gest, therefore, that any strain caused on chelation has been relieved through bond lengthening in the cyclobutane ring and As-C(5) bonds.

However other evidence, although indirect, should be considered. It has been calculated that the energy of the cyclobutane system is minimized if the CH_2 groups rock so as to increase the staggering of adjacent hydrogen atoms.[12] In addition, Meiboom and Snyder[13] have shown that the CH_2 groups are tilted 4° such that axial protons on the same side of the ring come together. This is true for the methyl groups here as the angle C(5')-C(6)-C(8) is much less than C(5')-C(6)-C(7), C(8) being axial. As C(6)-C(5)-As is 113.0 (2)°, $\sim$1° less than C(5')-C(6)-C(8), it is possible that the As· · ·As bite has not changed on chelation. However the aa Cl· · ·Cl distance in octachlorocyclobutane is 3.38 Å[14] and since the arsenic-carbon bond length is greater than chlorine-carbon bond length, one might expect that As· · ·As would be greater in the uncoordinated state than the chelated state. From the microwave spectrum of bromocyclobutane,[15] the C-C-Br angle is calculated to be 131° (a rather large value), much greater than C(6)-C(5)-As in this compound, but by how much the large angle would be reduced by substituents on adjacent carbons to the bromine substituent is not known.

Registry No. (1,3-Dimethylarsino-2,2,4,4-tetramethylcyclobutane-*As,As*)tetracarbonylchromium, 38566-51-7.

Acknowledgments. We wish to thank Dr. W. R. Cullen for crystals of the compound and for helpful discussions. This work was made possible by grants from the National Research Council of Canada.

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Importance of Donor Atom Distortions. Crystal Structure, Absolute Configuration, and Optical Activity of $(-)_{589}$-*trans*-Dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) Nitrate

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The crystal structure and absolute configuration of $(-)_{589}$-*trans*-dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) nitrate have been determined from three-dimensional X-ray data collected by counter methods. The salt crystallizes in the monoclinic space group $P2_1$, with two formula units per cell. The unit cell dimensions are $a = 13.18$ (2), $b = 8.88$ (2), $c = 6.40$ (1) Å, and $\beta = 99.2$ (1)°. The observed and calculated densities are 1.65 (1) and 1.63 g cm^{-3}, respectively. 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 $R_1 = 0.026$ using 1733 observations for which $F_o^2 > 2\sigma(F_o^2)$. The structure consists of discrete complex cations and anions. The inner coordination sphere of the cobalt atom is octahedral, with the tetradentate linear tetramine occupying the equatorial plane and the two chlorine atoms the apices. The absolute configuration of the complex cation was determined by the Bijvoet method. The conformations of the two six-membered rings are chair. The five-membered ring adopts the gauche conformation, with absolute configuration δ. The configurations of the asymmetric secondary nitrogen atoms are both *R*. The observed circular dichroism spectrum of the complex ion is compared with that of the *trans*-dinitro analog and that of the *trans*-$[Co(R\text{-pn})_2Cl_2]^+$ ion, in the light of recently proposed regional rules.

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, acts as a tetradentate ligand and forms complexes with cobalt(III).[1] Coordination to the metal ion in ions of the type $[Co(3,2,3\text{-tet})X_2]^{n+}$, where X is a unidentate ligand, has been shown to occur preferentially with trans stereochemistry. Upon complex formation the secondary nitrogen atoms become centers of asymmetry, and the compound may be resolved into two enantiomeric forms, in which the absolute configurations of the asymmetric nitrogen atoms are either both *R*, or both *S*.[2] In addition there is a meso form, with absolute configurations of *R* and *S* at the nitrogen atoms. This resolution has been achieved for the complex cation where $X^- = NO_2^-$, and a three-dimensional, single-crystal X-ray structural analysis of the enantiomer $(+)_{546}$-$[Co(3,2,3\text{-tet})(NO_2)_2]Br$ has been reported.[3] In that analysis, the five-membered chelate ring adopts the gauche conformation, with absolute configuration δ.[4] The absolute configurations at the asymmetric nitrogen atoms are both *R*. Two additional sources of dissymmetry, apparently contributing to the observed optical activity in the solid state, were found. The four donor nitrogen atoms of the tetramine ligand in the equatorial plane of the coordination octahedron showed alternate deviations from the plane. Such deviations generate two nonorthogonal skew lines, which define a helical system at the cobalt atom. Second, the two trans ligands are not axially symmetric. The plane of one NO_2^- ligand was shown to be rotated by approximately 10° around the O_2N-Co-NO_2 axis relative to the plane containing the other NO_2^- ligand. A crystal structure analysis of a cation containing the same tetramine ligand, but with axially symmetric X ligands, is therefore of interest, and we present here the results of a three-dimensional, single-crystal X-ray analysis of $(-)_{589}[Co(3,2,3\text{-tet})Cl_2]NO_3$.

