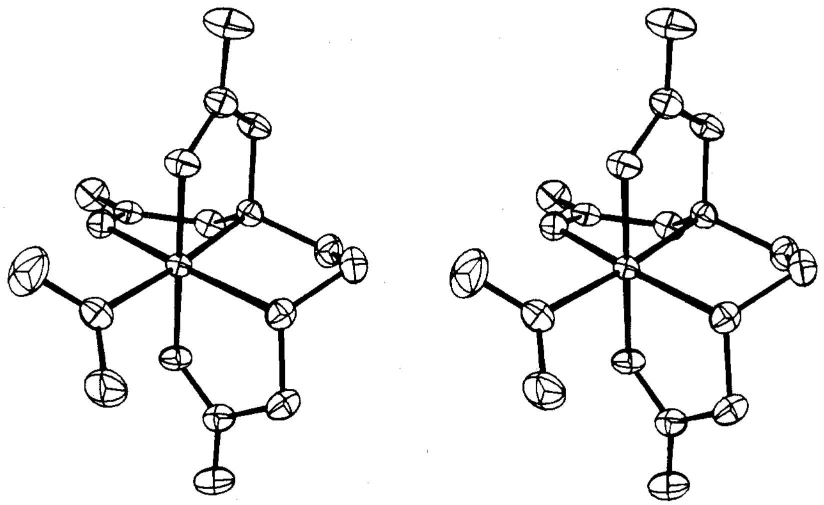

Figure 1. A stereoscopic view of the complex molecule $Co(O_8N_2C_6H_{11})(NO_2)$. The hydrogen atoms have been omitted for clarity. The thermal ellipsoids represent 50% probability.

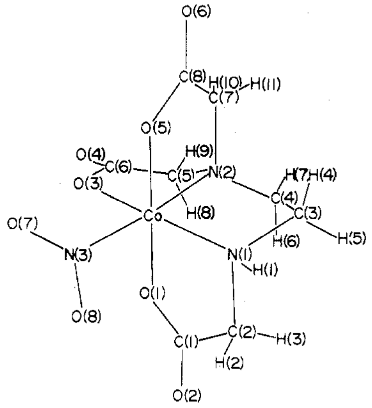

Figure 2. Diagram showing the atom numbering system used in this paper.

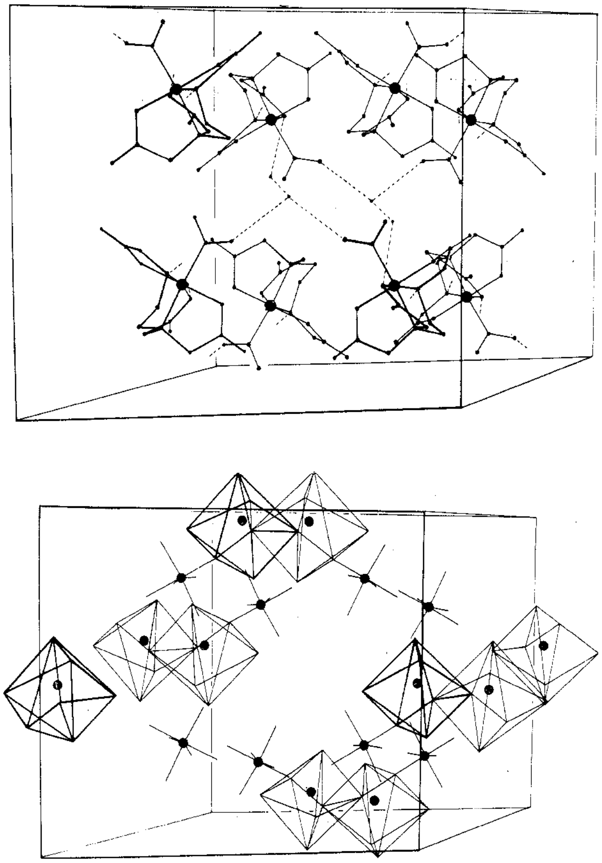

Figure 3. Two illustrations showing the unit cell contents viewed approximately down the *c* axis. The packing of the potassium polyhedra and the complex molecules are shown separately for clarity. The potassium ions are represented as shaded circles at the centers of the polyhedra. Hydrogen bonds are shown as broken lines.

associated bond angles given in Table III. Angles including hydrogen atoms are not listed. The atom numbering scheme is shown in Figure 2. In the ethylenediaminetriacetic acid-cobalt(III) complex the Co-N bond lengths are not significantly different, with a mean value of 1.960 (5) Å. However, the Co-O bond lengths show significant differences between the bond in the plane of the nitrogen ligators, 1.919 (2) Å, and the bonds axial to this plane, 1.883 (2) Å. These compare with the values of 1.915 (5) and 1.885 (15) Å found in the cobalt complex of ethylenediaminetetraacetic acid.[28] Table IV indicates that the axial glycinate chelate rings are relatively planar, unlike the in-plane glycinate or the ethylenediamine chelate rings. This planarity of the axially coordinated glycinate rings has been postulated, through nmr studies, as being the primary factor controlling the rates of deuterium exchange in complexes of this type. The angles subtended at the cobalt atom by the chelate rings lie in the range 83.3-87.7°, with the largest angle being associated with the ethylenediamine ring. The Co-N(nitro) bond length, 1.923 (3) Å, is significantly shorter than values reported for bromodinitrotriamminecobalt(III),[29] 1.98 Å, and for chlorodinitrotriamminecobalt(III),[30] 1.99 (5) Å. The nitro group N-O bond length, 1.231 (3) Å (mean), and the O-N-O bond angle, 119.6 (3)°, are comparable with those found in other complexes (1.22, 1.24 Å; 119° [29]) (1.22-1.25 Å; 118, 121° [30]) and with values for the NO_2^- ion in sodium nitrate[31] (1.236 (14) Å; 115.4 (17)°).

