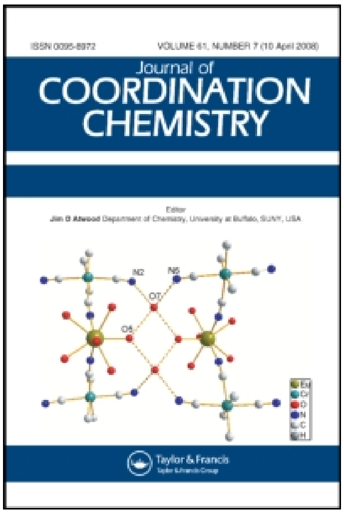

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The Crystal and Molecular Structure of the Unstable *Facial* Isomer of 1,4,7,10,13,16-Hexaazacyclooctadecanecobalt(III) Nitrate Monohydrate, *fac*-[Co(hexacyclen)]$(No_3)_3 \cdot H_2O$

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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE UNSTABLE *FACIAL* ISOMER OF 1,4,7,10,13,16-HEXAAZACYCLOOCTADECANE-COBALT(III) NITRATE MONOHYDRATE, *fac*-[Co(hexacyclen)]$(NO_3)_3.H_2O$

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The crystal structure of all-*facial*-[Co(hexacyclen)]$(NO_3)_3.H_2O$ (the geometric isomer which elutes first on cation exchange chromatography) is reported. In the centrosymmetric cation the cobalt(III) atom exists in a slightly distorted octahedron, and the cation has approximate C_3 symmetry. The Co–N distances average 1.997(3) Å and the average chelate angle is 83.6(1)°. In the crystal lattice the complex cations are linked by water molecules of crystallization thereby forming infinite chains and the nitrate groups are associated to both the cation and the water molecule. The compound crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions $a = 13.980(4)$, $b = 9.892(2)$, $c = 16.002(6)$ Å, $\beta = 111.34(4)°$ and $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.037$ for 1183 reflections with $I \geq 2.5\,\sigma(I)$.

Keywords: Cobalt(III), hexacyclen, facial isomer, structure, X-ray

INTRODUCTION

Complexes of the N_6-macrocyclic ligand 1,4,7,10,13,16-hexaazacyclooctadecane (abbreviated hexacyclen, or [18]aneN_6) with Co(III), Ni(II) and Cu(II) were first reported in 1978.[1,2] The stereochemistry of these complexes is of considerable interest since various isomers arise from coordination of this ligand. As a sexadentate the ligand can wrap around a metal atom to give two topological arrangements which may be designated as *fac* (with facial linkages from all pairs of coupled chelate rings, but alternatively designated *meso*,[1] or *symm*,[2] or 'D_3 configuration'[3]) or *mer* (having two meridional and four facial linkages, alternatively designated *racemic*, or *unsymm*, or 'D_2 configuration'). The *mer* further exists as two internal N–H diastereoisomers (and their enantiomers), and the existence of all these forms, their characterization by ^{13}C NMR spectroscopy, and their relative stabilities were first demonstrated for the $[Co(hexacyclen)]^{3+}$ system by Yoshikawa.[1]

Since this initial work, interest in complexes of this ligand and analogues has continued, with studies in solution (ESR, electrochemistry, electronic spectroscopy) and in the solid state (IR spectroscopy, magnetic susceptibility) being made with the complexes of Ni(II) and Ni(III),[4] Cu(II)[5,6] and Co(II).[7] Complexation constants have been determined for a range of M^{2+} metal ions (and also K^+ and La^{3+}), and

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show that the ligand has high sequestering ability for all metal ions.[8] Anion complexation with protonated forms of hexacyclen has been studied extensively by Kimura and coworkers using a range of anions.[9-13] The cobalt(III) complexes with hexacyclen, along with analogous ligands [21]aneN_6 (= hexacyclam) and tricyclohexano[18]aneN_6, were further examined by Royer, with respect to chromatographic separation of the *mer* diastereoisomers including partial optical resolution, and CD spectra.[3]

The abovementioned solution and solid state measurements have not yielded definitive structural information on the Co(II), Ni(II) and Cu(II) complexes, and despite the interest in these systems the only X-ray structure of a hexacyclen complex system appears to be of one of the diastereoisomers of *mer*-[Co(hexacyclen)]$^{3+}$ (as the perchlorate racemate).[3] The protonated ligand has also been of structural interest owing to the possibility of the abovementioned anion complexation.[14] There has been a recent pH titration study of hexacyclen.$3H_2SO_4$,[15] and the crystal structures of hexacyclen$H_6(NO_3)_6.H_2O$[16] and hexacyclen$H_4(NO_3)_2Cl_2.2H_2O$[17] have been determined.

