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Configurational Isomerism of Coordinated Tetraazamacrocycles. Crystal and Molecular Structure of Carbonato (1,7-Dimethyl-1,4,7,10-Tetraazacyclododecane)cobalt(III) Perchlorate

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The title compound was prepared according to three different procedures and was characterized by ion-exchange chromatography, NMR spectroscopy and X-ray crystallography. The compound crystalllizes in the orthorhombic space group Imcb with a = *18.458(4),* b = *13.608(3) and* c = *13.436(3)* Å. *The structure was solved by heavy-atom methods and refined to an R of 0.061. The geometry of the complex cation is octahedral with the macrocyclic ligand bonded through its four nitrogen atoms. Ion-exchange chromatography and NMR spectroscopy give no evidence of more than one stable configurational isomer of this complex.*

Introduction

Recently there have been numerous studies on tetraamino macrocycles, many of them devoted especially to the thermodynamic, kinetic and stereochemical behaviour of the ligands in their complexes with transition metals [1]. The 12-membered macrocycle 1,4,7,10-tetraazacyclododecane, cyclen, and its tetra-N-methyl derivative, Me_4cyclen, have been shown to form square-planar [2], square-pyramidal [3] and *cis*-octahedral complexes [4–6] adopting a nearly planar geometry in the two former cases and a butterfly-like folded configuration in the latter one. A trans-octahedral coordination has never been found for cyclen complexes, presumably because of the small size of the cavity provided by these 12-membered macrocycles.

Due to the presence of four potentially chiral nitrogen atoms a tetraamino macrocycle can give many configurational isomers even for a *cis*-octahedral complex. Thus, for cyclen in *cis*-octahedral complex of the type MAB (cyclen) (A, B = monodentate ligands) as many as twelve isomers are possible. In the case of the symmetrical di-N-methyl derivative, Me_2cyclen, twenty-four different isomers should be taken into account. However, most of them can be safely ruled out on the basis of strong repulsive interactions and angular strains. Nevertheless, the two configurations shown in Fig. 1 have been ascertained.

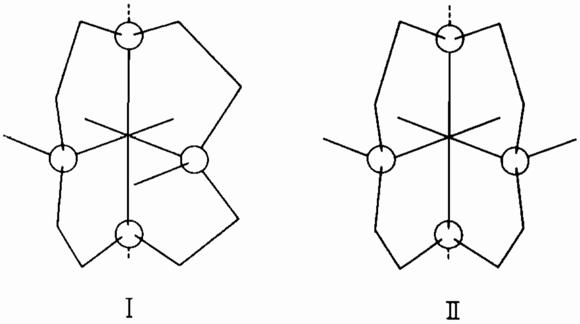

Fig. 1. Two possible structures for *cis*-octahedral complexes of a tetraazamacrocycle.

Configuration I has been found by X-ray crystallography in the cobalt(III) complexes: $[Co(CO_3)cyclen](ClO_4)\cdot H_2O$ [4], $[Co(NO_2)_2cyclen]Cl$ [5], $[Co(pd)cyclen](ClO_4)_2\cdot H_2O$, pd = pentane-2,4-dionate [6] and $[CoBr(Br_2H_2O)Et_4cyclen]$ [7], Et_4cyclen = 2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane, whereas configuration II was revealed in $[NiBr(H_2O)Me_2cyclen]Br$ [8]. In order to investigate the possible occurrence of stable isomers of *cis*-octahedral complexes with Me_2cyclen we have synthesized the complex $[Co(CO_3)Me_2cyclen](ClO_4)$. The present paper reports the results of the X-ray structure determination and the ^{13}C NMR study of the compound.

Experimental

Preparation of the Complex

The complex was prepared according to the following three procedures:

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a) A solution of Me_2cyclen [8] (0.2 g, 1 mmol) and $CoBr_2 \cdot 6H_2O$ (1 mmol) in water (20 ml) was stirred at room temperature for 2 days in the open air. The solution was evaporated to about 2 ml under vacuum and added to a solution of $NaClO_4 \cdot H_2O$ (2 mmol) in water (2 ml). Ethanol (20 ml) was added to precipitate the violet perchlorate complex which was collected by filtration and recrystallized from absolute ethanol.

