Crystal Structure of Dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) Chloride[1]

YOICHI IITAKA,[2a] MUNEKI SHINA,[2a] and EIICHI KIMURA*[2b]

The crystal and molecular structure of dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) chloride, [Co(cyclen)(NO$_2$)$_2$]Cl, has been determined by the X-ray diffraction method. The crystals are monoclinic, space group $P2_1$, with unit-cell dimensions $a = 7.63$ Å, $b = 13.00$ Å, $c = 7.62$ Å, and $\beta = 102.75°$. There are two formula units in the cell. The structure was solved by the heavy-atom method and refined by least-squares (using anisotropic temperature factors) to an R value of 0.026 for 1148 observed reflections. The cyclic ligand is coordinated to four octahedral sites around the central cobalt atom. The two nitro groups are cis to each other, which confirms the structure earlier deduced from the spectroscopic data. Of the two meridional "dien" rings forming cyclen, one has a pair of unsymmetric gauche ethylenediamine chelates with δ and λ chiralities, while the other consists of unsymmetric envelope chelates with λ and δ forms. The two "dien" rings are joined in a folded way at the two "angular" nitrogen atoms with a pseudo mirror plane bisecting the two "dien's" at the two "planar" nitrogens. The cyclen ring may also be viewed as containing two diastereomeric "β-trien" geometries, RR (or SS) and RS (or SR). A comparison of the bond parameters between the known smallest macrocyclic ring and the flexible linear ligands in the octahedral complexes affords a clear picture of the internal strains and the geometries.

Introduction

The structure determination of [Co(cyclen)(NO$_2$)$_2$]Cl was undertaken in order to provide information about the bonding of the 12-membered tetramine macrocycle.[3] A folded cis coordination about the cobalt ion was proposed on the basis of spectral data.[4,5] Since most known macrocyclic complexes contain 12 or more atoms in the macrocycle,[6-10] it was of primary interest to find out how the smallest cyclen macrocycle with the least flexibility accommodates itself to octahedral coordination. In particular, it was desired to see if there were signs of distortion from octahedral symmetry that would cause the considerably high visible absorption intensities compared with other tetramine analogs.[4,5] Since the stereochemistry of trien coordinated in β geometry that structurally lacks only one ethylene bridge of the cyclen has been fully investigated by Buckingham, *et al.,*[11-19] a compari-

son was of special interest in understanding more of the effects of intramolecular forces, *i.e.,* nonbonded interactions, valence deformations, bond length distortions, and torsional strains in determining the cyclen conformations.

Cis β-trien   Cis cyclen
complex   complex
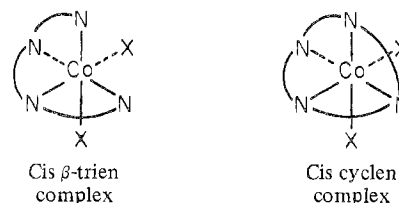
Experimental Section

1,4,7,10-Tetraazacyclododecane and [Co(cyclen)(NO$_2$)$_2$]Cl were prepared according to the methods of Stetter[20] and Collman,[4] respectively. The crystals were grown from an aqueous solution as dark red parallelepipeds. The specimen for the X-ray analysis was obtained by cleaving a large crystal to give a block of the size of approximately 0.2 × 0.2 × 0.4 mm. The lattice constants were determined by a least-squares method based on the angular settings of 13 reflections measured on a Rigaku four-circle X-ray diffractometer. Intensity data were also collected with the diffractometer by use of Zr-filtered Mo radiation. Integrated intensities were measured by a θ–2θ scan method with the scanning speed of 4° 2θ/min. The background was measured at each end of the scan for 10 sec.

A total of 1352 reflections were measured in the range $2\theta \leqslant 50°$, of which 1148 reflections having net intensities greater than the 3σ level were used for the following structure determination.

Crystal Data. Dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) chloride, [Co(C$_8$H$_{20}$N$_4$)(NO$_2$)$_2$]Cl·H$_2$O, FW 376.4, appears as monoclinic crystals, with $a = 7.627$ (5), $b = 13.003$ (10), $c = 7.616$ (5) Å; $\beta = 102.75$ (10)°; $U = 736.6$ Å^3; $d_x = 1.70$ g cm^{-3}; $Z = 2$. Absent reflections are $0k0$ when k is odd. The space group is $P2_1$. The linear absorption coefficient for Mo Kα radiation is 14.2 cm^{-1}.

Intensities were corrected for Lorentz-polarization factors but no correction was applied for absorption.

Determination and Refinement of the Structure. Structure was solved by the heavy-atom method. The electron density map, synthesized with the phases calculated by the contributions of cobalt and chlorine atoms, revealed the locations of all atoms except hydrogen. Refinement of the structure was carried out by the method of least squares with block-diagonal approximations. The R value was steadily reduced to 0.041 when the anisotropic thermal parameters of atoms were included. At this point, two cycles of difference Fourier and least-squares calculations were made in order to determine the hydrogen atom positions. The first difference Fourier synthesis clearly showed the locations of 15 hydrogen atoms out of 22. These atoms were then included in the least-squares calculations. The loca-

(1) Presented at the 30th National Meeting of the Chemical Society of Japan, Osaka, Japan, April 1974.

(2) (a) Faculty of Pharmaceutical Sciences, University of Tokyo. (b) Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine.

(3) The following abbreviations are used in this article: cyclen, 1,4,7,10-tetraazacyclododecane; dien, diethylenetriamine; trien, triethylenetetramine; cyclam, 1,4,8,11-tetraazacyclotetradecane; en, ethylenediamine; metrien, 5(R)-methyltriethylenetetramine; dimetrien, L-3,8-dimethyltriethylenetetramine; tetramine, any four nitrogen atoms attached to a metal ion; tetraammine, four ammonia molecules in complexes of cobalt(III).

