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Crystal Structure of *cis*-(1,4,8,11-Tetraazacyclotetradecane)ethylenediaminecobalt(III) Chloride Trihydrate

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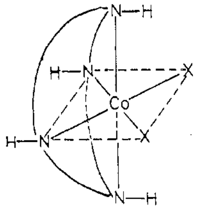
The crystal and molecular structure of *cis*-(1,4,8,11-tetraazacyclotetradecane)ethylenediaminecobalt(III) chloride trihydrate, *cis*-$[Co(C_{10}H_{24}N_4)(C_2H_8N_2)]Cl_3 \cdot 3H_2O$, has been solved by Patterson and Fourier methods. The crystals are orthorhombic, space group *Pbcn*, with $a = 29.840$ (2), $b = 9.489$ (1), and $c = 14.932$ (1) Å and with eight formula units per cell. Refinement by least-squares gave $R = 0.052$ on 2608 diffractometer observations. The crystal structure is composed of *cis*-Co(cyclam)en^{3+} cations, Cl^- anions, and water molecules held together by hydrogen bonds. The cyclic ligand is coordinated to four adjacent octahedral sites around the central cobalt atom and the ethylenediamine molecule occupies the remaining sites.

Introduction

The ligand substitution reactions of cis and trans cobalt(III) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) have been shown to proceed with complete retention of configuration.[2,3] However, cis complexes with unidentate ligands in aqueous solution eventually isomerize to a trans configuration.[4] The mechanism of isomerization of *cis*-$[Co(cyclam)Cl_2]^+$, and possibly of other cis complexes, has been shown to go by way of the labile *cis*-$[Co(cyclam)OHOH_2]^{2+}$ cation involving a facile internal proton transfer from a nitrogen to an oxygen.[4] The mechanism was discussed in terms of a certain proposed configuration of the folded macrocycle in which the two axial amine hydrogens are pointing toward the unidentate ligands (structure I). We have successfully prepared and grown suitable crystals of $[Co(cyclam)en]Cl_3 \cdot 3H_2O$ and report here its crystal and molecular structure in order to understand the configuration of the folded macrocycle. The crystal structures of two related complexes, viz., *cis*-$[Co(cyclen)(NO_2)_2]Cl^5$ and $[Ni(tetb)AcO]ClO_4 \cdot {}^1/_2H_2O^6$ (cyclen = 1,4,7,10-tetraazacyclododecane, tetb = *C-rac*-5,7,7,12,14,14-hexamethyl derivative of cyclam, and AcO = acetate anion), have been published. However, cyclen is only a 12-membered ring and tetb has an additional steric effect arising from the six methyl substituents. The configurations of the above complexes cannot be taken as representative of the folded cyclam in its cobalt(III) complexes.



I

Experimental Section

$[Co(cyclam)en]Cl_3 \cdot 3H_2O$ was prepared by warming a methanolic solution of *trans*-$[Co(cyclam)Cl_2]Cl^7$ with an excess of ethylenediamine. Pink crystals which separated from solution were collected, washed with acetone, and air-dried. Crystals suitable for diffraction studies were grown by slow diffusion of diethyl ether into a saturated methanolic solution of the compound. Anal. Calcd for $[Co(C_{10}H_{24}N_4)(C_2H_8N_2)]Cl_3 \cdot 3H_2O$: C, 30.8; H, 7.94; N, 17.5; Cl, 22.2. Found: C, 30.4; H, 7.96; N, 17.5; Cl, 21.9.

Preliminary oscillation and Weissenberg photographs showed the crystals to be orthorhombic, space group *Pbcn*. Values of cell dimensions were obtained from a least-squares fit to measurements made on *h*0*l* and *hk*0 Weissenberg photographs taken with a Straumanis-type camera using Cu Kα radiation (λ 1.5418 Å); they are $a = 29.840$ (2) Å, $b = 9.489$ (1) Å, $c = 14.932$ (1) Å, and $V = 4228$ Å^3. The density measured by flotation in a chlorobenzene–carbon tetrachloride solution is 1.50 g cm^{-3} and the calculated density for eight formula units of the trihydrate in the unit cell is 1.507 g cm^{-3}. The density analysis indicated three water molecules of crystallization; their presence was confirmed by the successful refinement of the structure.

Intensity data were collected on a Datex-automated General Electric XRD-5 diffractometer using iron-filtered Co Kα radiation (λ 1.7902 Å) and a scintillation counter. The crystal used was a square red prism of dimensions 0.1 × 0.15 × 0.1 mm, elongated along *b*. All reflections within one octant of the sphere of reflection extending to $2\theta = 150°$ were measured using θ–2θ scans at a scanning speed of 1° (in 2θ)/min; the background was counted for 50 s at each extreme. The scan ranges, with values of 1.8° at $2\theta = 10$ and 2.8° at $2\theta = 100°$, were adjusted to account for α_1–α_2 splitting. Four check reflections chosen from different parts of the reciprocal lattice were monitored every 40 reflections; at the end of the data collection each check reflection indicated a drop in intensity of about 2%.

