CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WESTERN ONTARIO,
LONDON 72, ONTARIO, CANADA

The Crystal Structure and Absolute Configuration of (+)$_{546}$-*trans*-Dinitro(1,10-diamino-4,7-diazadecane)cobalt(III) Bromide

BY NICHOLAS C. PAYNE

Received June 24, 1971

The crystal structure and absolute configuration of (+)$_{546}$-*trans*-dinitro(1,10-diamino-4,7-diazadecane)cobalt(III) bromide, (+)[Co{$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$}$(NO_2)_2$]Br, have been determined from three-dimensional X-ray data collected by counter methods. The crystals are monoclinic, with a = 7.848 (5), b = 14.756 (12), c = 6.397 (5) Å, β = 99.5 (1)°, and two formula units in space group $P2_1$. The structure was solved by application of Patterson and Fourier techniques and refined on F by full-matrix least-squares methods to a final residual R_1 = 0.038. The absolute configuration of the cation was determined by the Bijvoet method. The inner coordination sphere around the cobalt atom is approximately octahedral, with the tetradentate linear tetramine occupying the equatorial plane and two nitro ligands the apices. The conformation of the five-membered chelate ring is gauche, with absolute configuration δ. The two six-membered chelate rings assume the chair conformation. The configurations of the asymmetric secondary nitrogen atoms are both R.

Introduction

The linear tetramine 1,10-diamino-4,7-diazadecane, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (hereafter 3,2,3-tet), can act as a tetradentate ligand and form complexes with Co(III).[1] There are three possible geometrical forms of the [Co(3,2,3-tet)X_2]$^{n+}$ ion, two cis isomers, designated α and β, and one trans isomer. Coordination of 3,2,3-tet in complexes where X is a unidentate ligand appears to occur with a preference for the trans topology. A source of further asymmetry arises in the trans structure from the two secondary amine groups. There are three possible isomers, depending upon the configurations at the nitrogen atoms, the antimeric *RR* and *SS* forms and the internally compensated *RS* (meso) form.[1] A study of scale models suggests that for the *RS* (meso) configuration, the ethylene fragment in 3,2,3-tet will assume an eclipsed form, while both the *RR* and *SS* configurations result in a gauche conformation. In many cases, in the absence of strong hydrogen-bonding effects,[2] the gauche conformation of a chelated ethylenediamine ligand has been demonstrated to be energetically favored over the eclipsed form.[3] If the gauche conformation occurs, then resolution of the complex should be possible since the *RR* and *SS* configurations are antimeric. The two six-membered chelate rings formed upon coordination can assume skew, boat, or chair conformations. A consideration of nonbonding intramolecular repulsions suggests that the chair and skew forms will be more stable thermodynamically than the boat form.[4] The chair conformation has been observed in the tris(1,3-diaminopropane)cobalt(III) ion for the six-membered chelate rings.[5] In a recent letter, the optical properties of *trans-RR*-[Co(3,2,3-tet)Cl_2]$^+$ and *trans-RR*-[Co(3,2,3-tet)Br_2]$^+$ were reported.[6]

We present here the result of a crystal structure and absolute configuration determination of the (+) isomer of the [$(NO_2)_2$Co(3,2,3-tet)]$^+$ ion, which was undertaken to determine the absolute configurations of the asymmetric secondary nitrogen atoms and the conformations of the chelate rings. The optical properties of the enantiomer studied are presented in Figure 1.[7]

Experimental Section

A crystalline sample was supplied by Dr. J. N. MacB. Harrowfield and Dr. B. Bosnich. *trans*-Dinitro(1,10-diamino-4,7-diazadecane)cobalt(III) bromide crystallizes as transparent orange plates, elongated along [001]. A preliminary photographic X-ray examination showed monoclinic symmetry, Laue group $2/m$. Systematic absences restricted to $0k0$ when $k = 2n + 1$ suggested space groups $P2_1/m$-$C_{2h}{}^2$ or $P2_1$-$C_2{}^2$.[8] Since the material is optically active, space group $P2_1$ (no. 4) was chosen. Unit cell parameters were obtained from a least-squares refinement of diffractometer setting angles,[9] using Mo Kα_1 radiation (λ 0.70926 Å); a = 7.848 (5), b = 14.756 (12), c = 6.397 (5) Å, and β = 99.5 (1)°. The density of the crystals was determined by flotation in a mixture of chloroform and 1,2-dibromoethane, and the value observed, 1.87 (1) g cm^{-3}, is in agreement with the value 1.84 g cm^{-3} calculated for two formula units per cell. There are no crystallographic symmetry conditions imposed upon the ions.

A crystal was selected for data collection of approximate dimensions 0.15 mm × 0.05 mm × 0.05 mm and mounted with the long dimension [001] approximately parallel to the diffractometer ϕ axis. An optical examination identified the crystal faces as $(\bar{2}\bar{1}0)$, $(2\bar{1}0)$, $(1\bar{2}0)$, $(\bar{1}\bar{2}0)$, and (100) and forms {010} and {001}. The crystal was measured with a micrometer eyepiece in preparation for an absorption correction, for which μ(Mo Kα) = 41 cm^{-1}.