(4) J. P. Collman and P. W. Schneider, *Inorg. Chem.,* 5, 1380 (1966).

(5) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A,* 1549 (1968).

(6) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robinson, and M. L. Tobe, *Chem. Commun.,* 97 (1965).

(7) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.,* 4, 1102 (1965).

(8) M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.,* 94, 4134 (1972).

(9) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A,* 867 (1966).

(10) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A,* 1827 (1966).

(11) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.,* 6, 1032 (1967).

(12) D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, and A. M. Sargeson, *Chem. Commun.,* 583 (1969).

(13) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.,* 92, 3617 (1970).

(14) M. R. Snow, *J. Amer. Chem. Soc.,* 92, 3610 (1970).

(15) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.,* 8, 1293 (1969).

(16) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and H. C. Freeman, *Inorg. Chem.,* 9, 1921 (1970).

(17) H. C. Freeman, L. G. Marzilli, and I. E. Maxwell, *Inorg. Chem.,* 9, 649, 2408 (1970).

(18) R. J. Dellaca, V. Janson, W. T. Robinson, D. A. Buckingham, L. G. Marzilli, I. E. Maxwell, K. R. Turnbull, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.,* 57 (1972).

(19) D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *J. Amer. Chem. Soc.,* 96, 1713 (1974).

(20) H. Stetter and K. H. Mayer, *Chem. Ber.,* 94, 1410 (1961).

Table I. Final Atomic Parameters[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	42,139 (8)	0	7853 (8)	818 (9)	218 (3)	831 (9)	3 (9)	300 (7)	−7 (9)
Cl	364 (2)	−116 (2)	4638 (2)	112 (2)	61 (1)	110 (2)	−3 (2)	32 (2)	1 (2)
N(1)	1,941 (5)	35 (6)	−1043 (5)	103 (7)	36 (2)	81 (6)	−14 (7)	8 (5)	8 (7)
C(2)	1,179 (7)	1094 (5)	−1085 (7)	111 (11)	38 (4)	109 (11)	8 (5)	7 (9)	9 (5)
C(3)	1,474 (7)	1439 (4)	849 (7)	82 (10)	31 (3)	109 (10)	22 (5)	13 (8)	6 (5)
N(4)	3,432 (5)	1314 (3)	1573 (6)	81 (8)	22 (3)	97 (8)	2 (4)	11 (6)	−7 (4)
C(5)	4,133 (7)	1432 (4)	3522 (7)	119 (11)	35 (4)	75 (10)	−13 (5)	17 (8)	−24 (5)
C(6)	6,091 (7)	1086 (5)	3825 (7)	116 (11)	39 (4)	104 (11)	−6 (5)	2 (9)	−5 (5)
N(7)	6,049 (5)	28 (6)	3065 (5)	83 (6)	35 (2)	105 (7)	−1 (7)	15 (5)	3 (7)
C(8)	5,641 (8)	−756 (5)	4378 (9)	130 (11)	41 (4)	153 (12)	7 (6)	16 (9)	26 (6)
C(9)	4,151 (8)	−1477 (4)	3472 (8)	123 (11)	27 (4)	168 (13)	3 (5)	35 (10)	8 (6)
N(10)	2,859 (6)	−840 (3)	2138 (6)	94 (8)	27 (3)	106 (9)	4 (4)	24 (7)	8 (4)
C(11)	1,514 (8)	−1465 (4)	854 (8)	143 (12)	25 (3)	136 (12)	−6 (5)	32 (9)	−21 (5)
C(12)	631 (8)	−755 (5)	−633 (8)	138 (12)	41 (4)	137 (12)	−29 (6)	−2 (9)	2 (6)
N(13)	5,155 (7)	−1203 (4)	−151 (7)	155 (10)	34 (3)	162 (10)	14 (5)	82 (8)	1 (5)
O(14)	6,606 (6)	−1581 (4)	639 (7)	199 (11)	62 (4)	252 (12)	57 (5)	54 (9)	−22 (6)
O(15)	4,359 (7)	−1576 (4)	−1608 (6)	270 (12)	65 (4)	187 (11)	17 (6)	73 (9)	−59 (6)
N(16)	5,620 (6)	743 (4)	−618 (6)	126 (9)	35 (3)	121 (9)	1 (5)	73 (7)	3 (5)
O(17)	4,937 (7)	984 (5)	−2168 (6)	227 (11)	111 (5)	117 (9)	−38 (7)	65 (8)	36 (6)
O(18)	7,169 (6)	985 (5)	67 (7)	124 (9)	108 (5)	230 (11)	−35 (6)	66 (8)	27 (7)
O(W)	553 (12)	2512 (5)	4448 (12)	527 (25)	78 (5)	521 (25)	15 (10)	279 (20)	−8 (10)

Atom	x	y	z	β_{11}	Atom	x	y	z	β_{11}
H(N(1))	202 (8)	−30 (6)	−233 (8)	5 (2)	H(C(8))	667 (7)	−118 (5)	476 (8)	3 (1)
H(C(2))	188 (6)	158 (3)	−187 (6)	1 (1)	H'(C(8))	523 (11)	−32 (8)	548 (11)	9 (3)
H'(C(2))	−5 (10)	104 (7)	−180 (10)	7 (2)	H(C(9))	463 (7)	−198 (5)	288 (7)	3 (1)
H(C(3))	125 (8)	225 (5)	98 (8)	3 (1)	H'(C(9))	356 (9)	−187 (5)	437 (9)	4 (2)
H'(C(3))	73 (6)	106 (4)	161 (6)	2 (1)	H(N(10))	214 (8)	−40 (5)	273 (8)	4 (1)
H(N(4))	399 (10)	188 (6)	108 (10)	5 (2)	H(C(11))	204 (7)	−201 (5)	43 (7)	3 (1)
H(C(5))	410 (7)	219 (4)	376 (7)	3 (1)	H'(C(11))	52 (9)	−187 (6)	142 (9)	5 (2)
H'(C(5))	324 (8)	103 (5)	422 (8)	4 (1)	H(C(12))	10 (8)	−109 (5)	−169 (8)	3 (1)
H(C(6))	685 (7)	161 (4)	318 (7)	2 (1)	H'(C(12))	−34 (10)	−30 (7)	−30 (10)	8 (2)
H'(C(6))	678 (7)	95 (5)	518 (7)	3 (1)	H(W)	−73 (14)	304 (9)	447 (14)	12 (3)
H(N(7))	725 (6)	−17 (5)	296 (6)	3 (1)	H'(W)	21 (16)	169 (9)	443 (16)	14 (4)