A total of 2782 independent reflections were measured, of which 2608 had net intensities greater than zero. Observational variances $\sigma^2(I_i)$ were calculated from counting statistics including an additional term $(0.02S)^2$ (S = number of counts during the scan) to allow for instrumental variations.[8] Intensities and standard deviations were then corrected for Lorentz and polarization factors and placed on an absolute scale by Wilson's method.[9] No correction was made for absorption ($\mu r_{\min} \simeq 0.36$, $\mu r_{\max} \simeq 0.55$).

Structure Determination and Refinement

The positions of the cobalt atom and three chloride ions were assigned from a three-dimensional Patterson synthesis. After two structure factor Fourier calculations, the remaining nonhydrogen atoms including the oxygen atoms of the water molecules were located. The R index ($=\sum|\Delta F|/\sum|F_o|$) was 0.47.

Refinement was carried out mainly by full-matrix least-squares methods. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weight w equal to $1/\sigma^2(F_o^2)$. Atomic scattering factors for Co, C, N, and O atoms and Cl^- ions were obtained from ref 10 and those for hydrogen atoms were from Stewart, Davidson, and Simpson.[11] The real part of anomalous dispersion correction was applied to the scattering factors for Co.[12] Calculations were carried out on an IBM 370/155 computer under the CRYM system at the California Institute of Technology.

After several cycles of least-squares adjustment of the coordinates and anisotropic temperature factors of the nonhydrogen atoms the R value was reduced to 0.12. A difference map was calculated from which all of the hydrogen atoms were located. During the course of refinement one of the water molecules was proved to be disordered. Inspection of the difference map suggested that the oxygen atom of this disordered molecule could best be represented by two sites, O(3) and O(4), each with an occupancy factor of 0.5.

With this new arrangement the atomic coordinates and anisotropic temperature factors of the nonhydrogen atoms, a scale factor, and a secondary extinction parameter g^{13} were adjusted by a few further cycles until convergence was reached. The coordinates and isotropic temperature factors of 36 hydrogen atoms were then adjusted, to convergence, in a separate full-matrix refinement based on reflections with $2\theta < 100°$; the four partial hydrogen atoms associated with O(3) and O(4) were assigned positions consistent with linear hydrogen bonds and were not adjusted.

Finally, in the last two cycles, 236 parameters were adjusted: coordinates and anisotropic temperature factors of the nonhydrogen atoms, a scale factor, and a secondary extinction parameter g. The

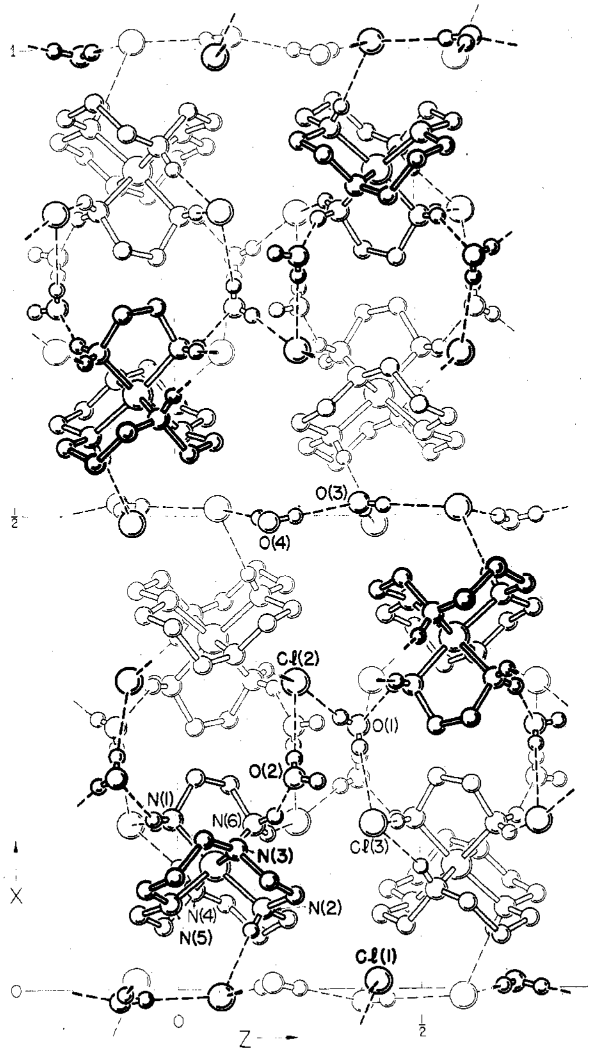


Figure 1. Drawing of the structure, as viewed along the *b* direction. The hydrogen bonding involving O(3) and O(4) comprises two disordered arrangements related to one another by a twofold axis at (for example) $x = 0, z = {}^1/_4$.

positional parameters were kept in one matrix and the rest of the parameters in another.