In the cobalt(III) complex system the *fac* isomer is relatively unstable, being present in equilibrium conditions in solution (charcoal) at $\leqslant 1\%$.[1,2] However, we have recently been able to prepare the *fac* isomer in increased proportion, for use in the examination of the kinetics of its isomerization to the *mer* isomers,[18] and this availability prompted the present X-ray structure analysis. This was carried out to ascertain the detailed molecular structure of the *fac* cation, and to compare this solid state structure with that calculated by molecular mechanics.[1]

EXPERIMENTAL

Preparation

The *fac*-[Co(hexacyclen)]$^{3+}$ isomer was prepared by isomerization from the *mer*.[18] These two geometric isomers were separated chromatographically on SP-Sephadex using 0.1 M Na_3PO_4 eluent, and the first-eluted *fac* band was then absorbed on Dowex 50W-X2 resin, H^+ form, and was eluted with 1 M HNO_3. On rotary evaporation of the effluent the product crystallized, and was removed by filtration, and washed with ethanol and acetone. Found C, 27.5; H, 6.0; N, 24.2%; *fac*-$[Co(C_{12}H_{30}N_6)](NO_3)_3.H_2O$ requires C, 27.6; H, 6.2; N 24.2%.

Crystallography

Intensity data for 1687 reflections were measured on an Enraf-Nonius CAD4F diffractometer with the use of graphite monochromatized Mo$K\alpha$ radiation and the ω:2/3θ scan technique. The data were corrected for Lorentz and polarization effects and for absorption.[19] Of the reflections measured (θ_{max} 22.5°), 1525 were unique (R_{amal} 0.016) and of these 1183 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability. Crystal data and refinement details are given in Table I.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F.[19] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions, located from difference maps (except those for the water molecule of crystallization), were included in the model but their positions were not refined. Refinement with a weighting scheme of the form $w = [\sigma^2(F) + g(F)^2]^{-1}$ converged with final R 0.037, R_w 0.042, and g 0.0017.

TABLE I
Crystal and refinement details for *fac*-[Co(hexacyclen)](NO$_3$)$_3$.H$_2$O.

Formula	$C_{12}H_{32}CoN_9O_{10}$
M_r	521.4
Crystal system	monoclinic
Space group	$C2/c$
a, Å	13.980(4)
b, Å	9.892(2)
c, Å	16.002(6)
β (°)	111.34(4)
Vol. (Å^3)	2061(2)
Z	4
D_c (g cm^{-3})	1.680
F(000)	1084
μ, cm^{-1}	8.64
Transmission factors (max./min.)	0.881; 0.808
0 limits (°)	1.0-22.5
No. of data collected	1687
No. of unique data	1525
No. of unique reflections used with $I \geq 2.5\sigma(I)$	1183
R	0.037
g	0.0017
R_w	0.042
ρ_{max} (e Å^{-3})	0.69

TABLE II
Fractional atomic coordinates ($\times 10^4$) for *fac*-[Co(hexacyclen)](NO$_3$)$_3$.H$_2$O.