[a] The coordinates and temperature factors of cobalt are multiplied by 10^5; those of other nonhydrogen atoms are $\times 10^4$; the coordinates of hydrogen atoms are $\times 10^3$. The anisotropic temperature factors are of the form $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; and the isotropic temperature factors for hydrogen atoms are $T = \exp[-\beta_{11}(\sin^2\theta)/\lambda^2]$. The estimated standard deviations are given in parentheses in this and succeeding tables.

tions of the remaining 7 hydrogen atoms were easily found in the subsequent difference Fourier map. The positional and isotropic thermal parameters of the 22 hydrogen atoms were then refined by three cycles of least squares. The R value decreased to 0.027. Finally, two sets of three cycles of least-squares calculations were carried out in order to correct the F_c values for the anomalous dispersion effect. In each set, the dispersion corrections $\Delta f' = 0.3$ and $\Delta f'' = 1.0$ of the atomic scattering factor of cobalt for Mo Kα radiation[21] were taken into account for the calculation of the structure factors. The first set of the refinement, in which the structure factors were calculated by a right-handed coordinate system, gave an R value of 0.026, while the second set, which refined the antipode structure of the first set, gave an R value of 0.028. It may therefore be concluded that the structure refined by the first set represents the correct absolute configuration, but for the present study no further elaboration was made on this point. The weighting system adopted in the final least-squares calculations was as follows: $w = 0$, when $F_o \leqslant 5$; $w = 1$, when $5 < F_o < 30$; $\sqrt{w} = 30/F_o$, when $30 < F_o$. The final atomic parameters are given in Table I and the observed and calculated structure factors are compared in Table II (given in microfilm edition only). The atomic scattering factors for Co, Cl, O, N, and C atoms were taken from the "International Tables for X-Ray Crystallography" (cited as SX-68, SX-69, SX-8, SX-7, and SX-6, respectively),[21] and those for the H atoms were from Stewart, *et al.*[22]

Discussion of the Structure

Intermolecular Contacts. Figure 1 shows the projection of the crystal structure along the a axis. Intermolecular distances shorter than 3.5 Å are listed in Table III. Of the four nitrogen atoms in cyclen, N(1), N(7), and N(10) closely interact with the chloride anion. The remaining N(4) atom
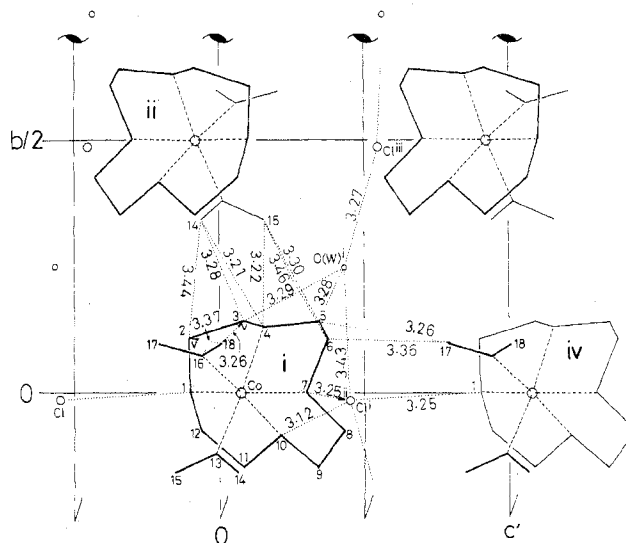
(21) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

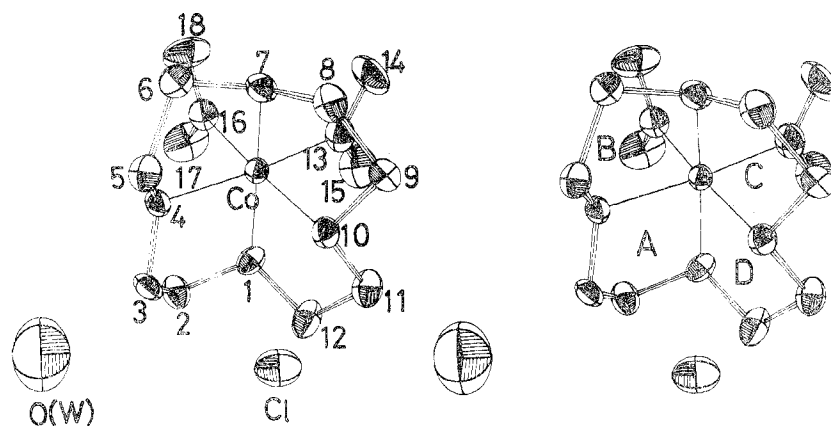(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

Figure 1. Projection of the crystal structure along the a axis. Interatomic distances shorter than 3.5 Å between the complex ions are shown by dotted lines. Code numbers for the symmetry operations are given in the footnote of Table III.

similarly hydrogen bonds with the nitro oxygen atoms, O(14) and O(15), in a neighboring complex cation. There are also several close contacts between the neighboring complex cations, especially between the nitro oxygen atoms and methylene groups of the immediate neighbor. The complex cations thus form a framework of the crystal structure. The chloride anions and water molecules are arranged alternately

Figure 2. Stereoscopic drawing of the structure by the ORTEP program.[23] Atoms are represented by ellipsoids of thermal vibrations, indicating the atoms lie within the ellipsoids with 50% probability.