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Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	$U(1,1)$[b]	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Co	0.25828 (3)	$^1/_4$	0.01556 (5)	209 (2)	227 (2)	168 (2)	9 (2)	39 (1)	1 (2)
Cl(1)	0.36812 (6)	0.27802 (12)	−0.21598 (11)	277 (3)	404 (7)	233 (3)	−30 (4)	91 (3)	32 (4)
Cl(2)	0.14830 (6)	0.22194 (13)	0.25005 (12)	316 (4)	476 (8)	234 (3)	7 (4)	119 (3)	14 (3)
N(1)	0.3614 (2)	0.3286 (3)	0.2521 (4)	330 (14)	246 (16)	229 (12)	−11 (12)	0 (10)	−9 (11)
N(2)	0.3040 (2)	0.0397 (3)	0.0716 (4)	273 (13)	242 (14)	238 (12)	13 (11)	24 (10)	−22 (11)
N(3)	0.1551 (2)	0.1679 (4)	−0.2165 (4)	229 (12)	375 (17)	218 (13)	5 (11)	20 (10)	−26 (12)
N(4)	0.2114 (2)	0.4587 (4)	−0.0565 (4)	347 (15)	299 (17)	318 (14)	64 (13)	29 (12)	27 (13)
C(1)	0.4660 (2)	0.2612 (6)	0.2968 (5)	260 (13)	362 (19)	310 (14)	−8 (17)	−10 (11)	−10 (17)
C(2)	0.4612 (3)	0.0933 (4)	0.3318 (5)	344 (17)	316 (18)	313 (16)	85 (15)	−22 (13)	−8 (15)
C(3)	0.4149 (2)	0.0061 (4)	0.1361 (5)	294 (15)	277 (19)	332 (16)	92 (14)	6 (13)	2 (14)
C(4)	0.2609 (3)	−0.0515 (4)	−0.1155 (5)	386 (18)	289 (15)	335 (17)	−17 (14)	−32 (13)	−75 (13)
C(5)	0.1516 (3)	0.0012 (4)	−0.1856 (6)	360 (18)	345 (20)	376 (18)	−53 (15)	−13 (14)	−43 (15)
C(6)	0.0503 (2)	0.2321 (6)	−0.2572 (5)	234 (13)	487 (27)	315 (15)	15 (16)	12 (11)	7 (17)
C(7)	0.0502 (3)	0.3992 (5)	−0.2997 (6)	299 (18)	573 (27)	361 (19)	112 (18)	−10 (14)	77 (19)
C(8)	0.1001 (3)	0.4909 (5)	−0.1125 (6)	376 (18)	410 (22)	395 (19)	167 (16)	73 (15)	20 (17)
N(5)	0.2589 (3)	−0.2912 (4)	0.3971 (6)	598 (21)	361 (18)	466 (19)	−89 (15)	−10 (16)	61 (14)
O(1)	0.2263 (4)	−0.1616 (5)	0.3899 (7)	1394 (43)	539 (26)	940 (35)	243 (27)	650 (30)	111 (25)
O(2)	0.3151 (3)	−0.3314 (4)	0.2668 (6)	815 (23)	440 (19)	718 (23)	45 (18)	94 (19)	−123 (17)
O(3)	0.2395 (5)	−0.3757 (7)	0.5291 (9)	1918 (57)	1148 (41)	1465 (52)	36 (35)	770 (47)	836 (37)

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] $U_{ij} = B_{ij}/(2\pi^2 a_i{}^* a_j{}^*)$ 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
H(1)[a]	0.3290	0.2392	0.5275
H(2)	0.3712	0.2462	0.4940
H(3)	0.5071	0.3157	0.4418
H(4)	0.5067	0.2865	0.1667
H(5)	0.4150	0.0701	0.4549
H(6)	0.5396	0.0514	0.3844
H(7)	0.4254	−0.1150	0.1661
H(8)	0.4564	0.0365	0.0056
H(9)	0.2645	0.0148	0.1991
H(10)	0.2611	−0.1721	−0.0704
H(11)	0.3065	−0.0382	−0.2405
H(12)	0.1042	−0.0221	−0.0625
H(13)	0.1173	−0.0527	−0.3316
H(14)	0.1918	0.1899	−0.3489
H(15)	0.0139	0.2129	−0.1170
H(16)	0.0058	0.1759	−0.3924
H(17)	−0.0283	0.4385	−0.3450
H(18)	0.0931	0.4203	−0.4304
H(19)	0.0626	0.4633	0.0219
H(20)	0.0892	0.6102	−0.1505
H(21)	0.2392	0.5275	0.0754
H(22)	0.2462	0.4940	−0.1855

[a] Hydrogen atoms are numbered sequentially around the tetramine ligand. Thus H(1) and H(2) are bonded to N(1) and H(3) and H(4) are bonded to C(1), etc.

Experimental Section

Dark green crystals of the salt were supplied by Dr. J. MacB. Harrowfield and Dr. B. Bosnich of the University of Toronto. *trans*-Dichloro(1,10-diamino-4,7-diazadecane)cobalt(III) nitrate crystallizes as prismatic crystals, elongated along [001]. A preliminary X-ray examination showed monoclinic symmetry, Laue group $2/m$. The systematic absences observed on Weissenberg and precession photographs of reciprocal lattice layers (0–2)kl, h(0–2)l, and hk(0–2) were $0k0$, when $k = 2n + 1$. These absences are consistent with space groups $P2_1/m\text{-}C_{2h}{}^2$ and $P2_1\text{-}C_2{}^2$.[5] Since the material is optically active, space group $P2_1$ (No. 4) was chosen and later confirmed by solution of the structure. The crystal selected for data collection was of approximate dimensions 0.16 mm × 0.12 mm × 0.10 mm and was a fragment of a larger crystal. An optical goniometric examination identified well-developed prismatic faces of the forms {100} and {110}, while fragmented basal faces are closely approximated as $(10\bar{3})$ and $(\bar{1}03)$. The crystal was measured with a micrometer eyepiece prior to application of an absorption correction (μ(Mo Kα) = 15.8 cm^{-1}).

