The PD_3 analog can be best prepared by chromatography on alumina deactivated with 8% D_2O; this method is preferential to several solution exchanges.

Registry No. $Cr(CO)_5PH_3$, 18116-53-5; $[(C_2H_5)_4N]$-$[CrCl(CO)_5]$, 14780-95-1; *cis*-$Cr(CO)_4(PH_3)_2$, 21676-58-4; $Cr(CO)_4DTO$, 21948-40-3; *cis*-$Mo(CO)_4(PH_3)_2$, 21676-59-5; *cis*-$W(CO)_4(PH_3)_2$, 21479-60-7; *fac*-$Cr(CO)_3(PH_3)_3$, 26068-81-5; $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; *fac*-$Mo(CO)_3(PH_3)_3$, 23623-68-9; *fac*-$W(CO)_3(PH_3)_3$, 38496-37-6; $Cr(CO)_5PD_3$, 38496-38-7; *cis*-$Cr(CO)_4(PD_3)_2$, 38496-39-8; *fac*-$Cr(CO)_3$-$(PD_3)_3$, 38496-40-1.

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Crystal Structure of (1,3-Dimethylarsino-2,2,4,4-tetramethylcyclobutane-*As,As*)tetracarbonylchromium at −150°

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The crystal structure of $\{Me_2As)\overline{CH(CH_3)_2C(Me_2As)CH(CH_3)_2C}\}Cr(CO)_4$ has been determined at −150° from the three-dimensional X-ray diffraction data collected by counter methods ($2\theta \leqslant 60°$) using Mo Kα radiation. The compound crystallizes in the tetragonal space group $I4_1cd$; the unit cell contains 8 molecules and has dimensions a = 12.115 (2), c = 27.514 (5) Å; d_m = 1.51 g/cm^3; d_c = 1.41 g/cm^3 for 8 molecules. The structure was determined from the Patterson function and refined by full-matrix least-squares techniques to R = 0.025 and R_w = 0.028 for 1437 observed reflections. A crystallographic twofold axis passes through the chromium atom and the midpoints of the two vectors joining nonbonded carbon atoms in the cyclobutane ring. The asymmetric unit is thus half of the molecule. The chromium atom has approximately octahedral coordination, Cr–As being 2.486 (1) Å. The carbonyl group trans to an arsenic atom has Cr–C = 1.841 (4) Å while those cis have Cr–C = 1.885 (4) Å. These Cr–C bond lengths are significantly different and reflect the superior π-acceptor properties of the carbonyl group. In the cyclobutane ring, the two independent carbon-carbon bond lengths are 1.570 (5) and 1.565 (5) Å. The cyclobutane group is nonplanar, the dihedral angle being 31.9 (5)°.

Introduction

Recently, Cullen[1] has shown that when arsenic atoms are substituted in the 1,3 positions of cyclobutane, a chelate complex can be formed with chromium carbonyl compounds. Using the geometry of cyclobutane as a model, arsenic atoms in the 1,3 positions and cis (axial-axial) positions (see ref 2 for nomenclature) would have a separation of ~3.6 Å. Since one might expect some nonbonded repulsion between arsenic atoms, the separation is probably greater in the hypothetical uncoordinated ligand. This ligand bite has to be shortened to form a chelate compound and this study was undertaken to ascertain if any distortions occur, especially of the cyclobutane ring on chelation. A second feature of interest was whether differences in the Cr–C bond lengths could be determined. It was expected that the use of low temperature would assist this aim.

Experimental Section

The pale yellow crystals of the compound were octahedral. A zero-level Weissenberg photograph with (110) as the rotation axis and precession photographs with (110) as the dial axis, taken with Cu Kα radiation, indicated that the crystals were tetragonal. The following spectra were observed: for hkl, $h + k + l = 2n$; for $0kl$, $l(k) = 2n$; for hhl, $2h + l = 4n$. The space group $I4_1cd$ is unequivocally indicated by these spectra and the Laue symmetry ($4/mmm$).

Crystal Data. $C_{16}H_{26}As_2CrO_4$, mol wt 436.04, crystallizes in the tetragonal space group $I4_1cd$, with a = 12.115 (2) Å, c = 27.514 (5) Å, U = 4038.2 Å^3 (cell at −150°), d_m = 1.5 (1) g/cm^3 (flotation in $ZnBr_2$ solution), d_c = 1.41 g/cm^3, Z = 8, $F(000)$ = 1760, λ(Cu Kα) 1.5418 Å, λ(Mo Kα_1) 0.70926 Å, and μ(Mo Kα) = 40.3 cm^{-1}.