A series of ω scans through intense reflections showed an average width at half-height of 0.1°. This value was considered satisfactory.[10]

Intensity data were recorded on a Picker four-circle automatic diffractometer. Molybdenum radiation was used for data collection, and the diffracted beam was filtered through 0.11 mm of Zr foil. At the takeoff angle of 1.1° the intensity of the beam was 80% of the maximum attainable. The counter was placed 32 cm from the crystal, with an aperture 4 mm × 4 mm. A symmetric scan range of 1° was sufficient, employing the θ–2θ scan technique, at a scan rate of 1°/min. Stationary-crystal, stationary-counter background measurements of 10 sec were made at each end of a scan. A unique data set (hkl) was first collected, for 2θ less than 50°. At higher 2θ values, there was

---

[1] M. D. Alexander and H. G. Hamilton, Jr., *Inorg. Chem.*, **8**, 2131 (1969).

[2] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 842 (1968).

[3] E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

[4] B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, **8**, 2567 (1969).

[5] Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Jap.*, **41**, 530 (1968).

[6] G. R. Brubaker and D. P. Schaefer, *Inorg. Nucl. Chem. Lett.*, **6**, 237 (1970).

[7] J. N. MacB. Harrowfield and B. Bosnich, private communication.

[8] "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1962.

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

[10] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

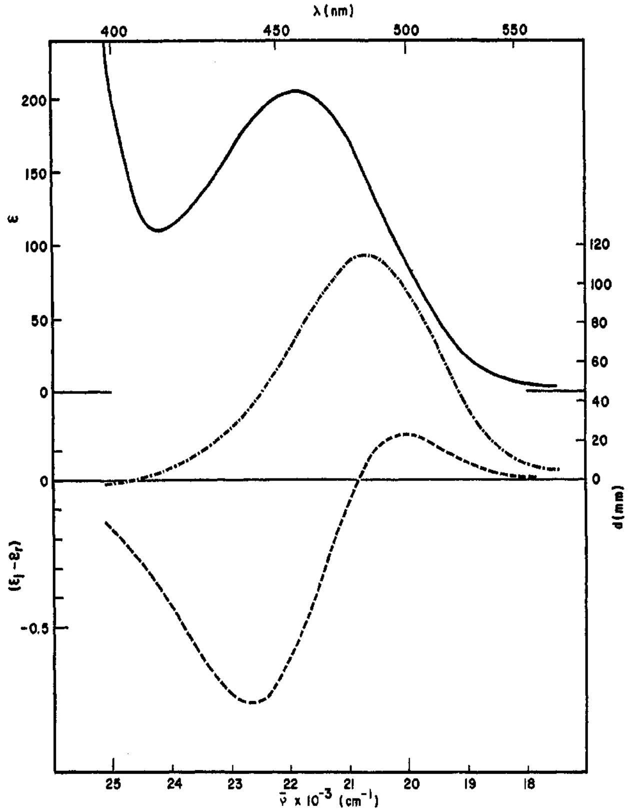

Figure 1.—Absorption and CD spectra of $(+)_{546}$[Co(3,2,3-tet)(NO$_2$)$_2$]Br: ——, electronic spectrum in water; - - - - -, CD spectrum in water; –·–·–, CD spectrum of a 1% KBr disk, sensitivity 5 mdeg cm^{-1}.

little or no intensity observed. The pulse height analyzer was set to accept a window of approximately 90% when centered on the Mo Kα_1 peak. Coincidence losses for strong reflections were minimized by insertion of copper foil attenuators with attenuator factors of approximately 2.0. During the collection of the data, three intense, axial reflections (100), (040), and (002) were monitored after every 100 reflections recorded. The intensities observed showed only a statistical variation throughout data collection. The Friedel pair data set ($\bar{h}\bar{k}\bar{l}$) was then collected under the same conditions. In all, 1438 (hkl) reflections were collected. The 1151 unique reflections for which $F^2 > 2\sigma(F^2)$ were used in the solution and refinement of the structure.

The data were then corrected for background and Lorentz-polarization effects. Standard deviations were assigned as described previously,[9] using a value of $p = 0.04$.[11] Absorption correction trials using $\mu = 41.0$ cm^{-1} for Mo Kα radiation showed transmission factors varying from 0.67 to 0.79, so an absorption correction was applied.[12]

Structure Solution and Refinement

Initial coordinates for the cobalt and bromine atoms were determined from a Patterson synthesis. The y coordinate of the cobalt atom was chosen as $^1/_4$ to fix the origin of the unit cell. Of the two possible Br positions determined from the Patterson synthesis, related by the mirror plane $y = {}^1/_4$, one was arbitrarily chosen at this point.

One cycle of full-matrix, least-squares refinement varying positional and isotropic thermal parameters of the two atoms gave values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.43$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.53$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and the weight w was calculated as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Br, Co, O, N, and C were taken from Cromer and Waber;[13] that of H was from Stewart, *et al.*[14] The real and imaginary anomalous dispersion corrections for Co and Br of Cromer were used.[15] A series of least-squares refinements and difference Fourier syntheses located the remaining nonhydrogen atoms. Two cycles of least-squares refinement of the 20 nonhydrogen atoms, with isotropic thermal parameters, reduced R_1 and R_2 to 0.097 and 0.128, respectively.