Unit cell dimensions were determined from a least-squares refinement[6] of 20 reflections centered on a Picker four-circle automatic diffractometer, using Mo Kα_1 radiation, λ 0.70926 Å. The values observed, at 21°, are $a = 13.18$ (2), $b = 8.88$ (2), $c = 6.40$ (1) Å, and $\beta = 99.2$ (1)° and correspond to a cell volume of 739 Å^3. The density of the crystals, calculated for two formula units per cell, 1.63 g cm^{-3}, is in good agreement with the value 1.65 (1) g cm^{-3}, determined by flotation in a mixture of carbon tetrachloride and dibromomethane. There can be no symmetry conditions imposed upon the ions.[5]

For data collection the crystal was mounted with the longest dimension [001] approximately parallel to the diffractometer ϕ axis. Several ω scans, with narrow source and open counter, through intense, low-angle reflections showed an average width at half-height of 0.09°, a value deemed satisfactory.[7] Three-dimensional intensity data of the form hkl were collected, out to a maximum 2θ of 55°, using Mo Kα radiation. The diffracted beam was filtered through 0.08 mm of niobium foil. Coincidence losses for strong reflections were minimized with copper foil attenuators. The θ–2θ scan technique was employed, with a scan range of 1°, at a scan rate of 1°/min. Stationary-crystal and stationary-counter background counts of 10 sec were made at each end of a scan. Throughout data collection, three intense axial reflections, (200), (040), and (004) were monitored after every 100 reflections recorded. The intensity of reflection (200) showed only statistical variations during data collection, while reflections (040) and (004) showed a 5% increase. These variations were considered negligible. During data collection a takeoff angle of 1.4° was employed. The counter aperture, of dimensions 4 mm × 4 mm, was placed 31 cm from the crystal. The Friedel pair reflection data, of form $h\bar{k}\bar{l}$, were then collected under the same conditions. In all, 1899 reflections of the form hkl were recorded. The raw data were then corrected for background and Lorentz-polarization effects, and standard deviations were assigned, according to the expression

$$\sigma(I) = [\mathrm{TC} + {}^1/_4(t_\mathrm{c}/t_\mathrm{b})^2(B_h + B_l) + (pI)^2]^{1/2}$$

where TC is the total integrated count, measured in a scan time t_c, B_h and B_l the background counts, each measured in times t_b. I, the corrected intensity, is given by $[\mathrm{TC} - {}^1/_2(t_\mathrm{c}/t_\mathrm{b})(B_h + B_l)]$. The value of p chosen was 0.04.[8] A series of absorption correction tests showed transmission factors varying by 7%, and an absorption correction was applied. Of the 1899 reflections measured, the 1733 reflections for which $|F_\mathrm{o}{}^2| > 2\sigma(F_\mathrm{o}{}^2)$ were considered "observed" and were used in structure solution and refinement.

Solution and Refinement of the Structure

A three-dimensional Patterson synthesis was calculated, from which the cobalt and chlorine atom positions were determined.[9] The y coordinate of the cobalt atom was chosen as $^1/_4$ to fix the origin of the cell. One cycle of full-matrix least-squares refinement, varying positional and isotropic thermal parameters, resulted in values of

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$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.40$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o^2|)^{1/2} = 0.51$. The weight applied to each observation was calculated from $4F_o^2/\sigma^2(F_o^2)$, and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Atomic scattering factors for Co, Cl, O, N, and C were taken from Cromer and Waber;[10] those for H, from Stewart, *et al.*[11] The real and imaginary anomalous dispersion corrections of Cromer were applied to the Co and Cl scattering factors.[12] The remaining 16 nonhydrogen atoms were located from a series of least-squares refinements and difference Fourier syntheses. Two cycles of least-squares refinement of the positional and isotropic thermal parameters of the 19 nonhydrogen atoms reduced R_1 and R_2 to 0.075 and 0.106, respectively.

Two possible enantiomeric structures exist, the one chosen, referred to as A, and its mirror image, which was generated by reflection in a mirror plane at $y = 1/4$, referred to as B. To distinguish between A and B, structure B was refined under identical conditions. Values of R_1 and R_2 of 0.091 and 0.121 were obtained. The R factor ratio test applied to the weighted agreement factors, R_2, shows that structure B may be rejected at the 0.005 level.[13] Further refinement was therefore continued on model A.