A small octahedral crystal (for absorption corrections, the crystal was assumed a sphere of 0.3-mm diameter) was used to measure cell dimensions and the intensity data. It was mounted on a single-crystal Cryo-Tip refrigerator (manufactured by Air Products and Chemicals, Inc.) with a general orientation in order to minimize intrinsic multiple reflection. Cell dimensions were obtained at 22 and −150° by least-squares analysis of the 2θ values $\{2\theta > 34°$; the function minimized was $\Sigma(\Delta\theta)^2\}$ of 11 reflections which had been accurately centered on a computer-controlled Picker diffractometer. Mo Kα_1 radiation was used and the takeoff angle was 1°. The errors in the cell dimensions are those determined in the least-squares process.

Intensity data were collected at −150°. The variation in temperature throughout the data collection was from −145 to −150°. The unique set of intensities was measured using the θ–2θ scan technique with Mo Kα radiation (niobium filtered) and a scintillation counter equipped with pulse height analysis. The takeoff angle was 2°. Each reflection was scanned symmetrically for 1.3° (extended for spectral dispersion) at a scan rate of 2° min^{-1}. At each end of the scan range, the background scattering was counted 20 sec. Every 75 reflections, two standard reflections were measured and the maximum deviation of any individual standard from the mean was 3%. In this manner, intensities for 1506 reflections with $2\theta \leqslant 60°$ were measured.

Intensities were corrected for background (normalized to the scan time) and for the Lorentz-polarization factor. An absorption correction was applied by assuming the crystal to be a sphere, μR = 0.6. For each reflection, the esd in the intensity, σ_I, was determined from $\sigma_I = \{(TC) + (t_s/t_b)^2(B_1 + B_2) + (kI)^2\}^{1/2}$ where TC is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the background count time, and k is a constant set to 0.03.[3] If $I \leqslant 2.3\sigma_I$ (I is the net intensity), the reflection was considered unobserved. The number of observed reflections was 1437.

Structure Determination. In an ordered structure comprising 8 molecules per unit cell the chromium atom would be expected to lie on a crystallographic twofold axis with half of the molecule as the asymmetric unit. The chromium atom was placed at (0, 0, 0) and

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(1) W. R. Cullen, personal communication.

(2) P. Anderson, O. Bastiansen, and S. Furberg, Ed., "Selected Topics in Structure Chemistry," Universitetsforlaget, Oslo, 1967, p 91.

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

Table I. Positional (Fractional Coordinates) and Thermal (Å^2) Parameters

(a) Positional Parameters for Nonhydrogen Atoms

Atom	x	y	z
As	−0.11067 (3)[a]	0.08352 (3)	0.06658 (4)
Cr	0.0	0.0	0.0
C(1)	−0.0920 (4)	0.0641 (4)	−0.0451 (2)
O(1)	−0.1488 (4)	0.1037 (3)	−0.0738 (2)
C(2)	−0.0869 (3)	−0.1282 (4)	−0.0064 (2)
O(2)	−0.1369 (3)	−0.2074 (3)	−0.0153 (1)
C(3)	−0.1165 (3)	0.2437 (3)	0.0646 (2)
C(4)	−0.2692 (3)	0.0550 (3)	0.0684 (2)
C(5)	−0.0705 (3)	0.0542 (3)	0.1352 (1)
C(6)	−0.0549 (3)	−0.0719 (3)	0.1464 (1)
C(7)	−0.1182 (3)	−0.1575 (3)	0.1165 (2)
C(8)	−0.0807 (4)	−0.1007 (4)	0.1999 (2)