b) To a stirred aqueous slurry (5 ml) of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (0.7 g, 0.2 mmol) in an ice bath, a solution of Me_2cyclen (0.4 g, 2 mmol) was added dropwise. The green-brown suspension was heated at 40 °C and left for 15 minutes. After this period the violet solution was cooled at room temperature and added to a solution of $NaClO_4 \cdot H_2O$ (4 mmol) in water (2 ml). The remaining procedure was as described in a).

c) A solution of $[Co(CO_3)Me_2cyclen]ClO_4$ (0.3 g, 0.7 mmol) prepared according to the procedure a) and $HClO_4$ 70% (0.36 ml, 0.4 mmol) in water (4 ml) was refluxed for 1 hour. After rapid cooling to 0 °C, K_2CO_3 (0.6 g, excess) was added cautiously and the reaction mixture was kept in a refrigerator for 2 hours. The solid $KClO_4$ was removed by filtration and the violet solution of $[Co(CO_3)Me_2cyclen]ClO_4$ was further treated as described in a).

Anal. Calcd. for $C_{11}H_{24}N_4O_7ClCo$: C, 31.55; H, 5.77; N, 13.38. Found: C, 31.25; H, 5.69; N, 13.10.

Chromatographic Experiments

The reaction mixtures from the procedures a, b and c were chromatographed on the SP Sephadex C-25 cation exchange resin in a 3 cm X 85 cm column using 0.2 *M* sodium (+)-hydrogentartrate, 0.1 *M* disodium hydrogen phosphate and 0.2 *M* sodium chloride as eluents. A single well-defined band was observed in every case.

Spectroscopy

Proton decoupled ^{13}C NMR spectra were collected on a Varian FT-80A spectrometer at 20.0 MHz using D_2O as solvent; chemical shifts were reported in ppm from TMS with dioxane as secondary reference standard ($\delta_{diox.} = \delta_{TMS} + 67.4$). Recording conditions were as follows: aquisition time 2 s, and pulse width 11 μs, corresponding to a 90° pulse. The multiplicity of carbon atoms was determined by the 'attached proton test' (APT) technique, which easily allowed distinction between CH_2 and CH_3 groups [9]. Proton NMR spectra were obtained with a Perkin-Elmer R32 instrument operating at 90 MHz; chemical shifts were reported in ppm from internal TMS.

Crystallographic Procedures

Diffraction data were collected from a crystal of dimensions 0.18 X 0.18 X 0.18 mm by a $\omega-2\theta$ technique with variable scan width using a PW 1100 Philips diffractometer. Of the reflections collected, 1256 with $I > 3\sigma$ (F) were considered observed. Systematic absences for reflections hkl of the type $h + k + l = 2n + 1$ and of the type $l = 2n + 1$ and $k = 2n + 1$ for reflections h0l and hk0 respectively indicated the space groups I2cb and Imcb. The centrosymmetric space group Imab (the non-standard setting of No. 72-Ibam) was assumed on the basis of the successful structure solution and refinement. The details of the data collection are shown in Table I. Three standard reflections were monitored every 120 min. of exposure, and no significant variation was observed. The data were corrected for Lorentz and polarization effects, but not for absorption.

TABLE I. Crystallographic Experimental Data.

Molecular Formula:	$C_{11}H_{24}N_4O_7ClCo$
Molecular Weight:	418.7
Crystal System:	orthorhombic
a (A)	18.458(4)
b (A)	13.608(3)
c (A)	13.436(3)
V (A^3)	3374.8
Space Group:	Imcb
Z	8
ρ (calcd gcm^{-3})	1.65
F(000)	1744e
Radiation	MoKα (λ = 0.71069 A)
μ(MoKα) (cm^{-1})	12.1
Theta Range (deg)	2.5–30
Scan Speed (deg/sec)	0.05
Scan Width (deg)	0.3–1.0
Observed Reflections	1256
Weighting Scheme	$w = 1.0/(\sigma^2(F) + 0.001F^2)$

The structure was solved by heavy-atom techniques using the SHELX 76 program package [10] and a SEL 32/70 computer. A Patterson map showed that the Co atom is located on the mirror plane. Subsequent Fourier maps revealed location of all non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms gave a final R of 0.061 ($R_w = 0.060$). The perchlorate ion was found to be disordered. The two alternative orientations were refined with an occupancy factor of 0.5 for the oxygen atoms. The contribution from the hydrogen atoms (except those bonded to the nitrogen atoms) fixed by standard geometry was included during the refinement.

The final atomic parameters are listed in Table II.