Table III. Important Intermolecular Contacts (to 3.5 Å) in the Crystal between Nonhydrogen Atoms and Their Associated Hydrogen Atoms

Atoms	Dist, Å	Atoms	Dist, Å	Symmetry operation[a]
Cl- - - -O(W)	3.425 (7)	Cl- - -H'-O(W)	2.36 (10)[b]	i
O(W)- - - -Cl	3.271 (8)	O(W)-H- - -Cl	2.49 (10)[b]	iii
Cl- - - -N(1)	3.250 (4)	Cl- - -H-N(1)	2.39 (6)[b]	iv
N(7)- - - -Cl	3.250 (4)	N(7)-H- - -Cl	2.44 (5)[b]	v
Cl- - - -N(10)	3.119 (5)	Cl- - -H-N(10)	2.23 (7)[b]	i
N(4)- - - -O(14)	3.210 (7)	N(4)-H- - -O(14)	2.38 (8)[c]	ii
N(4)- - - -O(15)	3.216 (7)	N(4)-H- - -O(15)	2.36 (8)[c]	ii
C(2)- - - -O(14)	3.443 (8)	C(2)-H- - -O(14)	2.73 (4)	ii
O(18)- - - -C(2)	3.366 (8)	O(18)- - -H'-C(2)	2.81 (9)	v
C(3)- - - -O(14)	3.284 (8)	C(3)-H- - -O(14)	2.72 (6)	ii
O(18)- - - -C(3)	3.259 (7)	O(18)- - -H-C(3)	2.71 (5)	v
C(3)- - - -O(W)	3.286 (11)			i
C(5)- - - -O(15)	3.301 (8)	C(5)-H- - -O(15)	2.74 (6)	ii
C(5)- - - -O(17)	3.256 (7)	C(5)-H'- - -O(17)	2.77 (6)	iv
C(5)- - - -O(W)	3.283 (11)			i
C(6)- - - -O(15)	3.457 (8)	C(6)-H- - -O(15)	2.72 (5)	ii
C(6)- - - -O(17)	3.361 (8)	C(6)-H'- - -O(17)	2.70 (6)	iv
		C(3)-H- - -H'-C(11)	2.32 (9)	vi
		C(5)-H- - -H'-C(9)	2.37 (8)	vii

[a] Applied to the second atom: (i) x, y, z; (ii) $1 - x$, $0.5 + y$, $-z$; (iii) $-x$, $0.5 + y$, $1 - z$; (iv) x, y, $1 + z$; (v) $1 + x$, y, z; (vi) $-x$, $0.5 + y$, $-z$; (vii) $1 - x$, $0.5 + y$, $1 - z$. [b] Hydrogen bond is suggested. [c] Bifurcated hydrogen bond.

along the diad screw axis forming hydrogen bonds between them.

Description of the [Co(cyclen)(NO₂)₂]⁺ Cation. Figure 2[23] is a stereoscopic view of the complex cation, which also shows the chloride anion and water oxygen atom involved in the same asymmetric unit. The atoms are drawn by ellipsoids showing thermal vibrations. Intramolecular bond distances and angles with their estimated standard deviations are given in Tables IV and V. Four nitrogen atoms of the macrocycle and two nitro groups are coordinated to the cobalt ion in approximately octahedral locations with the nitro groups in a cis position, confirming the structure earlier deduced from visible and infrared spectral data.[4]

The folded macrocycle may adopt two distinct nonenantiomeric structures with the opposite configurations to each other at the "planar" N(4) atom, in analogy to the structures proposed for Co(III) complexes of *cis*-cyclam.[7] The crystal analysis has established one of the configurations having obviously less nonbonded interactions and torsional strains.[24]

(23) C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table IV. Intramolecular Bond Distances within [Co(cyclen)(NO₂)₂]⁺

Atoms	Dist, Å	Atoms	Dist, Å
Co-N(1)	1.970 (3)	C(6)-N(7)	1.491 (9)
Co-N(4)	1.948 (4)	N(7)-C(8)	1.507 (9)
Co-N(7)	1.976 (3)	C(8)-C(9)	1.517 (8)
Co-N(10)	1.947 (5)	C(9)-N(10)	1.499 (7)
Co-N(13)	1.923 (5)	N(10)-C(11)	1.492 (7)
Co-N(16)	1.931 (5)	C(11)-C(12)	1.501 (8)
N(1)-C(2)	1.491 (9)	C(12)-N(1)	1.513 (9)
C(2)-C(3)	1.509 (8)	N(13)-O(14)	1.239 (7)
C(3)-N(4)	1.483 (6)	N(13)-O(15)	1.240 (7)
N(4)-C(5)	1.470 (6)	N(16)-O(17)	1.221 (6)
C(5)-C(6)	1.527 (8)	N(16)-O(18)	1.223 (6)