(b) Anisotropic Thermal Parameters for Nonhydrogen Atoms[b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As	0.0167 (2)	0.0175 (2)	0.0150 (1)	0.0027 (1)	−0.0010 (1)	−0.0008 (1)
Cr	0.0225 (4)	0.0176 (4)	0.0121 (3)	0.0017 (3)	0.0	0.0
C(1)	0.040 (2)	0.028 (2)	0.024 (2)	−0.003 (2)	−0.009 (2)	0.003 (2)
O(1)	0.070 (3)	0.048 (2)	0.047 (2)	−0.005 (2)	−0.034 (2)	0.017 (2)
C(2)	0.024 (2)	0.031 (2)	0.016 (2)	0.003 (2)	−0.002 (1)	0.000 (2)
O(2)	0.039 (2)	0.033 (2)	0.037 (2)	−0.010 (2)	−0.006 (1)	−0.005 (1)
C(3)	0.028 (2)	0.019 (2)	0.028 (2)	0.010 (2)	−0.002 (2)	0.001 (2)
C(4)	0.021 (2)	0.029 (2)	0.032 (2)	−0.001 (1)	−0.003 (2)	−0.002 (2)
C(5)	0.025 (2)	0.021 (2)	0.012 (1)	0.002 (1)	0.002 (1)	−0.002 (1)
C(6)	0.031 (2)	0.021 (2)	0.017 (2)	−0.001 (1)	0.002 (1)	−0.001 (1)
C(7)	0.020 (2)	0.023 (2)	0.020 (2)	−0.006 (2)	0.002 (1)	−0.000 (1)
C(8)	0.016 (2)	0.033 (2)	0.017 (2)	−0.007 (2)	0.006 (2)	0.006 (2)

(c) Positional and Isotropic Thermal Parameters for Hydrogen Atoms[c]

Atom	x	y	z	$\bar{U}_{\text{iso}}$
H(31)	−0.151 (6)	0.274 (7)	0.097 (3)	0.025
H(32)	−0.055 (5)	0.271 (6)	0.063 (3)	0.025
H(33)	−0.162 (5)	0.258 (4)	0.037 (2)	0.025
H(41)	−0.297 (5)	0.099 (5)	0.041 (2)	0.028
H(42)	−0.283 (4)	−0.013 (5)	0.065 (2)	0.028
H(43)	−0.295 (6)	0.080 (5)	0.098 (3)	0.028
H(51)	−0.117 (5)	0.087 (5)	0.148 (3)	0.019
H(71)	−0.097 (5)	−0.235 (6)	0.123 (2)	0.023
H(72)	−0.202 (5)	−0.152 (4)	0.126 (2)	0.023
H(73)	−0.110 (4)	−0.151 (4)	0.087 (2)	0.023
H(81)	−0.062 (5)	−0.049 (6)	0.228 (3)	0.027
H(82)	−0.147 (7)	−0.123 (6)	0.203 (3)	0.027
H(83)	−0.045 (6)	−0.165 (6)	0.207 (2)	0.027

[a] In this table, and all subsequent tables, the figure in parentheses is the esd in the least significant digit. [b] Expression of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [c] Hydrogen atoms were given isotropic temperature factors equivalent to those of the carbons to which they were attached.

the arsenic atom was located in a Patterson map. A structure factor calculation with these two atoms gave $R = 0.19$ with data to $\lambda^{-1} \sin\theta = 0.55$. An electron density map showed all nonhydrogen atoms, and when the coordinates and isotropic temperature factors were refined by the full-matrix least-squares technique (unit weights for each reflection; $\Sigma w(|F_o| - |F_c|)^2$ minimized), R was reduced to 0.04. Hydrogen atoms were located in an electron density difference synthesis which also indicated anisotropic thermal motion for the arsenic and chromium atoms and the carbonyl groups. Hydrogen atoms were fixed at calculated positions and further refinement with all data reduced R to 0.028. Another electron density difference map showed the other carbon atoms should have anisotropic thermal parameters and this was allowed for in subsequent least-squares refinement cycles. After convergence was reached with variation of the nonhydrogen parameters, the hydrogen atom coordinates only were refined with data out to $\lambda^{-1} \sin\theta = 0.48$ and this caused R_w ($R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$) to fall from 0.024 to 0.021 for this set. A final refinement cycle with hydrogen atoms fixed at their new positions led to $R = 0.025$ and $R_w = 0.028$ and all parameter shifts were less than 0.1σ. In the final refinement cycles, the weights were those determined from the counting statistics, $w = 1/\sigma_{F^2}$, where $\sigma_F = \sigma_I/(Lp) \cdot 2F_o$. The error of fit was 1.02 and there was no variation of $w(|F_o| - |F_c|)$ for ranges of F_o and $\lambda^{-1} \sin\theta$. A final electron density difference map had some peaks and troughs of height ~0.5 e Å^{-3} near the arsenic and chromium atoms. *Cf.* the height of a carbon atom of ~10.5 e Å^{-3}.