TABLE II. Final Atomic Parameters for (Carbonato) (1,7-Dimethyl-1,4,7,10-Tetraazacyclododecane)cobalt(III) Perchlorate.[a]

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2500	536(1)	2661(1)	27.2(5)	16.3(4)	26.4(5)	0	0	0.1(5)
Cl	0	2500	−563(2)	36(1)	56(1)	51(2)	0	−15(7)	0
O1	2500	136(4)	1298(4)	50(3)	23(3)	29(3)	0	0	−6(2)
O2	2500	1642(4)	1786(4)	36(3)	22(2)	25(3)	0	0	1(2)
O3	2500	1350(4)	153(4)	61(4)	36(3)	33(3)	0	0	0(3)
O4	−279(15)	3106(27)	122(27)	60(16)	200(23)	176(21)	25(13)	0(14)	−136(19)
O5	573(18)	2972(27)	−1154(27)	41(15)	138(20)	132(20)	−31(13)	27(11)	−26(16)
O41	−514(11)	3069(17)	−6(20)	54(13)	66(9)	114(14)	23(9)	35(11)	9(10)
O51	360(19)	3118(28)	−1153(24)	54(18)	148(20)	102(16)	−16(13)	20(11)	69(15)
N1	2500	1341(5)	3830(4)	28(3)	27(3)	22(3)	0	0	2(3)
N2	2500	−765(4)	3225(5)	71(5)	13(3)	36(4)	0	0	−1(3)
N3	1419(3)	480(4)	2814(4)	34(2)	48(3)	36(3)	−13(2)	1(2)	3(2)
C1	2500	1060(6)	1013(6)	29(4)	32(4)	26(4)	0	0	1(3)
C2	1810(3)	1233(4)	4386(4)	37(3)	40(3)	34(3)	5(3)	6(2)	−2(3)
C3	1230(3)	1235(5)	3582(5)	28(3)	58(4)	46(4)	5(3)	7(3)	0(3)
C4	1228(4)	−539(6)	3193(5)	64(5)	61(4)	54(4)	−40(4)	2(3)	6(4)
C5	1819(5)	−1233(5)	2870(5)	104(7)	32(3)	44(4)	−31(4)	−1(4)	0(3)
C6	1012(4)	672(7)	1868(5)	29(3)	93(6)	54(4)	−11(4)	−9(3)	1(4)

[a]The form of the thermal ellipsoid is $\exp[-2T^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2}2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Coordinates multiplied by 10^4, temperature factors by 10^3.

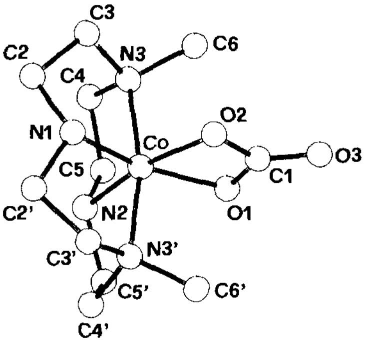

Fig. 2. Structure of the [Co(CO)$_3$)Me$_2$cyclen]$^+$ complex ion.

Results and Discussion

The complex [Co(CO)$_3$)Me$_2$cyclen]ClO$_4$ has been synthesized according to three different procedures (see Experimental). However, no evidence of the occurrence of different isomers in the reaction products was found when they were chromatographed through an ion-exchange resin with several eluents, a procedure which has been proved very effective in many other cases [11]. The products of the synthetic procedures show the same IR and NMR (^{13}C, ^{1}H) spectra.

TABLE III. Bond Lengths (A) and Angles (deg).