Two possible enantiomeric structures exist—that chosen up to this point, referred to as structure R, and its mirror image referred to as structure L. These are related in space group $P2_1$ by a mirror plane perpendicular to b. To distinguish between the two, the refinement on structure R was continued and, with isotropic thermal parameters, coverged at $R_1 = 0.080$ and $R_2 = 0.109$. The atomic positional parameters were then reflected across $y = {}^1/_4$ to give structure L and refined using isotropic thermal parameters and the same data. The refinement of structure L converged at $R_1 = 0.102$ and $R_2 = 0.136$. The R-factor ratio test applied to the weighted agreement factors, R_2, shows that the L structure may be conclusively rejected at the 0.005 level.[16]

It has been shown that the choice of the wrong enantiomer for the value of $\Delta f''$ applied to the scattering factor will lead to polar dispersion errors in the coordinates of atoms for which there are anomalous scattering effects.[17] An examination of the geometry of the refined cations showed the Co–N(1) and Co–N(3) vectors to be within 7° of the y axis. In space group $P2_1$ the error will be in the y coordinate.[18]

An incorrect choice of enantiomer should therefore result in a discrepancy between the Co–N(1) and Co–N(3) bond lengths. For the R structure values of Co–N(1) and Co–N(3) of 2.01 and 1.98 Å were observed, and for the L structure the values were 1.81 and 2.21 Å, respectively. The bond lengths observed for the L structure differ by 0.4 Å, and this model may therefore be rejected. On these two criteria the R structure was chosen as the correct enantiomer.

A difference Fourier synthesis at this stage revealed clear evidence of the 22 hydrogen atoms, thus justifying their inclusion in the model. Idealized coordinates were used, assuming tetrahedral coordination about both nitrogen and carbon atoms and C–H and N–H bond lengths of 1.0 Å. The contributions from the hydrogen atoms were thereafter included in calculations of F_c. One cycle of least-squares refinement, allowing the 22 nonhydrogen atoms to vibrate anisotropically, reduced R_1 and R_2 to 0.064 and 0.072. On the basis of this model the hydrogen atom coordinates were recalculated, and the refinement on F, employing 1151 reflections with $F_o^2 > 2\sigma(F_o^2)$, converged at $R_1 = 0.038$ and $R_2 = 0.039$. For all 180 variables in the full-matrix least-squares refinement the final shift was less than 0.1 esd. A statistical analysis of R_2 over various ranges of $|F_o|$ and $\lambda^{-1} \sin \theta$ confirmed that the weighting scheme was satisfactory and showed no unusual trends. The error in an observation of unit weight is 1.11 electrons. A comparison of F_o and F_c values showed that secondary extinction was not significant. A difference Fourier synthesis computed from structure factors based on the final model showed no features of chemical significance. The highest peak was of electron density 0.42 (9) e Å^{-3} at fractional coordinates (0.192, 0.467, 0.311). The final positional and thermal parameters are given in Table I.

The derived hydrogen atom positional parameters, which were not varied in the refinement, are listed in Table II. Structure amplitudes are presented in Table III, as $10|F_o|$ and $10|F_c|$ in electrons.[19]

Determination of the Absolute Configuration

The absolute configuration of the cation has been determined by the Bijvoet absorption-edge technique.[20] The values of the

---

[11] W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

[12] The programs used in this work were local modifications of a program library for the CDC 6000 series kindly supplied by Dr. J. A. Ibers. They include Hamilton's GONO9 absorption program, Ibers' NUCLS least-squares program, Zalkin's FORDAP fourier program, Johnson's ORTEP thermal ellipsoid plotting program, and the Busing–Levy ORFFE error function program.

[13] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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

[15] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[16] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

[17] T. Ueki, A. Zalkin, and D. H. Templeton, *ibid.*, **20**, 836 (1966).

[18] D. W. J. Cruickshank and W. S. McDonald, *ibid.*, **23**, 9 (1967).

[19] Table III, a listing of structure factor amplitudes, 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, by referring to code number INORG-72-1376. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

[20] J. M. Bijvoet, *Nature (London)*, **173**, 888 (1954); A. F. Peerdeman, A. J. Van Bommel, and J. M. Bijvoet, *Proc. Acad. Sci. Amsterdam, Sect. B*, **54**, 16 (1951).

TABLE I

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS[a]

	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	−0.08396 (13)	1/4	0.21342 (15)	255 (5)	411 (6)	241 (5)	14 (6)	74 (4)	11 (6)
Br	0.30487 (13)	0.47063 (11)	0.44233 (15)	625 (7)	579 (6)	590 (7)	−105 (6)	21 (5)	44 (6)
N(1)	−0.0924 (11)	0.3828 (5)	0.1800 (12)	495 (50)	424 (49)	440 (45)	−16 (38)	49 (38)	64 (38)
N(2)	−0.2971 (9)	0.2330 (5)	0.0064 (10)	335 (38)	629 (55)	291 (35)	53 (36)	27 (28)	−64 (34)
N(3)	−0.0882 (10)	0.1161 (5)	0.2495 (12)	507 (52)	383 (46)	525 (48)	57 (36)	224 (40)	−43 (38)
N(4)	0.1347 (9)	0.2623 (6)	0.4146 (10)	373 (36)	504 (47)	388 (37)	−6 (41)	25 (30)	13 (39)
N(5)	−0.2033 (8)	0.2643 (5)	0.4545 (10)	313 (36)	422 (44)	391 (37)	127 (38)	118 (30)	157 (41)
N(6)	0.0524 (9)	0.2453 (7)	−0.0176 (11)	350 (42)	750 (55)	300 (35)	105 (48)	27 (30)	93 (50)
O(1)	−0.1595 (9)	0.3278 (5)	0.5792 (10)	709 (46)	603 (44)	393 (35)	41 (40)	193 (32)	−193 (36)
O(2)	−0.3144 (9)	0.2115 (5)	0.4919 (11)	624 (48)	685 (49)	607 (45)	−40 (37)	359 (39)	−16 (35)
O(3)	0.1434 (9)	0.3088 (7)	−0.0460 (11)	501 (44)	1332 (72)	557 (44)	−225 (52)	206 (35)	119 (49)
O(4)	0.0418 (12)	0.1813 (7)	−0.1387 (12)	1254 (77)	897 (65)	552 (48)	316 (59)	546 (50)	57 (49)
C(1)	−0.2648 (14)	0.4314 (7)	0.1451 (17)	694 (71)	465 (55)	579 (63)	225 (55)	198 (54)	123 (50)
C(2)	−0.3848 (14)	0.3943 (8)	−0.0387 (16)	555 (67)	735 (80)	464 (61)	380 (59)	63 (52)	−6 (53)
C(3)	−0.4380 (12)	0.2987 (9)	0.0004 (15)	331 (53)	970 (89)	472 (55)	73 (56)	19 (46)	−53 (59)
C(4)	−0.3622 (14)	0.1387 (8)	0.0267 (17)	547 (68)	689 (74)	584 (65)	−207 (57)	29 (52)	−282 (57)
C(5)	−0.2119 (14)	0.0761 (7)	0.0723 (18)	627 (69)	510 (64)	611 (70)	−105 (57)	24 (54)	−88 (53)
C(6)	0.0756 (13)	0.0630 (7)	0.2809 (16)	613 (66)	484 (59)	654 (64)	146 (54)	253 (52)	52 (54)
C(7)	0.2080 (16)	0.0996 (9)	0.4530 (18)	714 (78)	694 (80)	574 (65)	422 (66)	166 (57)	177 (59)
C(8)	0.2699 (11)	0.1928 (9)	0.4173 (16)	286 (52)	903 (85)	551 (62)	192 (55)	65 (46)	39 (61)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] $U_{ij} = \beta_{ij}/2\pi^2 a_i^* a_j^*$ (Å). The values have been multiplied by 10^4. The thermal ellipsoid is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE II