Calculations were carried out as described in ref 4.

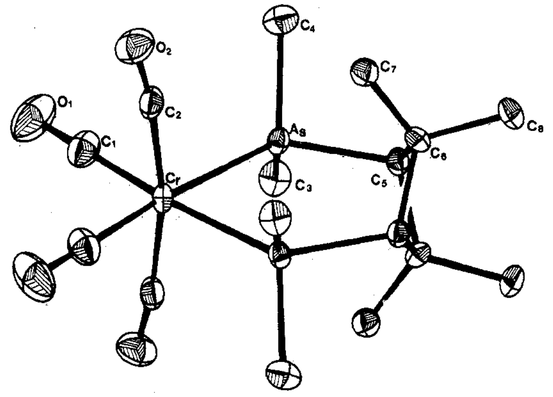

Figure 1. A diagram of the molecule indicating the atomic labeling used; 50% thermal ellipsoids are shown for the atoms.

Scattering factors for the non-hydrogen atoms were taken from

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(4) Programs used are listed in F. W. B. Einstein and R. D. G. Jones, *Inorg. Chem.*, **11**, 395 (1972), with the exception of the data reduction program which was written by Dr. M. M. Gilbert of this laboratory.

ref 5a and those for hydrogen from ref 5b while anomalous dispersion corrections for the arsenic and chromium atoms were taken from ref 5c.

Results

Coordinate and thermal parameters obtained in the last least-squares cycle are shown in Table I.[6] Interatomic distances and angles are listed in Table II. The equations to selected planar groupings are tabulated in Table III. Analysis of the thermal parameters of the nonhydrogen atoms (excepting the carbonyl groups) showed that these atoms could be described as a rigid body. However the correction to the bond lengths using this model were of the order of 0.001 Å (in keeping with the small thermal motion) and are therefore not judged to be significant. Figure 1 is a diagram of the molecule.

Discussion of the Structure

Even though the favored conformation for 1,3-disubstituted cyclobutanes in the free molecule would place the arsenic atoms in the equatorial-equatorial (ee) positions, the compound here has the arsenic atoms in the axial-axial (aa) positions in order that the cyclobutane can function as a chelate ligand. Hence the stability imposed on the ligand system by complex formation more than compensates for the small energy barrier in going from the ee to the aa conformation.

A crystallographic twofold axis passes through the chromium atom and the midpoints of the vectors joining the two sets of nonbonded carbon atoms in the cyclobutane group. The chromium atom has approximately octahedral geometry. Cr-As is 2.486 (1) Å. Two significantly different chromium-carbon bond distances are observed, Cr-C(1) = 1.841 (4) and Cr-C(2) = 1.885 (4) Å. The shorter distance is trans to an arsenic atom whereas the longer one is trans to another carbonyl group and reflects the superior π-acceptor properties of the carbonyl group. The carbon-oxygen distances are not significantly different, C(1)-O(1) = 1.150 (5) and C(2)-O(2) = 1.161 (5) Å. Similar variations in chromium-carbon bond lengths have been observed by Plastas, *et al.*,[7] for pentacarbonyltriphenylphosphinechromium and pentacarbonyl(triphenyl phosphite)chromium. It would be expected that metal-oxygen distances should vary somewhat less than metal-carbon distances in metal carbonyls since the variation of carbon-oxygen bond length with changes in the multiple bond character of the CO group is much less sensitive than for the metal-carbon bond.[8] In addition to this, it is also possible that, in cases where the metal-oxygen distance is constant and the metal-carbon distance varies, the variation may be due to inaccurate carbon atom placement. For the compounds studied by Plastas, *et al.*, even though chemical considerations indicate the phosphite is a better π acceptor than the phosphine, the corresponding metal-oxygen distances in each compound are the same.