Distances and angles associated with four hydrogen bonds are listed in Table V. Only one hydrogen bond directly links adjacent complex molecules. The other three involve water molecules, with O(9) acting as a hydrogen donor in two bonds but not as an acceptor because of its interaction

(28) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 81, 549 (1959).

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with the potassium ion, while O(10) forms two pairs of symmetry-related hydrogen bonds, including one with the nitro oxygen atom O(7). This last hydrogen bond stabilizes the nitro group so that the angle between the plane of this group and that of the coordination plane Co, O(3), N(1), N(2), N(3) is 35.9°.

The potassium ions are surrounded by seven oxygen atoms at distances of 2.672 (3)-2.877 (5) Å. One carboxyl oxygen atom in this group makes the shortest contact with one potassium ion and also the longest contact with an adjacent (symmetry-related) potassium. The polyhedra occur in pairs, sharing an edge, as shown in Figure 3.

The configuration of the complex illustrated in Figure 1 can be described using the proposed IUPAC nomenclature[32] as Δ, and the chelate ring conformations as δ-$\lambda\lambda\lambda$. The enantiomer is therefore described as Λ, λ-$\delta\delta\delta$. Ring conformations in complexes of this type have recently been discussed by Lee.[33] The dihedral angle α, defined as the angle between the plane which contains the ring carbon atoms and the cobalt atom and the plane which contains the ligator atoms and the cobalt atom, is listed in Table VI, together with the conventional torsional angle β.

Computer programs used were from the UCLA crystallographic library and included ORXFLS,[34] ORXFFE,[35] and ORTEP.[36]

Registry No. $KCo(C_8N_2O_6H_{11})(NO_2)\cdot 1.5H_2O$, 37448-69-4.

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Crystal and Molecular Structure of an Ortho-Metalated Benzylidineaniline-Manganese Carbonyl Complex, Tetracarbonyl-2-(*N*-phenylformimidoyl)phenylmanganese, $C_6H_5NCHC_6H_4Mn(CO)_4$

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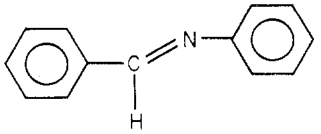
The structure of tetracarbonyl-2-(*N*-phenylformimidoyl)phenylmanganese, a product of the reaction of $CH_3Mn(CO)_5$ with benzylidineaniline, has been determined by a single-crystal X-ray structural analysis. Crystals of $C_6H_5NCHC_6H_4Mn(CO)_4$ are monoclinic, space group $P2_1/c$, with $a = 9.548$ (4), $b = 9.154$ (3), $c = 18.201$ (6) Å, $\beta = 102.07$ (2)°. Observed and calculated ($Z = 4$) densities are 1.48 and 1.47 (1) g/cm³, respectively. The structure determination was based upon 1530 independent nonzero intensity data with $2\theta \leqslant 50°$ collected by counter methods. Full-matrix anisotropic-isotropic least-squares refinement converged to a final conventional discrepancy factor of 0.071. The crystal structure is composed of monomeric molecular units, in which the manganese atom is coordinated in a distorted octahedral configuration to four carbonyl groups and to the chelating ligand. The ligand is bound *via* a metal-nitrogen bond and a metal-carbon σ bond to the ortho position of the benzylidine phenyl ring, forming a planar five-membered chelate ring. The conformation of the coordinated ligand closely resembles that of free benzylidineaniline; in particular, the aniline phenyl ring is twisted by 57.0° from the CC=NC plane. The Mn–C(phenyl) and Mn–N bond distances are 2.060 (8) and 2.070 (7) Å, respectively. Some apparently significant variation in the Mn–C(carbonyl) distances is observed.

Introduction

The Schiff base benzylidineaniline (bza, I) is isoelectronic with azobenzene (azb) and has been shown[1-4] to undergo ortho-metalation reactions similar to those observed for azobenzene.[5,6] In the resulting complexes, the bza has been proposed to be bound to the metal atom in a chelated fashion *via* a nitrogen→metal dative bond and a metal–phenyl carbon σ bond. This mode of coordination was first proposed by Cope and Siekman[7] for a series of palladium(II)-azobenzene derivatives and first demonstrated crystallographically in acetatobis[2-(phenylazo)phenyl]-rhodium.[8] Complexes of bza believed to have structure II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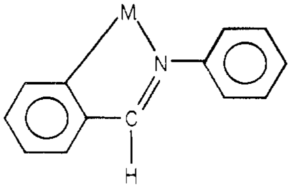
II

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