During the last cycle no shift in the parameters was greater than one-third of its standard deviation. The final *R* index for 2608 reflections with $|F_o|^2 > 0$ is 0.052, the "goodness-of-fit", $[\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, where $m = 2782$ measurements and $s = 236$ parameters, is 1.31, and the final value of the secondary extinction parameter *g*, as defined in ref 13, is $(7.9 \pm 0.3) \times 10^{-7}$. A three-dimensional difference Fourier synthesis calculated at the conclusion of the refinement indicated no peaks or troughs exceeded 0.3 e $Å^{-3}$. The heavy-atom parameters and their standard deviations are given in Table I; those of hydrogen atoms, in Table II. The standard deviations were calculated from the diagonal elements of the inverse matrices; since two separate matrices were used, the esd's may be slightly underestimated. Final structure factors are given in a separate table.[14]

Results and Discussion

Hydrogen Bonding and Molecular Packing. Figure 1 shows the projection of the structure viewed along the *b* axis. The hydrogen-bond distances and the angles subtended at the hydrogen atoms are given in Table III. The complex cations are arranged in layers perpendicular to the *a* axis with the chloride ions and water molecules sandwiched between layers. The shortest cation–cation approaches are 2.54 Å between H[C(5)b] and H[C(9)a] and 2.55 Å between H[C(8)a] and H[C(12)a]. The complex cations are linked through hydrogen bonding to the anions and water molecules. All nitrogen atoms, oxygen atoms, and chloride ions participate in the compact three-dimensional hydrogen-bonding system.

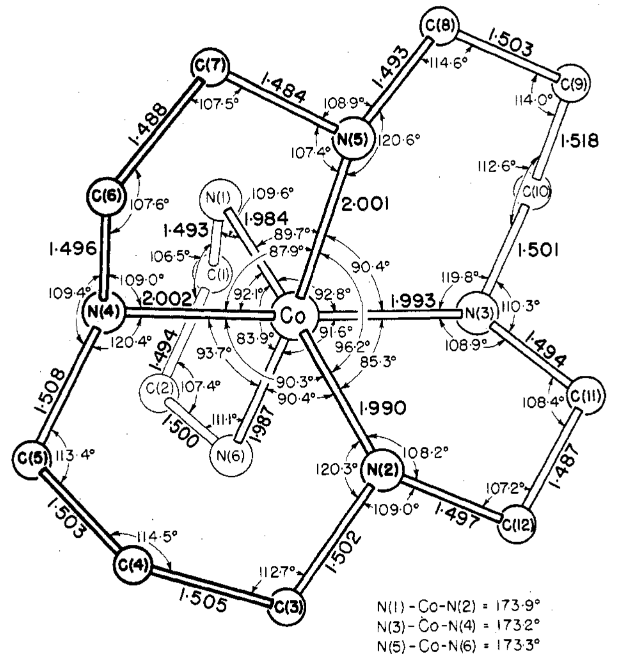


Figure 2. Bond distances and angles involving nonhydrogen atoms.

Molecular Geometry. Figure 2 shows the bond distances and angles involving nonhydrogen atoms. Standard deviations for bond lengths are estimated to be about 0.004 Å for those involving Co and 0.006 Å for those involving only C and N. The respective errors in angles are 0.2 and 0.4°. Bond lengths involving hydrogen atoms are listed in Table IV. Estimated standard deviations are about 0.05 Å.

The two Co–N(en) bonds average to 1.986 ± 0.003 Å, while the four Co–N(cyclam) bonds average to a marginally larger 1.996 ± 0.002 Å. Similar Co–N distances, averaging 1.981 Å, are found in two compounds involving the linear, tetradentate ligand "3,2,3-tet", which differs from cyclam in lacking one ethylene bridge and prefers to coordinate in a square-planar fashion; these latter compounds showed no significant difference between the Co–secondary N and Co–primary N distances.[15] On the other hand, there are notable differences among the C–N distances in cyclen[5] and trien (triethylenetetramine)[16] compounds. These differences have been attributed to angular strain; however, trans electronic effects may also be important. No such trans effect would be expected in the present compound.