DERIVED HYDROGEN ATOM POSITIONAL PARAMETERS

Atom	x	y	z	Atom	x	y	z
H(1)[a]	−0.035	0.397	0.056	H(12)	−0.156	0.070	−0.056
H(2)	−0.023	0.409	0.311	H(13)	−0.251	0.015	0.114
H(3)	−0.244	0.497	0.119	H(14)	−0.140	0.114	0.382
H(4)	−0.319	0.425	0.275	H(15)	0.124	0.064	0.146
H(5)	−0.326	0.395	−0.166	H(16)	0.050	−0.001	0.317
H(6)	−0.490	0.433	−0.066	H(17)	0.310	0.058	0.471
H(7)	−0.534	0.281	−0.115	H(18)	0.157	0.100	0.587
H(8)	−0.480	0.297	0.140	H(19)	0.312	0.194	0.279
H(9)	−0.247	0.238	−0.127	H(20)	0.368	0.207	0.534
H(10)	−0.437	0.120	−0.109	H(21)	0.187	0.322	0.383
H(11)	−0.431	0.136	0.145	H(22)	0.104	0.264	0.560

[a] Hydrogen atoms are numbered in order around the tetradentate ligand. Thus H(1) and H(2) are bonded to N(1) and H(3), H(4) is bonded to C(1), etc. For each atom $B = 5$ Å^2.

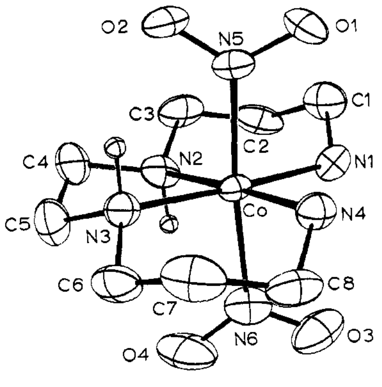

Figure 2.—Perspective view of the $[Co(3,2,3\text{-tet})(NO_2)_2]^+$ cation, showing the atom-numbering scheme. H(9) is bonded to N(2); H(14) is bonded to N(3). Atoms are plotted as 40% probability ellipsoids of thermal motion.

real and imaginary dispersion corrections applied to the atomic scattering factors were those listed by Cromer,[15] in electrons: for Co, $\Delta f' = 0.37$ and $\Delta f'' = 1.06$; for Br, $\Delta f' = -0.21$ and $\Delta f'' = 2.68$.

To confirm that the model chosen, structure R, was the correct enantiomer, its mirror image, structure L, was also refined under the same conditions. Idealized hydrogen atom positions were calculated for structure L, and the contributions were included in calculations of F_c. The refinement converged with $R_1 = 0.058$ and $R_2 = 0.066$ on 1151 observations with $F_o^2 > 2\sigma(F_o^2)$. Application of the R-factor ratio test shows that structure L may be rejected in favor of structure R at the 0.005 level.[16]

As discussed earlier, the wrong application of the anomalous dispersion correction to the atomic scattering factors leads to polar dispersion errors. In structure R, final values of the Co–N bond lengths, Co–N(1) of 1.971 (8) Å and Co–N(3) of 1.990 (8) Å, were determined. For structure L, values of Co–N(1) of 1.929 (10) Å and Co–N(3) of 2.031 (9) Å were found. The difference for structure L is 0.102 (13) Å, or approximately 8σ. Accordingly, we can also reject structure L on the basis of the cation geometry.