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	7500(−)	2500(−)	5000(−)
N(1)	8043(2)	908(3)	5799(2)
N(2)	8364(3)	2250(3)	4255(2)
N(3)	6594(3)	1130(3)	4168(2)
C(1)	7479(3)	683(4)	6420(2)
C(2)	8544(3)	3614(4)	3949(3)
C(3)	7936(3)	−306(4)	5208(3)
C(4)	6859(3)	−288(4)	4524(3)
C(5)	6719(3)	1288(4)	3290(2)
C(6)	7860(3)	1338(4)	3473(3)
N(4)	5000(−)	2533(6)	7500(−)
O(1)	5000(−)	1296(5)	7500(−)
O(2)	4899(5)	3202(6)	6816(4)
N(5)	4123(3)	2674(3)	3968(2)
O(3)	4492(2)	1507(3)	4041(2)
O(4)	3193(2)	2840(3)	3603(2)
O(5)	4704(2)	3661(3)	4268(2)
O(w1)	0000(−)	868(5)	7500(−)

Fractional atomic coordinates are listed in Table II, and the cation structure (drawn at 15% probability ellipsoids with ORTEP[20]) with the atom numbering scheme used is shown in Figure 1. The refinement was performed with the SHELX76[19] program system installed on a SUN 4/280 computer system. Scattering factors for Co^{3+} (corrected for f' and f'') were from the *International Tables for X-ray Crystallography*[21] and those for the remaining atoms were those incorporated in the SHELX76[19] program system. Listings of thermal parameters, hydrogen atom parameters, and the observed and calculated structure factors are available from the Editor.

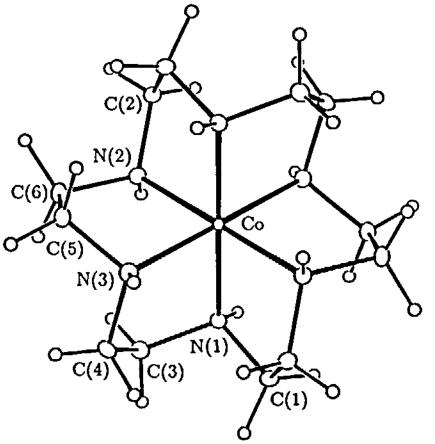

FIGURE 1 Molecular structure and crystallographic numbering scheme for the *fac*-[Co(hexacyclen)]$^{3+}$ cation.

RESULTS AND DISCUSSION

The crystal structure determination confirms the stoichiometry of the compound as $[Co(hexacyclen)](NO_3)_3.H_2O$. The cation is situated about a crystallographic centre of inversion so that only half of the cation comprises the crystallographic asymmetric unit. The remaining components of the asymmetric unit are (i) a nitrate group which is situated about a crystallographic 2-fold axis, (ii) a nitrate group in a general position, and (iii) a water molecule of crystallization situated about a crystallographic 2-fold axis.

In the cation, the cobalt atom exists in a slightly distorted octahedral N_6 geometry (Figure 1) and the disposition of the macrocyclic ring about the cobalt atom is the all-*facial* topology. Distortions from the ideal octahedral geometry may be traced to the restricted bite angle of the ethylenediamine chelate rings (av. 84°). The three unique Co–N distances are experimentally equivalent at 1.996(3) Å and are normal, as are the N–C and C–C bond parameters. The six ethylenediamine ring conformations alternate between δ and λ going around the macrocycle (starting at the δ of the N(1)–N(3) chelate).

A Dreiding model indicates that the molecular structure which should be adopted by this *fac* isomer on the basis of bond angle strain only is very rigid and is of symmetry D_{3d}. The normal bond distances and the idealized tetrahedral and 90° bond angles constrain the ring conformations to be alternating δ and λ around the macrocycle, all the pairs of the facial rings being related by mirror planes which bisect the faces of the octahedron. Although there seems to be little bond angle strain, the rigidity of the structure allows little conformational freedom. However, this symmetrical structure has large non-bonded hydrogen–hydrogen interactions across the mirror planes.

TABLE III

Bond distances (Å) and angles (°) for *fac*-[Co(hexacyclen)]$(NO_3)_3.H_2O$.