Co–N–C angles within the six-membered rings are all close to 120°, suggesting appreciable strain; nearly identical values were found in the six-membered chelate rings of the Co(3,2,3-tet) compounds.[15] Further evidence of strain may possibly be found in the C–N and C–C bond distances, which tend to be slightly longer (by an average of about 0.01 Å) in the six-membered rings than in five-membered rings; however, no such effect is apparent in the 3,2,3-tet compounds. The ten C–N bond lengths range from 1.484 to 1.500 Å with an average of 1.497 ± 0.002 Å and the seven C–C bond lengths range from 1.487 to 1.518 Å with an average of 1.500 ± 0.004 Å. These values are comparable with those observed in $[Co(cyclen)(NO_2)_2]Cl$[5] and $[H_2cyclam][ClO_4]_2$.[17]

A stereoscopic view of the complex cation is shown in Figure 3. The macrocycle is folded diagonally at N(3) and N(4) and coordinated to four adjacent sites of the cobalt ion; the ethylenediamine molecule occupies the remaining sites. Since the N–Co–N angles range from 83.9 to 96.2° the coordination around the central cobalt ion is that of a distorted octahedron.

Table I. Heavy-Atom Parameters and Their Standard Deviations (in Parentheses)[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1295 (1)	1994 (1)	772 (1)	185 (4)	220 (3)	186 (2)	−1 (2)	1 (2)	3 (2)
Cl(1)	82 (1)	3026 (1)	4128 (1)	235 (4)	547 (6)	462 (5)	−69 (5)	52 (4)	−97 (5)
Cl(2)	3239 (1)	2752 (1)	2457 (1)	324 (4)	372 (5)	412 (5)	20 (4)	60 (4)	63 (4)
Cl(3)	1738 (1)	1283 (1)	4037 (1)	363 (4)	366 (5)	426 (5)	14 (4)	82 (4)	129 (4)
N(1)	1791 (1)	1923 (3)	−112 (2)	249 (14)	282 (13)	227 (12)	6 (11)	−11 (11)	−10 (12)
N(2)	847 (1)	2039 (3)	1760 (2)	213 (14)	295 (13)	213 (12)	28 (12)	−9 (10)	37 (12)
N(3)	1473 (1)	3898 (3)	1208 (2)	213 (14)	277 (14)	214 (12)	16 (11)	−5 (10)	−16 (11)
N(4)	1041 (1)	166 (3)	335 (2)	228 (14)	237 (14)	268 (13)	3 (11)	−5 (12)	−24 (11)
N(5)	899 (1)	2870 (3)	−155 (2)	217 (11)	299 (14)	188 (12)	−10 (11)	17 (10)	1 (11)
N(6)	1736 (1)	1067 (3)	1577 (2)	246 (14)	279 (14)	265 (13)	−11 (12)	12 (12)	10 (11)
C(1)	2227 (1)	1743 (4)	366 (3)	217 (18)	336 (19)	365 (18)	9 (14)	26 (13)	4 (15)
C(2)	2151 (1)	655 (4)	1074 (3)	249 (18)	364 (19)	363 (19)	72 (15)	−7 (14)	20 (16)
C(3)	736 (1)	719 (4)	2268 (2)	313 (18)	368 (19)	250 (17)	−52 (15)	71 (14)	72 (14)
C(4)	566 (1)	−443 (4)	1672 (3)	360 (18)	377 (21)	346 (20)	−111 (15)	14 (16)	68 (17)
C(5)	899 (1)	−957 (4)	992 (3)	388 (18)	287 (20)	339 (20)	−16 (15)	−41 (16)	16 (16)
C(6)	663 (1)	466 (4)	−294 (3)	288 (18)	336 (18)	293 (17)	−30 (15)	−38 (14)	−39 (14)
C(7)	782 (1)	1753 (4)	−811 (2)	324 (18)	365 (19)	231 (16)	−25 (15)	−57 (14)	−26 (15)
C(8)	1046 (1)	4155 (4)	−652 (2)	317 (18)	277 (17)	255 (17)	18 (14)	4 (14)	71 (14)
C(9)	1182 (1)	5367 (4)	−65 (3)	374 (18)	238 (18)	364 (19)	2 (14)	16 (15)	51 (15)
C(10)	1575 (1)	5046 (4)	547 (2)	317 (18)	236 (15)	290 (18)	−68 (14)	13 (13)	−4 (14)
C(11)	1135 (1)	4395 (4)	1876 (2)	331 (18)	258 (17)	288 (18)	−18 (14)	32 (14)	−88 (14)
C(12)	983 (1)	3161 (4)	2410 (2)	288 (18)	353 (18)	250 (16)	14 (15)	38 (13)	−55 (16)
O(1)	2766 (1)	667 (3)	3743 (2)	363 (14)	494 (16)	435 (14)	−22 (12)	−13 (12)	37 (13)
O(2)	2221 (1)	3481 (3)	2421 (2)	335 (14)	441 (14)	368 (13)	−36 (11)	−49 (11)	0 (12)
O(3)[b]	4874 (2)	1074 (7)	1203 (5)	666 (43)	499 (36)	643 (39)	6 (31)	138 (36)	11 (33)
O(4)[b]	4935 (3)	1276 (9)	1933 (5)	1175 (64)	799 (49)	968 (56)	30 (53)	86 (61)	−123 (47)