Table V. Intramolecular Bond Angles within [Co(cyclen)(NO₂)₂]⁺

Atoms	Angle, deg	Atoms	Angle, deg
N(1)-Co-N(4)	85.2 (2)	C(5)-N(4)-C(3)	118.5 (4)
N(1)-Co-N(10)	84.3 (2)	Co-N(4)-C(3)	109.5 (3)
N(4)-Co-N(7)	85.4 (2)	C(6)-C(5)-N(4)	104.3 (4)
N(7)-Co-N(10)	84.3 (2)	N(7)-C(6)-C(5)	106.1 (5)
N(4)-Co-N(10)	95.4 (2)	C(8)-N(7)-Co	111.2 (4)
N(4)-Co-N(16)	88.7 (2)	C(8)-N(7)-C(6)	110.9 (5)
N(10)-Co-N(13)	91.4 (2)	Co-N(7)-C(6)	107.9 (4)
N(13)-Co-N(16)	84.5 (2)	C(9)-C(8)-N(7)	111.1 (5)
N(1)-Co-N(13)	95.7 (2)	N(10)-C(9)-C(8)	106.3 (5)
N(1)-Co-N(16)	96.1 (2)	C(11)-N(10)-Co	109.1 (3)
N(7)-Co-N(13)	95.2 (2)	C(11)-N(10)-C(9)	113.4 (4)
N(7)-Co-N(16)	96.0 (2)	Co-N(10)-C(9)	108.8 (3)
N(1)-Co-N(7)	164.4 (2)	C(12)-C(11)-N(10)	106.8 (5)
N(4)-Co-N(13)	173.1 (2)	N(1)-C(12)-C(11)	111.5 (5)
N(10)-Co-N(16)	175.9 (2)	O(14)-N(13)-Co	120.6 (4)
C(2)-N(1)-Co	108.3 (4)	O(14)-N(13)-O(15)	119.3 (6)
C(2)-N(1)-C(12)	111.1 (5)	Co-N(13)-O(15)	120.0 (4)
Co-N(1)-C(12)	110.9 (4)	O(17)-N(16)-Co	119.5 (4)
C(3)-C(2)-N(1)	106.3 (5)	O(17)-N(16)-O(18)	120.8 (5)
N(4)-C(3)-C(2)	104.5 (4)	Co-N(16)-O(18)	119.7 (4)
C(5)-N(4)-Co	109.5 (3)		

The cation molecule has approximate C_s symmetry with a near-mirror plane passing through Co, N(4), N(10), N(13), and N(16).

Of the four five-membered chelate rings (designated as A, B, C, and D in Figure 2), two rings (A and B) are enantiomeric to each other, having unsymmetric gauche conformations with δ and λ chiralities, while the other two rings (C and D), also reflectionally related, have unsymmetric envelope conformations with λ and δ chiralities.[25] The two "planar" nitrogen atoms, N(4) and N(10) of the cyclen ring, can be

(24) The conformational analysis of cyclen and the related complexes is to be reported separately.
(25) Since the absolute configuration of this complex remains undetermined, the present conformational assignment is tentative. For nomenclature, see ref 19.
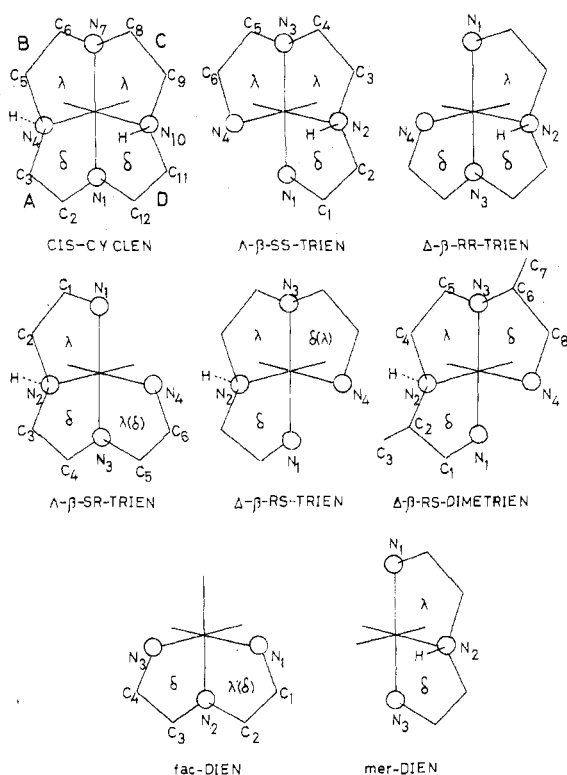
Figure 3. Comparison of coordination geometries for cis cyclen, cis β-trien, cis β-dimetrien, and dien chelate rings in cobalt(III) complexes. The chelate ring conformations in the cyclen complex are assigned for an arbitrary absolute configuration.
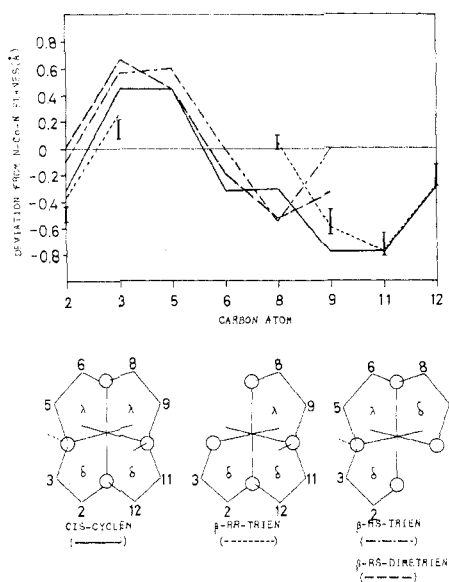

Figure 4. Comparison of deviations of carbon atoms from their respective N–Co–N plane. The data plotted in this and succeeding figures for β-*RR*- and β-*RS*-trien complexes are obtained from the energy-minimized coordinates,[13] which are free of intermolecular interactions.[16] The data obtained from the crystal structure of several β-*RR*-trien[16] and β-*RS*-dimetrien complexes[28] are also shown for comparison.

viewed as adopting the same configurations with N(2) atoms in β-*RS* (or *SR*)- and β-*RR* (or *SS*)-trien, respectively, which is illustrated in Figure 3, along with the conformational relationship.[26-29] It is interesting to note that the D (or C) ring involving N(10) has an envelope conformation almost identical with that of the central chelate ring in β-*RR*-trien or β-*SS*-metrien complexes,[27] while the B (or A) ring involving N(4) and the central chelate rings of β-*RS* (or *SR*)-trien[19] or -dimetrien complexes[28] take similarly puckered conformations (see Figure 4).