Distances			
Co–N(1)	1.996(3)	Co–N(2)	1.997(3)
Co–N(3)	1.996(3)	N(1)–C(1)	1.494(5)
N(1)–C(3)	1.501(5)	N(2)–C(2)	1.488(5)
N(2)–C(6)	1.495(5)	N(3)–C(4)	1.509(5)
N(3)–C(5)	1.485(5)	C(1)–C(2′)	1.513(5)
C(3)–C(4)	1.512(5)	C(5)–C(6)	1.515(6)
N(4)–O(1)	1.224(7)	N(4)–O(2)	1.242(5)
N(5)–O(3)	1.252(4)	N(5)–O(4)	1.226(4)
N(5)–O(5)	1.249(4)		
Angles			
N(1)–Co–N(2)	96.5(1)	N(1)–Co–N(3)	83.8(1)
N(1)–Co–N(2′)	83.5(1)	N(1)–Co–N(3′)	96.2(1)
N(2)–Co–N(3)	83.8(1)	N(2)–Co–N(3′)	96.2(1)
Co–N(1)–C(1)	111.9(2)	Co–N(1)–C(3)	107.5(2)
Co–N(2)–C(2)	107.2(2)	Co–N(2)–C(6)	111.8(2)
Co–N(3)–C(4)	111.7(2)	Co–N(3)–C(5)	107.2(2)
C(1)–N(1)–C(3)	110.1(3)	C(2)–N(2)–C(6)	110.9(3)
C(4)–N(3)–C(5)	111.0(3)	N(1)–C(1)–C(2′)	109.1(3)
N(2)–C(2)–C(1′)	106.9(3)	N(1)–C(3)–C(4)	107.0(3)
N(3)–C(4)–C(3)	109.2(3)	N(3)–C(5)–C(6)	107.4(3)
N(2)–C(6)–C(5)	108.8(3)	O(1)–N(4)–O(2)	122.2(4)
O(3)–N(5)–O(4)	119.8(3)	O(3)–N(5)–O(5)	119.8(3)
O(4)–N(5)–O(5)	120.4(3)		

The energy-minimized structure as calculated by Yoshikawa[1] has reduced symmetry C_3, since this structure allows these non-bonded interactions to be relieved. The X-ray determined structure is close to that predicted, in that it deviates from mirror symmetry and approximates C_3 as seen in Figure 1. Also, the interatomic parameters for the calculated and observed structures agree closely. However, no evidence for a disparity in the N–C bond distances as suggested by the calculations[1] was found in the crystal structure.

In the crystal lattice there are significant intermolecular contacts as expected in a salt of this type. Significant contacts between the cation, nitrate and water molecules are shown in Figure 2, and it can be seen that all six amine protons are involved in hydrogen bonding contacts. Thus H(n1) is 2.20 Å from O(w1), H(n2) is 2.10 Å from O(5) of the nitrate anion in a general position, and H(n3) is 2.08 Å from O(3) of the same nitrate so that this anion can be considered as bridging two amine protons; the corresponding angles are N–H–O(w1) 152°, N–H–O(5) 161°, and N–H–O(3) 167°. While the nitrate group in the general position interacts with the cation *via* the O(3) and O(5) atoms, the O(4) atom does not form any close contacts as evidenced by the short N(5)–O(4) bond distance of 1.226(4) Å. The nitrate group lying on the 2-fold axis interacts only with the water molecule *via* the two symmetry related O(2) atoms at 2.86 Å, and the non-interaction of the O(1) atom in any significant hydrogen bonding contacts is emphasized by the short N(4)–O(1) bond distance of 1.224(7) Å. The water molecule forms four contacts, two with symmetry-related H(n1) atoms bound to two complex cations and two further contacts with two O(2) atoms at 2.86 Å.

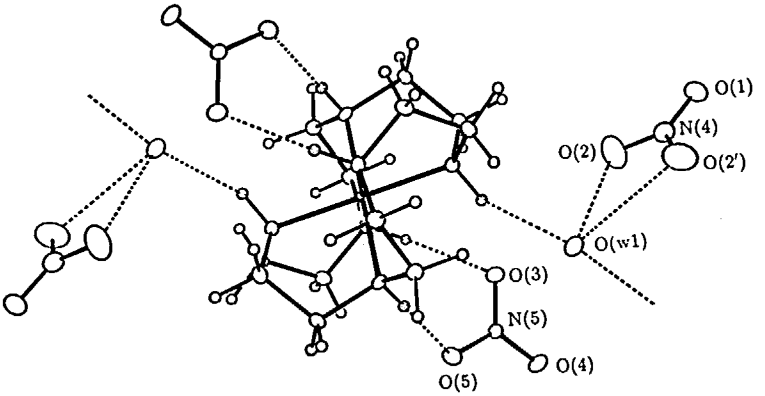

FIGURE 2 Hydrogen bonding characteristics in *fac*-[Co(hexacyclen)]$(NO_3)_3.H_2O$.