[a] The coordinates have been multiplied by 10^4. The anisotropic temperature factor is expressed in the form $\exp[-{}^1/_4(h^2a^{*2}B_{11} \cdots + 2klb^*c^*B_{23})]$. Values of B_{ij} are multiplied by 10^2. [b] These sites are half-populated.

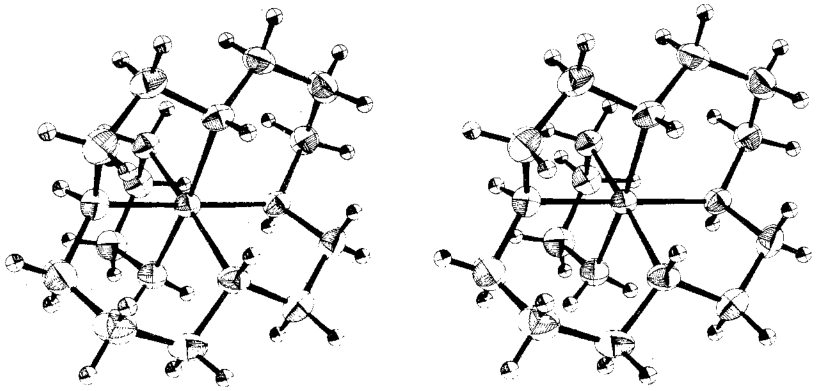
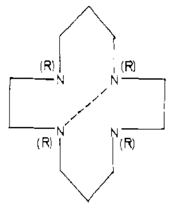


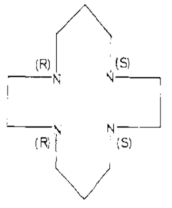
Figure 3. Stereoscopic view of the complex cation. Ellipsoids representing the thermal motions of the atoms are drawn at the 50% probability level.

Table V lists deviations from planes through some selected groups of atoms. Planes 1–3 show the gauche conformation adopted by the five-membered rings and planes 5 and 6 show the chair conformation adopted by the six-membered rings. The torsion angles are given in Table VI.

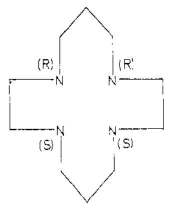
The folded macrocycle has approximate C_2 symmetry with a nearly twofold axis passing close to the midpoints between pairs of corresponding atoms. Details of this approximate twofold axis are given in a separate table.[14] The present finding confirms the earlier proposed configuration,[7] based on Dreiding stereomodels, for this macrocycle in the folded form. It seems reasonable to assume that this stable configuration also exists in other cis cobalt(III)–cyclam complexes. In terms of the helicity of the four nitrogen centers, the cis macrocycle with the *R,R,R,R* designation (structure II) is different from a trans macrocycle which can possibly assume two strain-free configurations, structures III and IV, although structure III is slightly more stable.[7,19] The *R,S* designation is based on the sequence rules of Cahn, Ingold, and Prelog.[20] A cis macrocycle is folded along the dotted line shown in structure II. This structure is consistent with the NMR spectrum of *cis*-$[Co(cyclam)(OH_2)_2](ClO_4)_3$[3] in which the four amine hydrogens are equally divided into two sets. Although the macrocycle and the ethylenediamine chelate force the coordination around the central cobalt ion to be distorted from a perfect octahedron, there is no excessive steric repulsion between nonbonded atoms and both five- and six-membered chelate rings adopt the most stable gauche and chair forms, respectively. The much greater specific rate of ligand substitution reaction of *cis*-$[Co(cyclam)Cl_2]^+$ [3] relative to that of ***trans***-$[Co(cyclam)Cl_2]^+$ by a factor of about 10^4 cannot be due entirely to an unstable chelate conformation or crowding of the cis cyclam substrate in the ground state, although the ring strain may be partially responsible for this increased reactivity. It is known, however, that *cis*-[Co(cyclam)NCSCl]$^+$ is not substantially more reactive than the trans isomer.[3] It is obvious that an overall cis to trans