There are 22 hydrogen atoms in each cation, which were evident in a difference Fourier synthesis. The contributions from the hydrogen atoms were therefore included in calculations of F_c. Idealized positional coordinates were computed, assuming a tetrahedral coordination about both the nitrogen and carbon atoms, with an N-H distance of 1.05 Å and a C-H distance of 1.10 Å. An isotropic thermal parameter of 5.0 Å^2 was assumed. Two cycles of least-squares refinement, including the hydrogen atom contributions and assigning anisotropic thermal parameters to the nonhydrogen atoms, reduced R_1 and R_2 to 0.038 and 0.070. The hydrogen atom positional parameters were then recalculated on the basis of the refined model, and two further cycles of full-matrix least-squares refinement, on F, with 171 variables and 1733 observations for which $F^2 > 2\sigma(F^2)$, converged at residuals of $R_1 = 0.026$ and $R_2 = 0.034$. In the final cycle of refinement no parameter shift exceeded 0.2 esd. The error in an observation of unit weight is 1.26 electrons. A comparison of F_o and F_c showed that secondary extinction was negligible. A statistical analysis of R_2 in terms of $|F_o|$ and $\lambda^{-1} \sin \theta$ showed no abnormal trends. A final difference Fourier synthesis computed from the final structure factors contained no features of chemical significance. The highest peak, at fractional coordinates (0.265, 0.235, 0.125) is of electron density 0.43 (6) e Å^{-3}.

Final positional and thermal parameters are presented in Table I, and those of the hydrogen atoms in Table II. Structure amplitudes are listed in Table III, as $10|F_o|$ and $10|F_c|$ electrons.[14]

Determination of the Absolute Configuration

The absolute configuration of the cation has been determined by the Bijvoet absorption edge technique, employing Mo K$\bar{\alpha}$ radiation.[15]

Each of the two enantiomeric structures, which are related by reflection in a mirror plane at $y = 1/4$, were further refined under the same conditions, including hydrogen atom contributions and assuming anisotropic thermal parameters. The model originally discarded, B, converged after two cycles of refinement with agreement factors $R_1 = 0.029$ and $R_2 = 0.040$. Application of the R factor ratio test shows that structure B may be rejected at the 0.005 level in favor of structure A.[13]

As confirmation, Bijvoet pairs of reflections were compared. A selection of structure amplitudes for structure A is listed in Table IV, for cases where $F_c(hkl)$ and $F_c(h\bar{k}l)$ differ by more than 15%, based on the final positional parameters. These observations confirm enantiomer A as the correct structure.

Table IV. Determination of Absolute Configuration

h	k	l	$F_c(hkl)$	Obsd relationship	$F_c(h\bar{k}l)$
1	1	$\bar{3}$	38.3	>	32.1
1	1	1	73.6	<	90.8
1	1	2	16.5	>	12.1
1	3	2	9.00	<	17.5
1	4	$\bar{2}$	26.3	<	32.9
1	4	0	42.2	~	28.2
3	4	0	19.9	<	24.7
4	4	0	8.99	<	14.0
5	2	0	17.9	<	24.9
5	1	$\bar{1}$	59.6	>	50.4

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
Cl(1)	H(1)	N(1)	3.42	2.52	144	$x, y, z - 1$
Cl(1)	H(7)	C(3)	3.47	2.85	116	$1 - x, 1/2 + y, \bar{z}$
Cl(2)	H(14)	N(3)	3.44	2.56	140	$x, y, 1 + z$
O(1)	H(11)	C(4)	3.28	2.67	115	$x, y, 1 + z$
O(1)	H(13)	C(5)	3.36	2.65	123	$x, y, 1 + z$
O(2)	H(2)	N(1)	3.08	2.17	144	$x, y - 1, z$
O(2)	H(21)	N(4)	2.95	1.92	165	$x, y - 1, z$
O(3)	H(22)	N(4)	3.11	2.15	149	$x, y - 1, 1 + z$

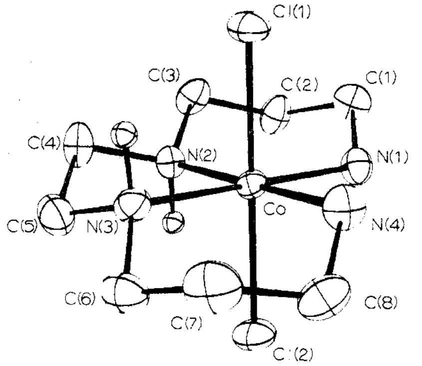

Figure 1. Perspective view of the [Co(3,2,3-tet)Cl$_2$]$^+$ cation, showing the atom-numbering scheme. H(9) is bonded to N(2); H(14) to N(3). Atoms are plotted as 50% probability ellipsoids of thermal motion.

Description of the Structure

The crystal is comprised of discrete ions, linked by a weak hydrogen-bonding network. Interatomic distances A···B for possible hydrogen bonds A-H···B are listed in Table V. The shortest nonbonding cation-cation approaches are 2.26 Å, between H(12) and H(19), and 2.21 Å, between H(13) and H(17).