The bonds extending from Co to the three nitrogens N(1), N(2), and N(3) of the meridional dien and β-trien groups are coplanar,[15,29] whereas for the cyclen complex the corresponding three nitrogen and cobalt atoms deviate significantly from the least-squares coordination planes indicating a distortion from the regular octahedron. [Distances (Å) of atoms from plane 1: Co, −0.145; N(1), 0.078; N(4), −0.012; N(7), 0.078. Distances (Å) of atoms from plane 2: Co, −0.124; N(1), 0.069; N(7), 0.069; N(10), −0.013.]

Bond Lengths. The distances from Co to N(4) and N(10) (mean 1.948 (5) Å) are considerably shorter than to N(1) and N(7) (mean 1.973 (3) Å), presumably serving to diminish the angular strain at the flattened N(4) and N(10), as was discussed for the similar situations in β-trien complexes.[13,16,19] A comparison of Co–N(secondary) bond lengths indicates no greater distortions in the macrocyclic than in the linear

tetramine complexes.[13,16,19] The two Co–N(nitro) bond distances (mean 1.930 Å) are comparable to 1.930 and 1.932 Å in the metrien[27] and dimetrien complexes[28] respectively. The intraligand C–C and C–N bond distances (mean 1.51 and 1.49 Å, respectively) do not vary significantly from the unstrained values.[13,16,29] The N–O bond distances (mean 1.31 Å) agree with those observed in other nitro complexes.[30]

Bond Angles and Nonbonded Interactions. The angles subtended by the A and B chelate rings at the cobalt atom (mean 85.3 (2)°) are close to 86° commonly observed for N–Co–N angles in β-trien,[16,19] meridional dien,[29] and ethylenediamine complexes,[31] while in the C and D rings these are significantly bent (mean 84.3 (2)°). The N–Co–N angle between the two nitro groups (84.5°) deviates greatly from the regular octahedron, to compare with 90 and 86.3° in bis-(ethylenediamine)[31] and dimetrien analogs,[28] respectively. The bond angles in the ligand skeleton involving the C and D rings agree well with those of the central ring of β-*RR*-trien complexes[13] as shown in Figure 5. The angles about the "angular" nitrogens, C(12)–N(1)–C(2) and C(6)–N(7)–C(8), are close to those of a strain-free tetrahedron.

Several bond angle strains found in the cyclen complex are obviously caused by other intramolecular forces, in particular, the nonbonded repulsion term. The N(4)–Co–N(10) angle of 95.4 (2)° is more distorted than the corresponding angle of 93° in *fac*-[Co(dien)(CN)₃][32] or 91.4–93.6° in β-*RR* (or *SS*)-trien complexes,[13,15] but comparable to 96.0° in β-*RS*-trien[19] and 95.6° in β-*RS*-dimetrien complexes.[28] Another significant angular distortion occurs at the "planar" nitrogen, C(3)–N(4)–C(5) = 118.5 (4)°, which is more opened than the corresponding angle of 115° in *mer*-[Co(dien)(gly)-

(26) The conformations of the ethylenediamine rings are all taken from the literature: β-trien, ref 16, 19; metrien, ref 27; dimetrien, ref 28; *fac*-dien, M. Kono, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B,* **29**, 739 (1973); *mer*-dien, ref 29.

(27) K. Tanaka, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B,* **29**, 733 (1973).

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

(29) For a review see H. Kuroya, *J. Chem. Soc. Jap.,* **92**, 905 (1971).

(30) K. Murmann and E. O. Schlemper, *Inorg. Chem.,* 12, 2625 (1973).

(31) K. Matsumoto and H. Kuroya, *Bull. Chem. Soc. Jap.,* **40**, 2985 (1967).

(32) S. Yamaguchi, S. Oi, K. Okawa, and H. Kuroya, paper presented at the 20th Coordination Chemistry Symposium, Tokyo, Japan, 1970.

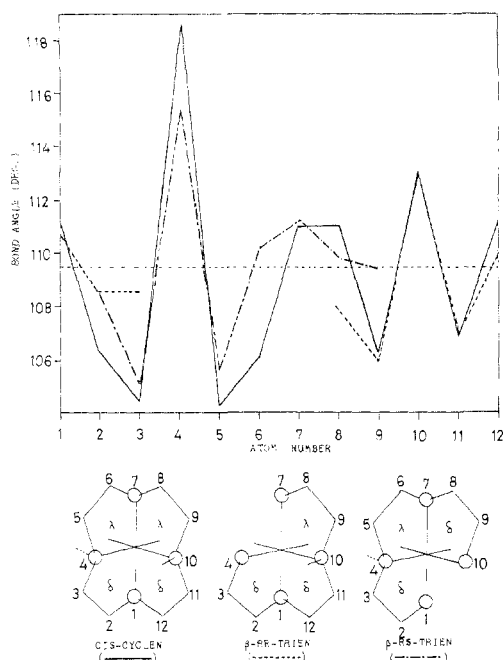Figure 5. Comparison of bond angles in the ligand skeletons at the indicated atoms.