TABLE IV

DETERMINATION OF ABSOLUTE CONFIGURATION

Indices	$F_c(hkl)$	Obsd relationship	$F_c(\bar{h}\bar{k}\bar{l})$	Indices	$F_c(hkl)$	Obsd relationship	$F_o(\bar{h}\bar{k}\bar{l})$
1 1 3	22.64	<	28.56	2 4 2	44.15	<	50.52
1 3 $\bar{1}$	58.31	<	66.72	2 6 0	31.92	<	38.24
1 5 0	43.59	>	38.44	3 2 $\bar{1}$	6.11	<	11.47
1 15 1	16.52	>	14.76	3 5 0	20.50	>	15.29
2 2 2	46.41	>	39.13	3 9 1	14.22	<	17.72

TABLE V

Possible A–H···B Interactions (A···B ⩽ 3.5 Å)

B	H	A	A–B, Å	B···H, Å	B···H–A, deg	Symmetry operator applied to A–H
Br	H(21)	N(4)	3.34	2.39	159	
O(1)	H(5)	C(2)	3.39	2.46	154	$x, y, 1 + z$
O(1)	H(9)	N(2)	3.40	2.49	152	$x, y, 1 + z$
O(2)	H(9)	N(2)	3.29	2.44	142	$x, y, 1 + z$
O(2)	H(20)	C(8)	3.23	2.56	125	$x - 1, y, z$
O(3)	H(7)	C(3)	3.25	2.68	112	$x + 1, y, z$
O(4)	H(22)	N(4)	3.29	2.40	148	$x, y, z - 1$
O(4)	H(18)	C(7)	3.33	2.42	151	$x, y, z - 1$

Nonbonding Interactions (A···B ⩽ 3.2 Å)

A	B	A···B, Å	Symmetry operator applied to B
O(1)	O(3)	3.10	$x, y, 1 + z$
O(1)	O(4)	3.08	$x, y, 1 + z$
O(1)	N(6)	3.08	$x, y, 1 + z$

Finally, Bijvoet pairs were compared. A selection of computed structure factors for structure R is given in Table IV for reflections where $F_c(hkl)$ and $F_c(\bar{h}\bar{k}\bar{l})$ differ by more than 10%, based on the final positional parameters. The observed relationships further confirm structure R as the correct choice. In no case was the enantiomeric structure L indicated.

Table VI

Selected Bond Distances (Å) and Bond Angles (deg)

Co-N(1)	1.971 (8)	N(1)-Co-N(2)	92.5 (3)	Co-N(1)-C(1)	120.0 (6)
Co-N(2)	1.972 (7)	N(1)-Co-N(3)	177.9 (3)	N(1)-C(1)-C(2)	112.1 (8)
Co-N(3)	1.990 (8)	N(1)-Co-N(4)	89.4 (3)	C(1)-C(2)-C(3)	111.8 (9)
Co-N(4)	1.978 (7)	N(1)-Co-N(5)	88.1 (3)	C(2)-C(3)-N(2)	113.3 (8)
Co-N(5)	1.943 (7)	N(1)-Co-N(6)	88.1 (4)	C(3)-N(2)-C(4)	110.5 (8)
Co-N(6)	1.964 (7)	N(2)-Co-N(3)	85.6 (3)	N(2)-C(4)-C(5)	108.9 (8)
		N(2)-Co-N(4)	177.3 (3)	C(4)-C(5)-N(3)	107.4 (8)
N(5)-O(1)	1.242 (9)	N(2)-Co-N(5)	94.6 (3)	C(5)-N(3)-C(6)	109.6 (8)
N(5)-O(2)	1.223 (9)	N(2)-Co-N(6)	89.8 (3)	N(3)-C(6)-C(7)	113.1 (9)
N(6)-O(3)	1.210 (11)	N(3)-Co-N(4)	92.6 (3)	C(6)-C(7)-C(8)	115.4 (9)
N(6)-O(4)	1.215 (12)	N(3)-Co-N(5)	89.8 (3)	C(7)-C(8)-N(4)	113.1 (8)
		N(3)-Co-N(6)	94.2 (4)	C(8)-N(4)-Co	119.3 (6)
N(1)-C(1)	1.52 (1)	N(4)-Co-N(5)	87.3 (3)		
C(1)-C(2)	1.49 (2)	N(4)-Co-N(6)	88.4 (3)		
C(2)-C(3)	1.47 (1)	N(5)-Co-N(6)	174.2 (4)		
C(3)-N(2)	1.50 (2)				
N(2)-C(4)	1.50 (1)	Co-N(5)-O(1)	118.3 (6)		
C(4)-C(5)	1.49 (1)	Co-N(5)-O(2)	122.6 (6)		
C(5)-N(3)	1.49 (2)	O(1)-N(5)-O(2)	119.1 (7)		
N(3)-C(6)	1.49 (1)	Co-N(6)-O(3)	119.6 (8)		
C(6)-C(7)	1.49 (2)	Co-N(6)-O(4)	121.3 (8)		
C(7)-C(8)	1.47 (1)	O(3)-N(6)-O(4)	119.0 (8)		
C(8)-N(4)	1.49 (2)				