The atom-numbering scheme is presented in a perspective drawing of the cation in Figure 1. For the purpose of clarity, of the hydrogen atoms only H(9), bonded to N(2), and H(14), bonded to N(3), are included. In Figure 2 a stereoview of the unit cell contents is shown. Atoms are plotted as 50% probability thermal ellipsoids.[9]

The inner coordination sphere of the cobalt atom is close to an ideal octahedron. A selection of intramolecular bond distances and bond angles is given in Table VI. The two trans chlorine atoms occupy the apices, with a mean Co-Cl distance of 2.255 (8) Å and a Cl-Co-Cl angle of 179.72 (3)°. When corrected for thermal motion, assuming a "riding" model, a mean Co-Cl distance of 2.262 (9) Å was obtained. In an analysis of a similar cation, (+)$_{589}$-*trans*-dichloro-

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(9) The computer programs used in this analysis include modifications for the CDC6400 at the University of Western Ontario of J. A. Ibers' NUCLS full-matrix least-squares program and W. R. Busing, K. O. Martin, and H. A. Levy's ORFFE function and error program. Patterson and Fourier syntheses were calculated with a version of A. Zalkin's FORDAP program, and illustrations were drawn with C. K. Johnson's ORTEP plotting program.

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

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

(13) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(14) Table III, a listing of structure factor amplitudes, will appear immediately following this article 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-73-1151.

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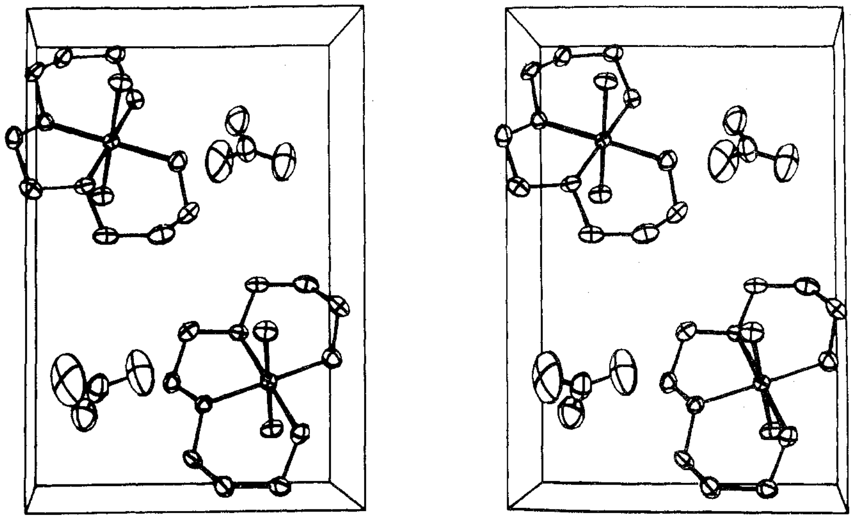

Figure 2. Stereoview of the contents of one unit cell. The horizontal axis, *y*, runs from 0 to 1, and the vertical axis, *x*, from $-^1/_2$ to $^1/_2$.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg)

Co-N(1)	1.991 (3)	Cl(1)-Co-Cl(2)	179.72 (3)
Co-N(2)	1.977 (4)	Cl(1)-Co-N(1)	91.72 (15)
Co-N(3)	1.985 (3)	Cl(1)-Co-N(2)	90.82 (9)
Co-N(4)	1.984 (4)	Cl(1)-Co-N(3)	89.03 (15)
Co-Cl(1)	2.247 (3)	Cl(1)-Co-N(4)	87.29 (10)
Co-Cl(2)	2.263 (3)	Cl(2)-Co-N(1)	88.01 (15)
N(1)-C(1)	1.489 (5)	Cl(2)-Co-N(2)	89.13 (9)
C(1)-C(2)	1.510 (7)	Cl(2)-Co-N(3)	91.24 (15)
C(2)-C(3)	1.515 (5)	Cl(2)-Co-N(4)	92.77 (10)
C(3)-N(2)	1.483 (5)	N(1)-Co-N(2)	92.4 (1)
N(2)-C(4)	1.482 (4)	N(2)-Co-N(3)	86.6 (1)
C(4)-C(5)	1.512 (5)	N(3)-Co-N(4)	91.1 (2)
C(5)-N(3)	1.495 (6)	N(4)-Co-N(1)	89.9 (2)
N(3)-C(6)	1.479 (5)	Co-N(1)-C(1)	120.2 (2)
C(6)-C(7)	1.508 (7)	N(1)-C(1)-C(2)	111.5 (3)
C(7)-C(8)	1.510 (6)	C(1)-C(2)-C(3)	113.7 (3)
C(8)-N(4)	1.481 (5)	C(2)-C(3)-N(2)	112.0 (3)
N(5)-O(1)	1.226 (6)	C(3)-N(2)-C(4)	110.3 (3)
N(5)-O(2)	1.254 (5)	N(2)-C(4)-C(5)	107.1 (3)
N(5)-O(3)	1.188 (6)	C(4)-C(5)-N(3)	107.3 (3)
		C(5)-N(3)-C(6)	111.0 (3)
		N(3)-C(6)-C(7)	112.7 (3)
		C(6)-C(7)-C(8)	113.5 (3)
		C(7)-C(8)-N(4)	112.1 (3)
		C(8)-N(4)-Co	119.7 (2)
		O(1)-N(5)-O(2)	118.9 (4)
		O(1)-N(5)-O(3)	120.3 (6)
		O(2)-N(5)-O(3)	120.8 (5)

{(+)$_{589}$-*N,N'*-bis((*S*)-2-amino-3-phenylpropyl)-*trans*-(*R*)-cyclohexane-1,2-diamine-δλδ}cobalt(III) perchlorate, with two molecules per asymmetric unit, a mean Co-Cl distance of 2.260 (8) Å was observed.[16] A value of 2.29 Å in *trans*-[Co(*R*-pn)$_2$Cl$_2$]Cl·HCl·2H$_2$O[17] was found.