II



III



IV

Table II. Hydrogen Atom Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

Atom	*x*	*y*	*z*	*B*, Å^2
H[N(1)a]	179 (1)	263 (5)	−49 (3)	5.4 (1.2)
H[N(1)b]	176 (1)	119 (4)	−47 (3)	3.2 (1.0)
H[N(2)]	62 (1)	233 (3)	150 (2)	2.3 (1.0)
H[N(3)]	172 (1)	378 (4)	151 (2)	1.8 (0.9)
H[N(4)]	128 (1)	−25 (4)	2 (2)	3.1 (1.0)
H[N(5)]	67 (1)	310 (4)	13 (3)	3.9 (1.1)
H[N(6)a]	163 (1)	34 (4)	185 (3)	5.0 (1.2)
H[N(6)b]	181 (1)	167 (4)	200 (2)	2.5 (1.0)
H[C(1)a]	229 (1)	275 (4)	62 (3)	3.9 (1.1)
H[C(1)b]	245 (1)	143 (4)	−8 (3)	4.4 (1.1)
H[C(2)a]	242 (1)	58 (4)	154 (3)	5.3 (1.2)
H[C(2)b]	207 (1)	−20 (4)	78 (3)	3.0 (1.0)
H[C(3)a]	52 (1)	103 (4)	267 (3)	3.3 (1.0)
H[C(3)b]	102 (1)	46 (4)	257 (3)	4.2 (1.1)
H[C(4)a]	50 (1)	−120 (4)	205 (2)	3.0 (1.0)
H[C(4)b]	29 (1)	−23 (4)	143 (3)	3.3 (1.1)
H[C(5)a]	116 (1)	−123 (4)	132 (3)	3.9 (1.1)
H[C(5)b]	80 (1)	−164 (4)	63 (3)	3.8 (1.1)
H[C(6)a]	39 (1)	62 (4)	6 (3)	3.0 (1.0)
H[C(6)b]	64 (1)	−34 (4)	−65 (2)	2.6 (1.0)
H[C(7)a]	106 (1)	159 (4)	−122 (3)	3.4 (1.1)
H[C(7)b]	55 (1)	208 (4)	−115 (2)	2.3 (0.9)
H[C(8)a]	80 (1)	449 (4)	−108 (3)	4.8 (1.2)
H[C(8)b]	128 (1)	388 (4)	−105 (2)	1.8 (0.9)
H[C(9)a]	92 (1)	576 (4)	31 (3)	2.8 (1.0)
H[C(9)b]	128 (1)	608 (4)	−42 (3)	3.2 (1.0)
H[C(10)a]	184 (1)	471 (4)	13 (3)	3.5 (1.1)
H[C(10)b]	163 (1)	593 (4)	91 (2)	2.4 (0.9)
H[C(11)a]	126 (1)	504 (4)	223 (2)	2.4 (0.9)
H[C(11)b]	92 (1)	480 (4)	154 (3)	3.0 (1.1)
H[C(12)a]	74 (1)	343 (4)	285 (3)	5.1 (1.2)
H[C(12)b]	123 (1)	277 (3)	275 (2)	1.9 (0.9)
H[O(1)a]	254 (2)	76 (5)	376 (3)	6.2 (1.3)
H[O(1)b]	285 (2)	123 (5)	337 (3)	6.7 (1.4)
H[O(2)a]	219 (2)	402 (5)	289 (3)	8.2 (1.5)
H[O(2)b]	242 (2)	323 (5)	241 (3)	8.0 (1.4)
H[O(3)a][b]	489	129	68	4.8
H[O(3)b][b]	493	24	111	4.8
H[O(4)a][b]	500	118	248	8.0
H[O(4)b][b]	498	49	170	8.0

[a] Values of the coordinates have been multiplied by 10^3. Temperature factors are in the form $\exp[-B(\sin^2 \theta/\lambda^2]$. [b] Assumed, half-populated sites.

Table III. Hydrogen-Bond Distances and Angles

Donor atoms	Acceptor atoms[a]	D···A, Å	H···A, Å	D–H···A, deg
N(1)	Cl(3^{VI})	3.30	2.46	160
N(2)	Cl(1^{V})	3.21	2.38	174
N(4)	Cl(3^{VI})	3.16	2.25	168
N(5)	Cl(1^{V})	3.31	2.50	163
N(6)	Cl(2^{VII})	3.41	2.64	148
N(1)	O(1^{II})	3.15	2.39	145
N(3)	O(2)	2.90	2.05	170
N(6)	O(2)	2.99	2.19	149
O(1)	Cl(2)	3.10	2.30	167
O(1)	Cl(3)	3.15	2.48	172
O(2)	Cl(2)	3.12	2.48	169
O(3)	Cl(1^{I})	3.22	2.41	180[b]
O(3)	Cl(1^{III})	3.00	2.18	180[b]
O(2)	O(1^{IV})	2.86	2.02	162
O(4)	Cl(1^{III})	3.49	2.66	180[b]
O(4)	O(3^{VIII})	2.85	2.01	180[b]