Table VI. Intramolecular Short Distances between Nonbonded Atoms

Atoms	Dist, Å	Atoms	Dist, Å
Between Nonhydrogen and Hydrogen Atoms, Less Than 2.42 Å			
C(2)- - -H′–C(12)	2.30 (9)	C(8)- - -H′–C(6)	2.41 (6)
C(6)- - -H′–C(8)	2.40 (10)	O(15)- - -H–N(1)	2.41 (7)
Between Hydrogen Atoms, Less Than 2.40 Å			
N(1)–H- - -H–C(12)	1.94 (9)	C(6)–H- - -H–N(7)	2.34 (9)
C(2)–H′- - -H′–C(12)	2.12 (10)	C(6)–H′- - -H–N(7)	2.32 (8)
C(3)–H- - -H–N(4)	2.13 (10)	C(6)–H′- - -H′–C(8)	2.08 (10)
C(3)–H′- - -H–N(10)	2.25 (8)	N(7)–H- - -H–C(8)	2.01 (9)
C(3)–H′- - -H′–C(12)	2.32 (10)	C(8)–H- - -H–C(9)	2.14 (8)
N(4)–H- - -H–C(5)	2.07 (9)	C(9)–H- - -H–C(11)	2.40 (7)
C(5)–H- - -H–C(6)	2.36 (8)	N(10)–H- - -H′–C(11)	2.38 (9)
C(5)–H′- - -H′–C(8)	2.39 (10)	C(11)–H- - -H–C(12)	2.27 (8)
C(5)–H′- - -H–N(10)	2.24 (9)		

$(NO_2)]Cl^{33}$ but close to those of β-RS-trien $(117.8°)^{19}$ and β-RS-dimetrien $(117.9°)$ complexes.[28] These two significant bendings can be interpreted as due to reducing the close non-bonded repulsions, such as N(10)–H- - -H′–C(3), N(10)–H- - -H′–C(5), C(3)–H′- - -H′–C(12), and C(5)–H′- - -H′–C(8) (see Table VI), in a similar discussion for the β-RS-trien configuration.[19] Probably assisting these angle deformations is the N(1)–Co–N(7) angle contracted to 164.4 (2)°, which is an unusual deviation from the octahedral value. The corresponding angles are in the range 170–172° for β-RR- and RS-trien, β-RS-dimetrien,[34] and *mer*-dien configurations.[33] Further distortions are found at N(1)–C(2)–C(3) and N(7)–C(6)–C(5) angles (mean 106.2°), an unexpected compression for the β-RS-trien structure $(111.8°)$,[19] which may help reduce the nonbonded interactions, C(2)–H′- - -H′–C(12) and C(6)–H′- - -H′–C(8).

Torsion Angles. Torsion angles about C–N and C–C bonds in cyclen are listed in Table VII and compared with β-trien rings in Figure 6. The agreement for cyclen and β-RR-trien is generally good. The higher torsional strain in the apical

(33) S. Yamaguchi, S. Oi, H. Kuroya, K. Okawa, and J. Fujita, paper presented at the 22nd National Meeting of Chemical Society of Japan, Tokyo, Japan, 1969.
(34) Computed using the coordinates given in ref 13, 19, and 28.

Table VII. Torsion Angles about the Bond Involved in the Ligand[a]

Atoms	Angle, deg	Atoms	Angle, deg
Co–N(1)–C(2)–C(3)	−40.8	Co–N(7)–C(8)–C(9)	10.6
N(1)–C(2)–C(3)–N(4)	54.8	N(7)–C(8)–C(9)–N(10)	−36.1
C(2)–C(3)–N(4)–Co	−44.0	C(8)–C(9)–N(10)–Co	46.2
Co–N(4)–C(5)–C(6)	44.6	Co–N(10)–C(11)–C(12)	−45.3
N(4)–C(5)–C(6)–N(7)	−55.5	N(10)–C(11)–C(12)–N(1)	34.9
C(5)–C(6)–N(7)–Co	40.8	C(11)–C(12)–N(1)–Co	−9.6

[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.
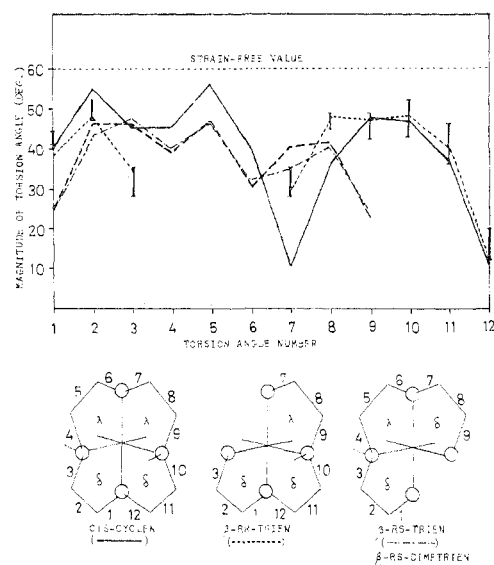

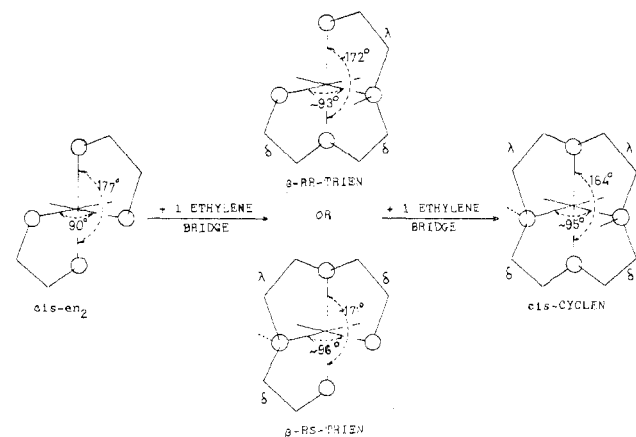Figure 6. Comparison of torsion angles along the ligand skeleton.

Figure 7. Effect of adding ethylene bridges to cobalt(III)–tetramine complexes. The given values for cis-(en)$_2$ are computed using [Co(en)$_2$(NO$_2$)$_2$][Co(en)(mal)$_2$] crystal structure coordinates,[31] and the β-trien complexes used are the energy-minimized structures.[13]

ring of β-RR-trien (torsion angle numbers 2 and 3 in Figure 6) may serve to alleviate the nonbonded interactions between the apical and the central chelate rings. The less torsional strain in the other outer chelate ring of the β-RR-trien (numbers 7 and 8 in Figure 6) occurs at the expense of the higher angular distortions (see angle numbers 8 and 9 in Figure 5). The agreement of the cyclen and the β-RS-trien rings is rather poor. Generally higher torsional strain for the β-RS-trien rings is compensated by the lower angular distortions. The large discrepancies at the torsion angles in the apical ring derive from their opposite conformational relations.