The tetradentate linear tetramine ligand occupies the equatorial plane. The mean Co-primary N atom distance is 1.988 (4) Å, and the mean Co-secondary N atom distance is 1.981 (4) Å. These values agree well with those of 1.974 (4) and 1.981 (9) Å observed in the [Co(3,2,3-tet)(NO$_2$)$_2$]$^+$ cation[3] and in other determinations. The five C-C distances in the tetramine ligand have a mean of 1.511 (1) Å, and the six C-N bonds, a mean of 1.485 (2) Å. Values of 1.482 (5) and 1.498 (5) Å were determined in the [Co(3,2,3-tet)(NO$_2$)$_2$]$^+$ cation. The presence of steric strain in the chelate rings is demonstrated by the inter-ring angles. The five-membered chelate ring, with a gauche conformation, subtends an angle of 86.6 (1)° at the cobalt atom. The mean of the two angles at the cobalt atom subtended by the six-membered chelate rings is 91.7 (7)°. The mean of the angles at the two secondary nitrogen atoms is 110.6 (6)°. The angles at the carbon and nitrogen atoms are significantly distorted from the tetrahedral value upon coordination. The mean angle at a ring carbon atom in a six-membered ring is 112.6 (4)°, while the mean value in the five-membered ring is 107.2 (1)°. These values are in good agreement with those of 113.1 (5) and 108.1 (7)°, respectively, observed in the *trans*-dinitro analog. Similar values for both five- and six-membered rings have been summarized in a review by Saito.[18]

The five-membered chelate ring adopts the gauche conformation, of absolute configuration δ.[4] The two six-membered rings have chair conformations. In the five-membered ring, the carbon atoms C(4) and C(5) deviate from the plane formed by Co, N(2), N(3) by 0.38 and −0.34 Å, respectively. Deviations of 0.30 and −0.35 Å were observed in the *trans*-dinitro derivative. The dihedral angle between the planes containing N(2), C(4), C(5) and N(3), C(4), C(5) is 63.9 (3)°, compared to 49.2° in the [Co(3,2,3-tet)(NO$_2$)$_2$]$^+$ cation.[3]

Some selected least-squares planes are presented in Table VII. The four donor nitrogen atoms show deviations from the equatorial plane. N(1) and N(3) are displaced by −0.023 (3) and −0.022 (3) Å, while N(2) and N(4) are displaced in the opposite sense, by 0.019 (2) and 0.025 (3) Å. These deviations are similar in magnitude, but opposite in sign to those observed in the dinitro cation, where N(1) and N(3) were displaced 0.036 and 0.037 Å, and N(2) and N(4) were displaced by −0.036 and −0.035 Å from the equatorial plane. In both cases the absolute configuration of the five-membered ring is δ, with C(4) displaced from the Co, N(2), N(3) plane in a direction which is defined as positive.

The nitrate anion is planar within experimental error. The mean N-O bond distance is 1.223 (19) Å, and the mean O-N-O angle is 120.0 (6)°.

Discussion

Rules which would allow the prediction of absolute configurations from the Cotton effects associated with d-d transitions have been sought for some time.[19-22] The

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Table VII. Selected Least-Squares Planes

Plane 1, through Co, N(1), N(2), N(3), N(4)
Plane equation: $10.19x + 0.81y - 4.76z = 2.76$
Displacements from the Plane, Å

Co	−0.0013 (4)	N(4)	0.034 (3)
N(1)	−0.014 (3)	C(4)	0.40
N(2)	0.026 (2)	C(5)	−0.34
N(3)	−0.013 (3)		

Plane 2, through N(1), N(2), N(3), N(4)
Plane Equation: $10.19x + 0.81y - 4.76z = 2.77$
Displacements from the Plane, Å

N(1)	−0.023 (3)	N(4)	0.025 (3)
N(2)	0.019 (2)	C(4)	0.40
N(3)	−0.022 (3)	C(5)	−0.33

Plane 3, through N(5), O(1), O(2), O(3)
Plane Equation: $9.50x + 2.66y + 3.21z = 2.97$
Displacements from the Plane, Å

N(1)	−0.007 (4)	O(2)	0.002 (4)
O(1)	0.006 (6)	O(3)	0.008 (7)

optical activity observed has been attributed to three sources of asymmetry in the metal complexes: first, configurational asymmetry, due to the helical arrangement of chelate rings around the metal atom, especially in octahedral *cis*-bisdiamine and trisdiamine complexes; second, a conformational contribution, arising from a dissymmetric, puckered chelate ring; and, third, a vicinal contribution caused by the presence of an asymmetric center on the chelate ring. In *trans*-bisdiamine complexes of Co(III), containing the CoN_4X_2 chromophore, any observed Cotton effects have been considered to originate from the second and third sources. Recently, two further sources of dissymmetry were recognized: that arising from dissymmetrically arranged amine hydrogen atoms and that due to dissymmetric distortions of the donor atoms.[21] We have completed single-crystal structure analyses of two Co(III) complexes of 3,2,3-tet, containing the CoN_4X_2 chromophore, where $X^- = Cl^-$ and NO_2^- in an attempt to examine the applicability of various regional rules. For such complexes, to a first approximation, the sources of dissymmetry expected would be the conformational effect of the gauche five-membered ring, the vicinal effect of the asymmetric, coordinated, secondary nitrogen atoms, and possible distortions of the donor atoms. The two six-membered rings possess an effective plane of symmetry and may therefore be neglected as sources of dissymmetry at this stage.