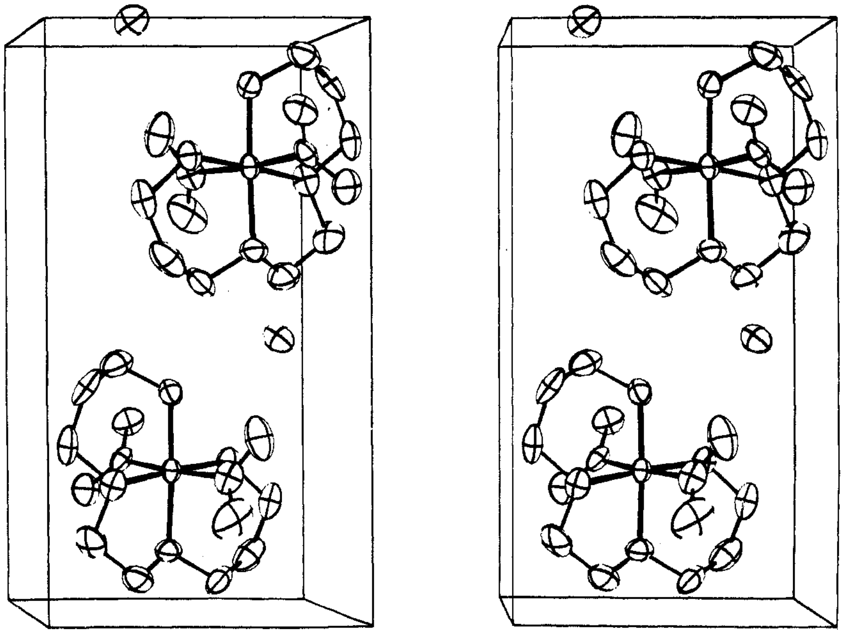

Figure 3.—Stereoview of the contents of one unit cell. The horizontal axis, *a*, runs from $-1/2$ to $1/2$, and the vertical axis, *b*, runs from 0 to 1.

Description of the Structure

The structure consists of essentially discrete ions, held together by a weak hydrogen-bonding network. Intermolecular distances A···B for possible hydrogen bonds A-H···B are listed in Table V. The shortest approach of a hydrogen atom to the bromide ion is H(21) at 2.39 Å. The closest H···H approach between two molecules is 2.29 Å.

A perspective drawing of the cation, together with the atom-numbering scheme used, is given in Figure 2. In order to highlight the absolute configurations at the two asymmetric nitrogen atoms, N(2) and N(3), the hydrogen atoms H(9) and H(14) bonded to these atoms are included. A stereoview of the contents of one unit cell is presented in Figure 3.

The cobalt atom is surrounded by six nitrogen atoms at the apices of a slightly distorted octahedron. The two nitro groups occupy trans positions, with a N-Co-N angle of 174.2 (4)°. A selection of intramolecular bond distances and angles is given in Table VI. The mean Co-primary N atom bond length is 1.974 (4) Å, the Co-secondary N atom bond length mean is 1.981 (9) Å, and the mean distance for the $Co-NO_2$ bonds is 1.954 (7) Å. These values are comparable to those observed in $(-)_{546}$-*cis*-*β*-$[Co(NO_2)_2$-$(3,8\text{-}Me_2trien)]ClO_4$[21] and $(+)_{589}$-*cis*-dinitrobis$[(-)_{589}$-1,2-propylenediamine]cobalt(III) chloride.[22] The mean N-O distance in the nitro groups is 1.223 (7) Å. When corrected for thermal motion, assuming the oxygen atom to ride on the nitrogen atom, the mean bond length is 1.257 (7) Å. The mean O-N-O angle is 119.0 (7)°. Comparable means of 1.23 Å and 119.5°,

---

[21] M. Ito, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **26**, 1408 (1970).

[22] G. A. Barclay, E. Goldschmied, and N. C. Stephenson, *ibid.*, **26**, 1559 (1970).

respectively, were observed in $(-)_{546}$-*cis*-*β*-[Co$(NO_2)_2$-(3,8-Me_2trien)]ClO_4.[21]

The mean C–C distance in the chelate rings is 1.482 (5) Å, and the mean C–N distance is 1.498 (5) Å. Both values are significantly shorter than expected for C–C and C–N single bonds. The five-membered ring adopts the gauche conformation, with absolute configuration δ.[23] The absolute configurations of the asymmetric secondary nitrogen atoms are both *R*.[24] Both six-membered chelate rings assume a chair conformation. The N–Co–N angle for the five-membered ring is 85.6 (3)°; the mean value for the two six-membered rings is 92.6 (3)°. The mean angle at the ring carbon atoms in the six-membered rings is 113.1 (5)° and in the five-membered chelate ring is 108.1 (7)°. The mean angle at the secondary nitrogen atoms is 110.1 (5)°, and the mean Co–NH_2–C angle is 119.6 (4)°. The bond angles in the six-membered chelate rings are significantly distorted from the tetrahedral value.

Some selected least-squares planes are given in Table VII. Plane 1, containing the Co atom and the two NO_2 ligands, is at an angle of 92° to the equatorial plane containing the Co atom and the four coordinated nitrogen atoms, plane 2. The plane formed by the nitro group N(5), O(1), O(2) makes a dihedral angle of 9.5° with the plane formed by the other nitro group, N(6), O(3), O(4). The deviations from an ideal octahedron evidenced by the amine nitrogen atoms result in displacements of 0.036 and 0.037 Å from the equatorial plane for N(1) and N(3) and displacements of −0.036 and −0.035 Å for atoms N(2) and N(4). These and other distortions from ideal geometries in the 3,2,3-tet ligand may be attributed to steric strain esulting from coordination to the Co(III) atom.