[a] Symmetry transformations with respect to the coordinates listed in Table I are as follows: (I) $-x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2$; (II) $-x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2$; (III) $x + {}^1/_2, y - {}^1/_2, -z + {}^1/_2$; (IV) $-x + {}^1/_2, y + {}^1/_2, z$; (V) $-x, y, -z + {}^1/_2$; (VI) $x, -y, z - {}^1/_2$; (VII) $-x + {}^1/_2, y - {}^1/_2, z$; (VIII) $1 - x, y, {}^1/_2 - z$. [b] Assumed.

Table IV. Bond Distances (Å) Involving Hydrogen Atoms

N(1)–H[N(1)a]	0.87	C(6)–H[C(6)a]	0.97
N(1)–H[N(1)b]	0.88	C(6)–H[C(6)b]	0.94
N(2)–H[N(2)]	0.84	C(7)–H[C(7)a]	1.03
N(3)–H[N(3)]	0.86	C(7)–H[C(7)b]	0.91
N(4)–H[N(4)]	0.93	C(8)–H[C(8)a]	1.02
N(5)–H[N(5)]	0.84	C(8)–H[C(8)b]	0.95
N(6)–H[N(6)a]	0.86	C(9)–H[C(9)a]	1.03
N(6)–H[N(6)b]	0.89	C(9)–H[C(9)b]	0.91
C(1)–H[C(1)a]	1.05	C(10)–H[C(10)a]	1.06
C(1)–H[C(1)b]	0.99	C(10)–H[C(10)b]	1.01
C(2)–H[C(2)a]	1.06	C(11)–H[C(11)a]	0.88
C(2)–H[C(2)b]	0.96	C(11)–H[C(11)b]	0.91
C(3)–H[C(3)a]	0.92	C(12)–H[C(12)a]	1.01
C(3)–H[C(3)b]	0.99	C(12)–H[C(12)b]	0.96
C(4)–H[C(4)a]	0.93	O(1)–H[O(1)a]	0.68
C(4)–H[C(4)b]	0.92	O(1)–H[O(1)b]	0.82
C(5)–H[C(5)a]	0.95	O(2)–H[O(2)a]	0.87
C(5)–H[C(5)b]	0.89	O(2)–H[O(2)b]	0.65

Table V. Deviations of the Atoms from the Least-Squares Planes (Å)[a]

Plane 1: Co, N(1), N(6)

$A = 0.3167, B = 0.8965, C = 0.3097, D = 3.2771$

Co	0.000	N(1)	0.000	N(6)	0.000
C(1)	0.479	C(2)	−0.191		

Plane 2: Co, N(2), N(3)

$A = -0.6668, B = 0.4185, C = -0.6166, D = -2.4953$

Co	0.000	N(2)	0.000	N(3)	0.000
C(11)	0.254	C(12)	−0.425		

Plane 3: Co, N(4), N(5)

$A = -0.7378, B = 0.0697, C = 0.6714, D = -1.9442$

Co	0.000	N(4)	0.000	N(5)	0.000
C(6)	0.221	C(7)	−0.474		

Plane 4: N(2), N(4), C(3), C(5)

$A = 0.9471, B = -0.0738, C = 0.3123, D = 3.0783$

N(2)	−0.008	N(4)	0.008	C(3)	0.009
C(5)	−0.008	Co	0.801	C(4)	−0.668

Plane 5: N(3), N(5), C(8), C(10)

$A = -0.7499, B = 0.5342, C = 0.3902, D = -0.6313$

N(3)	0.015	N(5)	−0.016	C(8)	0.017
C(10)	−0.017	Co	−0.805	C(9)	0.669

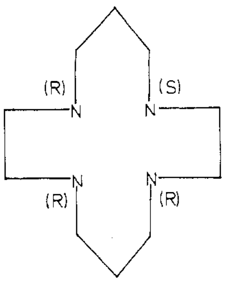
[a] The equation of the plane, with the coefficients *A*, *B*, and *C* equal to direction cosines with respect to the crystallographic axes, is $Aax + Bby + Ccz + D = 0$.