The optical properties of the $[Co(3,2,3\text{-tet})Cl_2]^+$ ion are presented in Figure 3.[23] The absorption spectrum is very similar to that of the *trans*-$[Co(R\text{-pn})_2Cl_2]^+$ ion, which has been extensively studied.[24,25] By analogy, we can assign the absorption maximum at 16,000 cm^{-1} to the $^1A_{1g} \rightarrow {}^1E_g$ transition, and the maximum at 21,500 cm^{-1} to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition, both originating from the $^1A_{1g} \rightarrow {}^1T_{2g}$ manifold. Likewise, the circular dichroism spectrum of the 3,2,3-tet complex is very similar to those of *trans*-$[Co(R\text{-pn})_2Cl_2]^+$ and *trans(Cl)*-$[Co(R\text{-pn})(NH_3)_2Cl_2]^+$.[21] Thus, the ^1E_g transition shows a negative circular dichroism band, in both methanol solution and the solid-state KBr disk spectrum, while the sign of the $^1A_{2g}$ transition reverses in changing from the solution to the solid-state spectrum. In the diamine complexes, which contain R-pn, with a preferred ring configuration of λ, both the $^1A_{2g}$ and the ^1E_g bands show positive signs of circular dichroism in the solid-state spectrum. In the *trans*-$[Co(3,2,3\text{-tet})Cl_2]^+$ ion, where the absolute configuration of the ring is δ, the sign of the ^1E_g band is negative and is of opposite sign to that observed for the λ configuration of the R-pn ring in the diamine complexes. By contrast, in the solid state, the sign of the $^1A_{2g}$ band is positive and of the same sign as that observed for the opposite absolute configuration of the R-pn ring in the diamine complexes. We might therefore conclude that, in the solid-state spectra, an additional source of dissymmetry is affecting the observed circular dichroism of the $^1A_{2g}$ transition, in addition to the conformational dissymmetry of the chelate ring. If this dissymmetry is responsible for the sign of the $^1A_{2g}$ band, then it is similar in both types of complex.

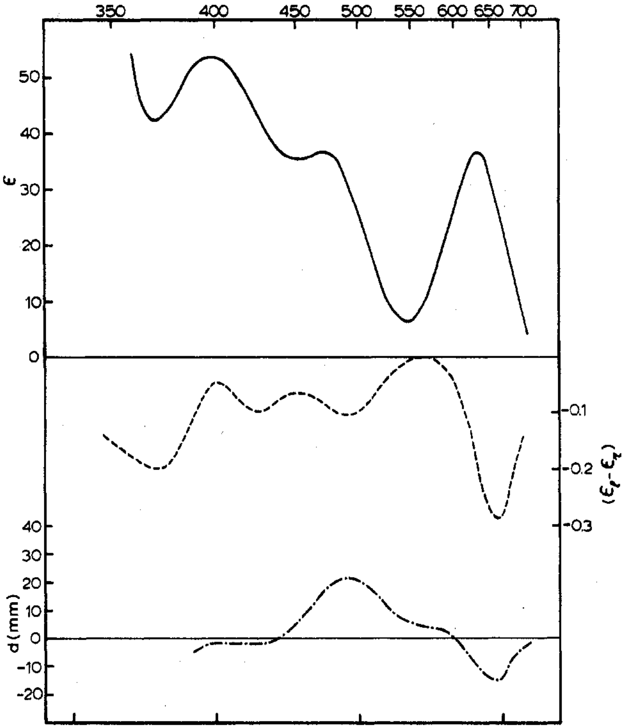

Figure 3. Absorption and CD spectrum of $(-)_{589}[Co(3,2,3\text{-tet})Cl_2]NO_3$: ——, electronic spectrum in methanol; - - - - - -, CD spectrum in methanol; -·-·-·-, CD spectrum of a 1% KBr disk, sensitivity 5 mdeg cm^{-1}.

An examination of the displacements of the donor nitrogen atoms from the equatorial plane of the coordination octahedron suggests a possible reason for this sign inversion. If these distortions are assumed to remain constant in sense in both the crystalline state, in which the structural analysis was performed, and the KBr disk, for which the circular dichroism was recorded, then the sign of the $^1A_{2g}$ band appears to depend upon the sense of the distortion. This assumption is supported by the invariance of the signs, the positions, and the relative intensities of the circular dichroism spectra recorded from a freshly prepared disk, an aged disk, and a Nujol mull pressed between two microscope slides.[23] Thus, in the structural analysis of the *trans*-$[Co(R\text{-pn})_2Cl_2]^+$ ion,[17,25] a calculation of a least-squares plane through the four donor nitrogen atoms shows that these atoms deviate alternatively, positively and negatively, by a mean value 0.030 (1) Å from the plane. The ring carbon atoms deviate from the plane in the opposite direction to the nitrogen atom to which they are bonded, so for a ring of absolute configura-