Co–O(1)	1.910(6)	C(1)–O(1)	1.314(9)
Co–O(2)	1.909(5)	C(1)–O(2)	2.307(9)
Co–N(1)	1.915(6)	C(1)–O(3)	1.222(9)
Co–N(2)	1.925(6)	C(2)–C(3)	1.520(9)
Co–N(3)	2.007(5)	C(4)–C(5)	1.506(12)
N(1)–C(2)	1.484(6)	Cl–O(4)	1.34(3)
N(2)–C(5)	1.488(8)	Cl–O(5)	1.47(3)
N(3)–C(3)	1.496(8)	Cl–O(41)	1.44(2)
N(3)–C(4)	1.518(8)	Cl–O(51)	1.33(2)
N(3)–C(6)	1.499(8)		
O(1)–Co–O(2)	68.6(2)	Co–N(3)–C(6)	113.8(4)
O(1)–Co–N(2)	96.6(3)	C(3)–N(3)–C(6)	110.0(5)
O(1)–Co–N(3)	95.0(1)	C(3)–N(3)–C(6)	110.4(6)
O(2)–Co–N(1)	93.1(3)	C(4)–N(3)–C(6)	109.0(5)
O(2)–Co–N(3)	95.4(2)	O(1)–C(1)–O(2)	110.4(6)
N(1)–Co–N(2)	101.7(3)	O(1)–C(1)–O(3)	125.8(7)
N(1)–Co–N(3)	86.4(1)	O(2)–C(1)–O(3)	123.8(7)
N(2)–Co–N(3)	85.7(2)	N(1)–C(2)–C(3)	104.2(5)
Co–O(1)–C(1)	90.4(4)	C(2)–C(3)–N(3)	108.9(5)
Co–O(2)–C(1)	90.6(4)	N(3)–C(4)–C(5)	108.0(5)
Co–N(1)–C(2)	110.9(3)	C(4)–C(5)–N(2)	104.5(5)
Co–N(2)–C(5)	105.5(4)	O(4)–Cl–O(5)	112(5)
Co–N(3)–C(3)	106.0(3)	O(41)–Cl–O(51)	107(2)
Co–N(3)–C(4)	107.4(4)		

The structure of the complex ion [Co(CO$_3$)Me$_2$cyclen]$^+$ is given in Fig. 2. The octahedral coordination sphere around the Co ion consists of four nitrogen atoms of the macrocyclic ligand and the carbonato moiety bonded to the central metal ion by two oxygen atoms. The complex ion exhibits the point symmetry C_s with the Co(III) ion, the carbonato group and the nitrogen atoms N(1) and N(2) located on the mirror plane (Table III).

Generally, the geometrical features of the complex resemble those found in the analogous Co(III) compound with cyclen [4]. The Co–O and Co–N distances in the coordination plane are nearly equal, ranging from 1.909(5) to 1.925(6) Å. On the other hand, the apical Co–N bonds are slightly longer (2.007(5) Å). As in the case of the cyclen analogue, the Me_2cyclen ligand adopts the configuration I (Fig. 1) where one of the terminal groups of the nitrogen atoms points out with respect to the macrocyclic plane, in a direction opposite to that of the three others. A comparison of the configuration found here with that present in the Ni–Me_2cyclen complex [8] (four terminal groups on the same side of the macrocyclic plane) shows no significant differences in bond lengths and angles within the Me_2-cyclen ligand. An insight of the stereochemistry of the $[Co(CO_3)Me_2cyclen]ClO_4$ complex in aqueous solution is given by its $^{13}C\ \{^1H\}$ NMR spectrum. This exhibits five resonances of equal integrated intensities in the range 66.9–46.3 ppm, indicating five non-equivalent sets of pairs of carbon nuclei.

The APT technique shows that the methyl carbons should be attributed the highest-field singlet (46.3 ppm) confirming the presence of a symmetry plane relating the two methyl groups in the complex present in solution. The resonances of the methylene groups, which are only two in the free ligand (45.9 and 55.5 ppm) [8] due to its high symmetry, are both split into two distinct signals upon metal coordination. This resonance pattern rules out the occurrence of another symmetry plane normal to the previous one (*i.e.* configuration II, Fig. 1) and is in agreement with the configuration I in much the same way as is found in the solid state.

By comparing the ^{13}C resonances found in the cobalt complex with those found in the free ligand, a small down-field shift is observed upon coordination for the methyl carbons (0.8 ppm). Larger deshieldings are experienced by methylene carbon nuclei, the peaks at 66.9 and 64.1 ppm being tentatively attributed to the methylene groups adjacent to the $N-CH_3$ (55.5 ppm in the free ligand) whereas the peaks at 49.1 and 48.0 ppm are assigned as those of methylene groups adjacent to NH groups.

The ^1H NMR spectrum does not give further information with respect to the ^{13}C spectrum. Actually, only a sharp singlet is found for the methyl hydrogens (2.0 ppm), confirming the equivalence of the two groups. The methylene protons exhibit complex multiplets between 2.5 and 3.1 ppm. On the other hand, the protons of the NH groups show a broadened resonance, probably as a result of quadrupole coupling, between 6.4 and 7.0 ppm. This does not allow us to draw conclusions about the non-equivalence of the two protons.

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