Table VI. Torsion Angles[a] (deg)

Co–N(1)–C(1)–C(2)	43.4	Co–N(2)–C(3)–C(4)	−58.0
N(1)–C(1)–C(2)–N(6)	−49.5	N(2)–C(3)–C(4)–C(5)	63.2
C(1)–C(2)–N(6)–Co	33.8	C(3)–C(4)–C(5)–N(4)	−62.0
Co–N(4)–C(6)–C(7)	35.8	C(4)–C(5)–N(4)–Co	55.2
N(4)–C(6)–C(7)–N(5)	−53.1	Co–N(5)–C(8)–C(9)	−54.3
C(6)–C(7)–N(5)–Co	44.6	N(5)–C(8)–C(9)–C(10)	60.8
Co–N(3)–C(11)–C(12)	36.4	C(8)–C(9)–C(10)–N(3)	−63.0
N(3)–C(11)–C(12)–N(2)	−51.3	C(9)–C(10)–N(3)–Co	59.1
C(11)–C(12)–N(2)–Co	41.7		

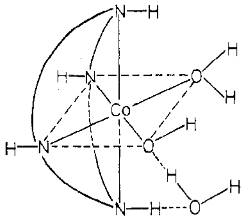
[a] The torsion angle A–B–C–D is defined as that angle between the planes containing A, B, and C and B, C, and D with normal sign convention.

isomerization would require the inversion of two adjacent nitrogen centers, whether the trans product is in the form of structure III or IV. This analysis nicely explains the observation[4] that two of the four amine protons were exchanged in the course of isomerization of *cis*-[Co(cyclam)-Cl_2]$^+$. With the aid of Dreiding stereomodels, it was shown[7] that only in the case of structure V for the macrocycle would cis and trans isomers be of comparable stability. It was then suggested[4,7] that only through this structure V could one expect a cis to trans change by a single edge displacement. Therefore, the process of isomerization probably only requires the ex-



V

change of one axial amine proton, i.e., N(3) or N(4), with concurrent inversion of the nitrogen center giving an unstable cis isomer of structure V. The initially formed trans isomer of structure V is a relatively unstable structure and it may be too labile, with respect to the inversion of a second nitrogen center by means of a second proton exchange to give structure III or IV, to allow detection. The great extent of hydrogen bonding involved in the structure suggests that Poon and Tobe's internal conjugate-base mechanism of isomerization[4] is highly reasonable. It seems, however, that a direct hydrogen bonding between one axial amine proton and the coordinated hydroxide in the isomerizing species[4] *cis*-[Co(cyclam)OHOH$_2$]$^{2+}$ is rather unlikely in terms of the distance and direction of bonding between the two and that a water molecule, as shown in structure VI, may be needed to transmit this hydrogen-bonding effect.



VI

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Registry No. *cis*-[Co(cyclam)en]Cl$_3$·3H$_2$O, 59109-91-0; *trans*-[Co(cyclam)Cl$_2$]Cl, 15220-74-3; ethylenediamine, 107-15-3.

Supplementary Material Available: A listing of structure factor amplitudes and a table giving the details of the approximate twofold symmetry of the cyclam group (12 pages). Ordering information is given on any current masthead page.

References and Notes

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Thiocarboxamido and Carbene Complexes Containing Chelating Carbon–Sulfur Linkages. Crystal and Molecular Structures of Dimethylthiocarboxamido(triphenylphosphine)tricarbonylmanganese, $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$, and (Dimethylamino(thiomethoxy)carbene)(triphenylphosphine)tricarbonylmanganese Tetrafluoroborate, $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$

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The structures of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (I) and its methylated derivative $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$ (II) have been determined by single-crystal x-ray diffraction techniques. The compounds crystallize as follows: I, space group $P\bar{1}$, $a = 9.605\ (11)$ Å, $b = 11.005\ (12)$ Å, $c = 11.516\ (12)$ Å, $\alpha = 77.71\ (6)°$, $\beta = 97.83\ (6)°$, $\gamma = 97.62\ (7)°$; II, space group $P2_1$, $a = 9.581\ (12)$ Å, $b = 16.559\ (9)$ Å, $c = 8.727\ (15)$ Å, $\beta = 101.81\ (6)°$. Full-matrix least-squares refinements yielded conventional R factors of 0.089 for I and 0.091 for II. In these complexes the thiocarboxamido and amino(thiomethoxy)carbene ligands are coordinated through both carbon and sulfur atoms. Their structural and bonding features are compared with those of related compounds, and the factors which lead to this unusual mode of bonding are discussed.

Introduction

Recently we have reported a series of thiocarboxamidomanganese and -molybdenum carbonyl complexes in which the dimethylthiocarboxamido group (C(S)N(CH$_3$)$_2$) acts as a chelating, three-electron donor ligand, coordinated through carbon and sulfur atoms.[1] Although a number of other thiocarboxamido complexes are known, only one other compound, $[MoS(CSN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$, has been reported which shares this unusual structure;[2] in other thiocarboxamido complexes[3-7] the ligand acts as a mono-