TABLE VII
SELECTED LEAST-SQUARES PLANES[a]

Plane 1, through Co, N(1), N(2), N(3), and N(4)
Plane equation:[b] $-6.601x + 0.896y + 8.435z = 19.209$

	Displacement from plane, Å		Displacement from plane, Å
Co	−0.003	C(3)	0.75
N(1)	0.036	C(4)	0.286
N(2)	−0.036	C(5)	−0.330
N(3)	0.037	C(6)	−0.71
N(4)	−0.035	C(7)	−0.42
C(1)	0.81	C(8)	−0.81
C(2)	0.39		

Plane 2, through Co, N(5), N(6), O(1), O(2), O(3), and O(4)
Plane equation: $6.405x - 5.085y + 4.625z = -16.438$

	Displacement from plane, Å		Displacement from plane, Å
Co	−0.022	O(2)	−0.068
N(5)	−0.016	O(3)	−0.088
N(6)	0.015	O(4)	0.083
O(1)	0.097		

Angles between Plane Normals

Atoms in plane A	Atoms in plane B	Angle, deg
Co, N(2), C(4)	Co, N(3), C(5)	18.2
N(5), O(1), O(2)	N(6), O(3), O(4)	9.5

[a] Least-squares plane calculations were performed with a local modification of the program written by V. Schomaker, J. Wader, R. E. Marsh, and G. Bergman, *Acta Crystallogr.*, **12,** 600 (1959). [b] Plane constants are given with respect to the crystallographic axes.

The degree of puckering in the five-membered ring is evidenced in two ways. The deviations of the carbon atoms C(4) and C(5) from the plane formed by the Co, N(2), and N(3) atoms are 0.30 and −0.35 Å, respectively. The dihedral angle between the planes defined by N(2), C(4), C(5) and N(3), C(4), C(5) is 49.2°. Comparable deviations of −0.35 and 0.29 Å and of −0.35 and 0.35 Å were observed in the ethylenediamine chelate rings in $(+)_{495}$-L-glutamatobis-(ethylenediamine)cobalt(III) perchlorate.[25] Dihedral angles of 43 and 52° were observed in D-[Co$(en)_3$]$Br_3 \cdot H_2O$.[26]

The gauche conformation of the five-membered chelate ring and the chair conformations of the two six-membered rings are those predicted on the basis of nonbonding intramolecular interactions.

The observed circular dichroism spectrum of the $(+)_{546}$-*trans*-[Co(3,2,3-tet)$(NO_2)_2$]$^+$ ion arises mainly from the asymmetry of the optically active five-membered chelate ring, of absolute configuration δ, which contains the two asymmetric secondary nitrogen atoms. The two six-membered rings effectively possess a plane of symmetry, passing through the cobalt atom, C(2), and C(7), and therefore may be considered to make no contribution to the spectrum. From this structural determination it is apparent that there are two further sources of asymmetry present in the solid state. The coordination of the tetramine ligand to the cobalt atom results in deviations of the four nitrogen donor atoms from the equatorial plane of the coordination octahedron. These deviations, of mean value 0.036 (1) Å, are of a tetrahedral nature. In addition, the N(5)–Co–N(6) angle is not 180°, but 174.2 (4)°. The least-squares plane including Co, N(5), N(6), O(1), O(2), O(3), and O(4) is given in Table VII. The perpendicular deviations from this plane of O(1), 0.097 Å, and that of O(3), −0.088 Å, are in opposite directions, as are those of O(2), −0.068 Å, and O(4), 0.083 A. These deviations are equivalent to a rotation of one NO_2 group relative to the other around the N(5)–Co–N(6) axis, a further source of asymmetry in the molecule. An examination of the intramolecular interactions provides a possible explanation for the observed geometry. O(1) deviates from the plane in a positive sense, toward H(22) at 2.29 Å, the axial hydrogen atom bonded to N(4). O(2) deviates in a negative sense, owing to a nonbonding repulsive interaction with H(14) at 2.18 Å, the axial hydrogen atom bonded to N(3). The other nitro ligand interacts in a similar fashion with the remaining six-membered ring. O(3) deviates in a negative sense, toward H(1) at 2.10 Å, the axial hydrogen atom bonded to N(1). O(4), owing to a nonbonding repulsion from H(9) at 2.43 Å, the axial hydrogen atom bonded to N(2), deviates in a positive sense. No significant intermolecular interactions were observed, and the nonbonding repulsion between H(9) and O(4) and between H(14) and O(2) appears to be the main reason for the observed geometry. Thus it appears that in *trans*-diacidotetraminecobalt(III) complexes and anal-

---

(23) IUPAC Information Bulletin No. 33, 1968; *Inorg. Chem.*, **9,** 1 (1970).

(24) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5,** 385 (1966).

(25) R. D. Gillard, N. C. Payne, and G. B. Robertson, *J. Chem. Soc. A*, 2579 (1970).

(26) K. Nakatsu, *Bull. Chem. Soc. Jap.*, **35,** 832 (1962).

ogous bis-diamine complexes, where the diacido ligands are not axially symmetric, there can exist a further source of asymmetry in the molecule which may contribute to the observed optical activity.

Acknowledgment.—We thank Professor J. A. Ibers for providing the computer programs used, Dr. B. Bosnich for helpful discussions, and the National Research Council of Canada for financial support.

Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. V.[1] Crystal Structure of Bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$

By M. D. Brice and B. R. Penfold*

Received October 5, 1971

The crystal and molecular structure of bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$, has been determined by three-dimensional X-ray analysis. The crystals are monoclinic; space group C_{2h}^6-$C2/c$, with four molecules in a unit cell of dimensions $a = 16.368$ (3), $b = 9.450$ (2), $c = 18.906$ (4) Å, and $\beta = 106.79$ (2)°. X-Ray data were collected by counter methods using Mo Kα radiation. Full-matrix least-squares refinement with Co atoms treated anisotropically led to a final value of the conventional R factor of 0.054 for the 1650 independent reflections having $F^2 > \sigma(F^2)$. The crystal structure consists of discrete dimeric molecular units each with a crystallographic dyad axis and with idealized symmetry D_3-32. These are derived from the parent compound $CH_3CCo_3(CO)_9$ by elimination of the terminal methyl group and direct linkage of the triply bridging carbon atoms. The central formally single C–C bond is extremely short at 1.37 (1) Å. The two Co_3 triangles are semieclipsed to minimize nonbonded repulsions and the mean Co–Co bond length is 2.456 (2) Å.