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tion λ, the donor atom distortions give rise to a dissymmetry of absolute configuration δ. The equivalent calculation for the *trans*-[Co(3,2,3-tet)Cl_2]$^+$ ion shows deviations of the donor atoms of mean value 0.022 (1) Å, but in this case the carbon atoms deviate from the plane in the same sense as the nitrogen atoms (Figure 4). The absolute configuration of the ring is δ, and the donor atoms form an additional dissymmetry of configuration δ. Thus both the *trans*-[Co(*R*-pn)$_2$$Cl_2$]$^+$ ion and the *trans*-[Co(3,2,3-tet)Cl_2]$^+$ ion have donor atom distortions which result in the formation of an additional source of dissymmetry of absolute configuration δ, and the observed circular dichroism spectra for both species have positive $^1A_{2g}$ bands in the solid state, in spite of the different absolute configurations of the chelate rings. The ^1E_g band, negative in the 3,2,3-tet species and positive in the diamine species, appears to depend in sign on the absolute configurations of the rings which are δ and λ, respectively. This conclusion is similar to that reached recently in a regional rule based on an octahedral pseudoscalar potential.[21] However, if the observed distortions are responsible for the sign of the $^1A_{2g}$ band, the donor atoms appear to interact with the pseudoscalar potential with a different sign to the interaction of the alkyl groups in the chelate ring, rather than the same sign, as was assumed in the discussion of the potential.

Further evidence, though qualitative in nature, for the importance of the donor atom distortions may be adduced from the variation in sign of the $^1A_{2g}$ band in changing from solution to the solid-state KBr disk. Similar effects and solvent dependence were observed for the analogous diamine complexes.[21] The sign of the ^1E_g band remains unchanged, though it varies in intensity. This is to be expected, for this transition is mainly dependent upon the absolute configuration of the ring, and to invert the ring would involve inversion of the entire tetramine moiety. The sign of the $^1A_{2g}$ band, dominated by the relatively small donor atom distortions, might be expected to be more sensitive to solvent effects.

Extension of this argument to the *trans*-[Co(3,2,3-tet)-(NO_2)$_2$]$^+$ ion is only partially successful. It is generally accepted that, owing to the different ligand field strengths of Cl^- and NO_2^-, the ^1E_g band in the CoN_4X_2 chromophore shifts to around 22,000 cm^{-1}, while the $^1A_{2g}$ band around 21,000 cm^{-1} remains relatively unchanged in energy.[26] In solution, such a spectrum is observed, and in accordance with the δ configuration of the ring, a negative ^1E_g band is seen. In the solid KBr disk, this band changes sign, and a broad, positive band is observed. In solution and, apparently in the solid state, the $^1A_{2g}$ band is positive in sign. It has been shown that the donor atom distortions in *trans*-[Co(3,2,3-tet)(NO_2)$_2$]$^+$ are of the opposite sense to the deviations of the carbon atoms to which they are bonded (Figure 4), forming a donor atom dissymmetry of absolute configuration λ.[3] By our previous argument, this should give rise to a negative $^1A_{2g}$ band, not a positive band as is observed. A strict comparison is difficult, however, owing to the broadness of the band in the KBr disk spectrum and the uncertainty of the additional dissymmetry caused by the nonaxially symmetric NO_2^- groups. We do however see a consistent picture for the compounds with the CoN_4Cl_2 chromophore. Attempts to examine rigorously the sector occupancy of the remaining atoms of the tetramine in the pseudoscalar potential yielded various results, and in general any sign may be obtained by a judicious placing of the nodes of the potential. A recent study[27] of complexes of 5-(*R*)-methyl-1,10-diamino-4,7-diazadecane, applying the hexadecant rule, concluded that the sign of the ^1E_g band can be correlated with the ring chirality, while the sign of the $^1A_{2g}$ band does not always correlate with that predicted by the sector rule.[20] An empirical correlation was noticed, however, with the chirality of the asymmetric, secondary nitrogen atoms.[27]

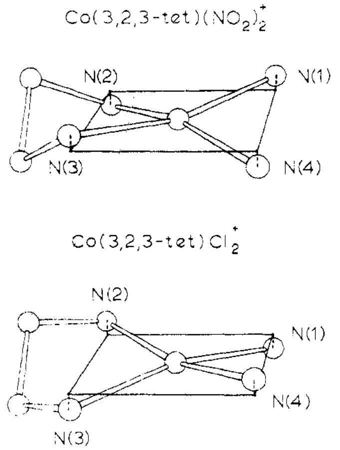

Figure 4. Donor atom distortions in [Co(3,2,3-tet)X_2]$^+$ cations.

We conclude therefore, that distortions of the donor atoms from an ideal octahedral geometry may give rise to additional sources of dissymmetry. Such sources may contribute markedly to the sign of the circular dichroism, especially in complexes where the prime sources of dissymmetry are either conformational or vicinal in origin. Unfortunately, the uncertainty in knowing the exact nature of these donor atom distortions, without a detailed structural analysis, precludes any ready applicability of the proposed regional rule to such systems.

Registry No. (−)-*trans*-dichloro-(1,10-diamino-4,7-diazadecane)cobalt(III) nitrate, 38217-29-7.

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