The crystal structure can thus be regarded as being comprised of infinite chains of complex cations bridged by water molecules, as seen in Figure 2. The crystallographically different nitrates both associate through only two of the oxygen atoms on the periphery of the infinite chains, and show no marked orientation towards the cations. By contrast, tetrahedral oxyanions such as phosphate are presumed to associate strongly and in a directed sense through three oxygen atoms to N–H protons of a particular octahedral face since they are found to cause marked enhancement of the proportions of facial isomers of cobalt(III)–polyamine complexes.[18]

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REFERENCES

1. Y. Yoshikawa, *Chem. Lett.*, 109 (1978).
2. R.W. Hay, B. Jeragh, S.F. Lincoln and G.H. Searle, *Inorg. Nucl. Chem. Lett.*, **14**, 435 (1978).
3. D.J. Royer, G.J. Grant, D.G. Van Derveer and M.J. Castillo, *Inorg. Chem.*, **21**, 1902 (1982).
4. A. Bencini, L. Fabbrizzi and A. Poggi, *Inorg. Chem.*, **20**, 2544 (1981).
5. K. Miyoshi, H. Tanaka, E. Kimura, S. Tsuboyama, S. Murata, H. Shimizu and K. Ishizu, *Inorg. Chim. Acta*, **78**, 23 (1978).
6. M.I. Mitewa, P.R. Bontchev, D.R. Vassileva, K.S. Kabassanov, E.N. Zhecheva and D.R. Mechandjiev, *J. Coord. Chem.*, **17**, 287 (1988).
7. M. Mitewa, P.R. Bontchev, D. Vassileva, E. Zhecheva, D. Mechandjiev and K. Kabassanov, *Inorg. Chim. Acta*, **134**, 17 (1987).

8. M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc. Dalton Trans.*, 2536 (1980).
9. T. Yatsunami, A. Sakonaka and E. Kimura, *Anal. Chem.*, **53**, 477 (1981).
10. E. Kimura, A. Sakonaka, T. Yatsunami and M. Kodama, *J. Am. Chem. Soc.*, **103**, 3041 (1981).
11. E. Kimura, M. Kodama and T. Yatsunami, *J. Am. Chem. Soc.*, **104**, 3182 (1982).
12. E. Kimura, A. Sakonaka and M. Kodama, *J. Am. Chem. Soc.*, **104**, 4984 (1982).
13. E. Kimura, A. Watanabe and M. Kodama, *J. Am. Chem. Soc.*, **105**, 2063 (1983).
14. B. Dietrich, M.W. Hosseini, J.M. Lehn and R.B. Sessions, *J. Am. Chem. Soc.*, **103**, 1282 (1981).
15. R.I. Gelb, L.M. Schwartz and L.J. Zompa, *Inorg. Chem.*, **25**, 1527 (1986).
16. T.N. Margulis and L.J. Zompa, *J. Heterocyclic Chem.*, **20**, 975 (1983).
17. J. Cullinane, R.I. Gelb, T.N. Margulis and L.J. Zompa, *J. Am. Chem. Soc.*, **104**, 3048 (1984).
18. G.H. Searle, to be published.
19. G.M. Sheldrick, "SHELX76. Program for Crystal Structure Determination", (University of Cambridge, England, 1976).
20. C.K. Johnson, ORTEPII, *Report ORNL-3794, Oak Ridge National Laboratory*, Tennessee (1971).
21. W.C. Hamilton and J.A. Ibers, Editors, "International Tables for X-ray Crystallography", Vol. IV, pp. 99, 149 (Birmingham, Kynoch Press, 1974).