The two independent carbon-carbon bond distances in the cyclobutane ring are equal within experimental error, 1.570 (5) and 1.565 (5) Å. This is slightly longer than the values determined in other cyclobutane derivatives in recent years: *e.g.*, 1.558 (3) Å by Raman spectra[9] and 1.548 (3) Å by electron diffraction[10] for cyclobutane; 1.555 (15) Å from electron diffraction studies of several halogen derivatives of cyclobutane.[2] There is a folding of the cyclobutane ring about C(6)· · ·C(6′), the dihedral angle [C(5)-C(6)-C(6′)] - [C(5′)-C(6)-C(6′)] being 31.9 (5)°, a value not much different from that found in free cyclobutane of 35°[2] and that in halogenated derivatives of 33°. Hence in the formation of the chelate compound, there has been virtually no change in the angle of fold. It might have been expected that this angle would have increased on chelation due to the pulling together of the arsenic atoms (As· · ·As in 3.360 Å in the complex). A difference is observed between the arsenic-methyl carbon and the arsenic-ring carbon bonds, the latter being the longer. Since the angle C(3)-As-C(4) is 98.2 (2)°, one might expect As-C(3) and As-C(4) to have more p-orbital character contribution from the arsenic atom than As-C(5), and As-C(5) to have more s-orbital character contribution than As-C(3) and As-C(4).[11] As a result, As-C(5) should be shorter than As-C(3) and As-C(4), contrary to observation. One might sug-

Table II. Molecular Geometry

(a) Interatomic Distances, Å

As-Cr	2.486 (1)	C(3)-H(31)	1.01
As-C(3)	1.943 (4)	C(3)-H(32)	0.81
As-C(4)	1.952 (4)	C(3)-H(33)	0.95
As-C(5)	1.982 (4)	C(4)-H(41)	0.95
		C(4)-H(42)	0.83
Cr-C(1)	1.841 (4)	C(4)-H(43)	0.89
Cr-C(2)	1.885 (4)	C(5)-H(51)	0.80
C(1)-O(1)	1.150 (5)	C(7)-H(71)	0.94
C(2)-O(2)	1.161 (5)	C(7)-H(72)	0.99
C(5)-C(6)	1.570 (5)	C(7)-H(73)	0.85
C(5)-C(6′)	1.565 (5)	C(8)-H(81)	0.95
C(6)-C(7)	1.529 (5)	C(8)-H(82)	0.85
C(6)-C(8)	1.544 (5)	C(8)-H(83)	0.85

(b) Interatomic Angles, Deg

Cr-As-C(3)	113.9 (1)	Cr-C(1)-O(1)	179.2 (4)
Cr-As-C(4)	118.5 (1)	Cr-C(2)-O(2)	172.9 (4)
Cr-As-C(5)	119.8 (1)	As-C(5)-C(6)	113.0 (2)
C(3)-As-C(4)	98.2 (2)	As-C(5)-C(6′)	113.6 (2)
C(3)-As-C(5)	102.4 (2)	C(6)-C(5)-C(6′)	88.8 (3)
C(4)-As-C(5)	100.7 (2)	C(5)-C(6)-C(5′)	86.8 (3)
As-Cr-As′	85.04 (3)	C(5)-C(6)-C(7)	119.7 (3)
As-Cr-C(1)	89.9 (1)	C(5)-C(6)-C(8)	112.5 (3)
As-Cr-C(1′)	174.7 (2)	C(5′)-C(6)-C(7)	118.3 (3)
As-Cr-C(2)	95.9 (1)	C(5′)-C(6)-C(8)	114.5 (3)
As-Cr-C(2′)	92.0 (1)	C(7)-C(6)-C(8)	104.9 (3)
C(1)-Cr-C(1′)	95.1 (3)		
C(1)-Cr-C(2)	86.9 (2)		
C(1)-Cr-C(2′)	85.8 (2)		
C(2)-Cr-C(2′)	169.2 (2)		

Table III. Equations of Planes to Selected Atomic Groupings of the Form $AX + BY + CZ + D = 0$ Where X, Y, and Z are in Å and Are along a, b, and c

Plane no.[a]	Atoms in plane	A	B	C	D	χ^2
1[b]	C(5), C(6), C(6′)	0.218	−0.167	−0.961	3.872	
2	C(5′), C(6), C(6′)	−0.218	0.167	−0.961	3.872	
3	Cr, As, As′, C(5), C(5′)	0.603	0.798	0.0	0.0	14.2[c]

[a] The dihedral angle between planes 1 and 2 is 31.9 (5)°. [b] C(5′) lies 0.591 (3) Å from this plane. [c] Although these atoms do not define a plane from statistical considerations, the maximum deviation of any atom in the plane is 0.010 (4) Å.

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(6) A listing of observed and calculated 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. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1148.

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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)°, ~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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[13] S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52**, 3857 (1970).

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Contribution from the Department of Chemistry, University of Western Ontario, London 72, Ontario, Canada

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 $O_2N\text{-}Co\text{-}NO_2$ 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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