Introduction

The compound $Co_6(CO)_{18}C_2$ was first reported by Allegra, Peronaci, and Ercoli,[2] who prepared it by warming bromomethinyltricobalt enneacarbonyl, $BrCCo_3(CO)_9$, in anhydrous toluene. They assumed that it was a dimer containing two connected $-CCo_3(CO)_9$ units of the type first characterized in $CH_3CCo_3(CO)_9$.[3]

A number of further products of the reaction between $YCCo_3(CO)_9$ (Y = Cl, Br) and arenes have been isolated[4,5] and structurally characterized[1,5–7] and all have proved to be based on the $-CCo_3(CO)_9$ structural entitity containing a CCo_3 tetrahedron. Study of the detailed geometries of these molecules pointed to the desirability of a precise structure determination of $[CCo_3(CO)_9]_2$, a preliminary account of which we have reported.[8]

Experimental Section

Preparation of $[CCo_3(CO)_9]_2$.—The compound was prepared by Dr. B. H. Robinson, University of Otago, from $BrCCo_3(CO)_9$ and toluene using the method previously reported.[2] Dark brown air-stable irregularly shaped crystals were obtained by recrystallization from the solvent.

Crystallographic Data.[9]—$Co_6C_{20}O_{18}$, mol wt 881.8, is monoclinic with $a = 16.368$ (3), $b = 9.450$ (2), $c = 18.906$ (4) Å, $\beta = 106.79$ (2)°; $V = 2801$ Å^3; $d_{obsd} = 2.10$ (2) g/cm^3; $Z = 4$; $d_{calcd} = 2.09$ g/cm^3; μ(Mo Kα) = 13.5 cm^{-1}. Systematic absences occurred for hkl reflections when $(h + k)$ was odd and for $00l$ reflections when l was odd. Possible space groups are therefore C_{2h}^6-$C2/c$ or C_s^4-Cc. The centrosymmetrical space group $C2/c$ was indicated both by intensity statistics of the full data set and a by the distribution of peaks in a three-dimensional Patterson map and was confirmed by the subsequent successful structure solution and refinement. This space group requires molecular symmetry C_i-$\bar{1}$ or C_2-2.

Unit cell dimensions and their estimated standard deviations were obtained at room temperature (23 ± 2°) with Mo Kα_1 radiation (λ 0.7093 Å) using the least-squares procedure described below. The experimental density was determined using a calibrated density gradient column containing a mixture of bromoform and *m*-xylene.

Diffraction data were obtained from a crystal fragment whose shape approximated to that of a parallelepiped with faces defined by the forms {001}, {010}, and {20$\bar{1}$}. Crystal cross sections normal to these faces were 0.15, 0.25, and 0.32 mm, respectively. All quantitative data were obtained from a Hilger-Watts four-circle diffractometer controlled by a PDP-8I computer using Zr-filtered Mo Kα radiation. A preliminary mosaicity check of the crystal by means of open-counter ω scans showed that the width at half-height of intense low-angle reflections was acceptably low at 0.10°. The crystal was mounted on a goniometer head in random orientation and 12 strong high-angle reflections were accurately centered through a circular 1.0-mm diameter diffracted-beam collimator. The setting angles so obtained formed the basis for a least-squares refinement of lattice constants and an orientation matrix. The method was as outlined by Busing[10] and adapted to our own system.

Intensity data were collected by use of an X-ray beam takeoff angle of 3° and in the bisecting mode ($\omega = \theta$). A diffracted beam collimator of circular cross section, diameter 5 mm, was positioned 23 cm from the crystal. The θ–2θ scan technique was used, counts being recorded at equal steps of 0.01° in θ. Scans were symmetric about the Mo K$\bar{\alpha}$ counter setting and 15-sec stationary-crystal, stationary-counter background counts were recorded at each end of the scan. For reflections in the range $0.1° < \theta < 18°$, the θ-scan range was 0.4° with counting for 1.5 sec at each step. For reflections in the range $18° < \theta < 23°$ the scan range was 0.6° with counting for 1 sec at each step, so that the total scan counting time was 60 sec in each case. Attenuators were automatically inserted in the primary beam if the total scan count exceeded 150,000. The intensities of three

---

[1] Part IV: R. J. Dellaca and B. R. Penfold, *Inorg. Chem.*, **10**, 1269 (1971).

[2] G. Allegra, E. M. Peronaci, and R. Ercoli, *Chem. Commun.*, 549 (1966).

[3] P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

[4] B. H. Robinson, J. L. Spencer, and R. Hodges, *Chem. Commun.*, 1480 (1968).

[5] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2204 (1970).

[6] G. Allegra and S. Valle, *Acta Crystallogr., Sect. B*, **25**, 107 (1969).

[7] R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197 (1970).

[8] M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *J. Chem. Soc. D*, 72 (1971).

[9] Here and throughout this paper, the figures given in parentheses are estimated standard deviations in the least significant digits quoted.

[10] W. R. Busing in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 319.