Implications of This Structure. The present crystal analy-

sis has demonstrated that fusing the chelated linear tetramine ligand with an ethylene group generally imposes on the existing chelated rings the extra potential energies more in terms of the nonbonded repulsion and the angular strain than in terms of the bond length and the torsion, and that the *RS* (or *SR*) structure having more nonbonded interactions and angle deformations than the *RR* (or *SS*) form[13,19] is subjected to more configurational and conformational changes compared with the latter.

The angular strain around cobalt atom is seen to increase at the two bond angle bendings as ethylene bridges in tetramine ligands increase (Figure 7). The strain-free tetraammine geometry adopts an undistorted octahedron. Addition of an ethylene bridge to a slightly distorted bis(ethylenediamine) complex forms two diastereomeric trien isomers: β-*RR* (or *SS*) with less strain and β-*RS* (or *SR*) with more strain. A further ethylene bridging yields the cyclic 12-membered ring with even more angular distortions around the cobalt atom. This very qualitative picture might account partially for the increasing visible absorption intensities as one goes from *cis*-[Co(NH₃)₄X₂]⁺ to *cis*-[Co(en)₂X₂]⁺, *cis*-β-*RR*-[Co(trien)X₂]⁺,

cis-β-*RS*-[Co(trien)X₂]⁺, and finally to *cis*-[Co(cyclen)-X₂]⁺.[4,19,35,36]

(35) In view of the close similarities to β-trien geometries which are known to have rigid conformations[16] it is concluded that the conformation of the cyclen complex in solution is close to that found in the solid state.

(36) In correspondence with the gradual expansion of the N–Co–N angle, the X–Co–X angle becomes narrower: *cis*-[Co(en)₂X₂]⁺ (90°),[31] racemic β-*RR*- and/or *SS*-[Co(trien)Cl(H₂O)]²⁺ (88.6°),[15] *cis*-β-*RS*-[Co(dimetrien)(NO₂)₂]⁺ (86.3°),[28] and *cis*-[Co(cyclen)-(NO₂)₂]⁺ (84.5°).

X-Ray Photoelectron Spectroscopy of Azaporphyrins

YOSHIO NIWA,*[1a] HIROSHI KOBAYASHI,[1b] and TOSHIKAZU TSUCHIYA[1a]

The X-ray photoelectron spectra of azaporphyrins were studied. The nitrogen 1s spectra of the free bases revealed that each inner proton is localized on one of the central nitrogens even if the meso methine bridges in porphyrins are substituted by aza nitrogens. An intramolecular hydrogen-bonding interaction between the meso-bridging aza nitrogen and the inner proton is quite impossible. In the metal complexes, the central and meso-bridging nitrogens are close in their charge density. With an increase in the number of aza substitutions in the meso bridge, the net electron donation from ligand to metal decreases and thus the metal positive charge increases. The shifts of nitrogen 1s and metal $2p_{3/2}$ binding energies in azaporphyrins are attributed to an electron-withdrawing effect by meso-bridging nitrogens but not to a contraction of the hole in molecular center. For a given ligand, the nitrogen 1s binding energy varies slightly with metals but the carbon 1s spectra of the metal complexes are essentially the same in their profile and position as the spectrum of the free base. The observations were explained by an extended Huckel molecular orbital calculation.

Introduction

The location of free-base protons in metal-free porphines has been the subject of long debate. Proposed structures are (a) two pyrrole and two aza groups (bonded structure), (b) shared protons (bridged structure), and (c) hydrogen-bonded models somewhere between. It is clear from various studies that the central protons are localized on a diagonally opposed pair of nitrogens in porphyrin free bases. However, the position of central protons in phthalocyanine free base (H₂Pc) is still a matter of controversy.[2]

By X-ray photoelectron spectroscopy, we showed evidences for the bonded structure of H₂Pc and tetraphenylporphine free base (H₂TPP).[3] Zeller and Hayes (Z-H) also concluded the bonded structure of H₂TPP; however, they could not draw a definite conclusion from their broad unresolved N 1s

photoelectron peak of H₂Pc.[4] Z-H suggested that an intramolecular hydrogen bonding prevents the resolution of distinct N 1s peaks in H₂Pc.

The authors who concluded the bridged structure of H₂Pc emphasized the presence of meso-bridging aza nitrogens.[5-7] The lone pair of the meso-bridging nitrogens in H₂Pc is equally effective in attracting protons as that of the inner nitrogens and thus an inner proton forms hydrogen bonds between two inner and one bridge nitrogens, while the lack of meso-bridging nitrogens in porphine leaves the inner proton localized on one of the central nitrogens.

One object of the present work is to elucidate the effect of meso-bridging aza nitrogens on the location of the inner protons. For this purpose, we measured the N 1s photoelectron spectra of tetrabenzmonoazaporphine free base (H₂-TBMAP) and tetrabenztriazaporphine free base (H₂TBTAP)

(1) (a) National Chemical Laboratory for Industry. (b) Department of Chemistry, Tokyo Institute of Technology.

(2) Reviews are found in the following references: Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.,* 60, 799 (1974); A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta,* 25, 62 (1972).

(3) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.,* 60, 799 (1974).

(4) M. V. Zeller and R. G. Hayes, *J. Amer. Chem. Soc.,* 95, 3855 (1973).

(5) B. D. Berezin, *Russ. J. Phys. Chem.,* 39, 165 (1965).

(6) I. Chen, *J. Mol. Spectrosc.,* 23, 131 (1967).

(7) E. B. Fleischer, *Accounts Chem. Res.,* 3, 105 (1970).