# The Crystal and Molecular Structure of $\Delta$-(8-Methyl-1,3,6,10,13,16,19-heptaazabicyclo[6.6.6]icosane)cobalt(III) Perchlorate Monohydrate

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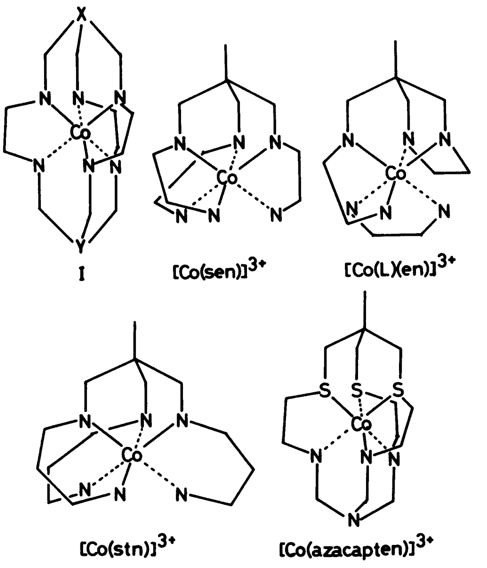
The structure of $\Delta$-(8-methyl-1,3,6,10,13,16,19-heptaazabicyclo[6.6.6]icosane)cobalt(III) perchlorate monohydrate, $\Delta$-[Co($C_{14}H_{33}N_7$)]($ClO_4$)$_3$·$H_2O$, has been determined by single crystal X-ray diffraction techniques. Crystal data are the following: space group $P2_12_12_1$, a=16.379(2) Å, $b$=16.388(2) Å, $c$=9.753(1) Å, $V$=2617.9(5) Å$^3$, Z=4, 3983 nonzero structure factors ($|F_o|>3\sigma(|F_o|)$), $R$=0.0447, and $R_w$=0.0491. The geometry of the cation can be approximated very closely by a composite of [Co(sen)]$^{3+}$ and [Co(sep)]$^{3+}$, where sen=1,1,1-tris(4-amino-2-azabutyl)ethane and sep=1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane.

The macrotricyclic hexaamine cage complexes of cobalt(III), with a commom basic structure **I** in Fig. 1, have several interesting properties. We have recently reported that these complexes are 3 to 6 orders of magnitude more acidic than ordinary cobalt(III) amine complexes and exploited this property to show the dominance of double hydrogen bonding in the ion association of these complexes.[1] It was implicitly assumed there that for favorable double hydrogen bonding, the complexes all take the ($lel$)$_3$ conformation, where ($lel$)$_3$ refers to the C–C vectors of "ethylenediamine" (en) moieties parallel to the cap-to-cap axis of the molecule. In contrast to this, the [Co(diNOsar-H)]$^{2+}$ (**I** with X=Y=C–$NO_2$) ion has been reported[2] to have the ($ob$)$_3$ conformation, where diNOsar-H is the deprotonated form of 1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane and ($ob$)$_3$ refers to the C–C vectors of "en" rings oblique to the cap-to-cap axis of the compound. Thus, it seemed to be interesting to investigate the conformation of [Co(azamesar)]$^{3+}$ (**I** with X=C–$CH_3$, Y=N), where azamesar=8-methyl-1,3,6,10,13,16,19-heptaazabicyclo[6.6.6]icosane. Further, we found that under some conditions, [Co(azamesar)]$^{3+}$ undergoes fragmentation reaction, which might result from steric strain.[3] Though the nature of this reaction is not clear as yet, steric strain has been shown to play an important role in determining spectroscopic[4] and chemical properties[5] as well as electron self-exchange rates in hexaamine cobalt(III) complexes. For example, complexes of type **I** exchange electron some $10^5$-fold faster than the parent [Co(en)$_3$]$^{3+}$ ion[6] and Geselowitz[7] proposed a ligand strain as a mojor factor for this difference. Therefore, examination of ligand strain might be considered to contribute to the elucidation of these problems.



I [Co(sen)]$^{3+}$ [Co(LXen)]$^{3+}$

[Co(stn)]$^{3+}$ [Co(azacapten)]$^{3+}$

Fig. 1. Schematic illustration of complexes.

## Experimental

**Material.** The compound was synthesized, according to the method of Creaser et al.,[8] by the reaction of aqueous ammonia and formaldehyde with $\Delta$-[Co(sen)]$^{3+}$, which had been prepared[4] and optically resolved[9,10] by the methods reported previously, where sen=1,1,1-tris(4-amino-2-azabutyl)ethane. The crystals were grown by slow evaporation of an aqueous solution into orthorhombic blocks elongated along the c axis.

**Crystal Data.** A yellow crystal of [Co($C_{14}H_{33}N_7$)]($ClO_4$)$_3$·$H_2O$ with dimensions of 0.32×0.24×0.20 mm was used for the data collection. The determination of cell constants and the collection of the intensity data were carried out at about 25 °C on a Rigaku AFC-5 automated four-circle diffractometer with Mo$K\alpha$ radiation made monochromatic by a graphite plate ($\lambda$=0.71073 Å). The cell constants, determined by a least-squares method using 50 independent reflections (25°<2$\theta$<30°), were $a$=16.379(2) Å, $b$=16.388(2) Å, $c$=9.753(1) Å, and $V$=2617.9(5) Å$^3$. The space group was determined to be $P2_12_12_1$ ($D_2^4$, No. 19) from the systematic absences for $h00$ ($h$=2$n$+1), $0k0$ ($k$=2$n$+1), and $00l$ ($l$=2$n$+1). The measured density of 1.73 g cm$^{-3}$ obtained by a flotation method agrees well with the calculated value of 1.712 g cm$^{-3}$ for $Z$=4. The intensity data were collected for $+h$, $+k$, $+l$ and $-h$, $-k$, $-l$ by the $\theta$—2$\theta$ scan technique to a maximum 2$\theta$ value of 60° at a scan rate of 3° min$^{-1}$ (40 kV, 25 mA). Scan widths ($\Delta\theta$) were calculated from the formula $\Delta\theta$=(1.1+0.5tan$\theta$)°. The intensity measurements were automatically repeated until $\sigma_c(|F_o|)/|F_o|$ became less than 0.05, where $\sigma_c(|F_o|)$ is a standard deviation calculated from counting statistics. The maximum

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number of repetition was 3. Three reference reflections monitored after every cycle of 100 measurements showed no significant variation in intensity during the data collection. Out of 5632 independent reflections measured, 3983 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination. They were corrected for Lorentz-polarization effects, but no absorption correction was applied since the linear absorption coefficient of $\mu(\mathrm{Mo}\,K\alpha)=10.65\,\mathrm{cm}^{-1}$ was low.

**Structure Determination and Refinement.** The structure was solved by standard heavy-atom techniques. The position of Co atom was determined from the three-dimensional Patterson map. The remaining atoms except hydrogen atoms were all revealed in subsequent Fourier syntheses. After all the non-hydrogen atoms were refined isotropically, a series of refinements using anisotropic thermal parameters for all non-hydrogen atoms reduced an $R$ value, $\sum||F_o|-|F_c||/\sum|F_o|$, to 0.0614 and an $R_w$ value, $[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, to 0.0724, where $F_o$ and $F_c$ are the observed and calculated structure factors, respectively. The weighting scheme used was $w=[\sigma_c^2+(0.015|F_o|)^2]^{-1}$. All the hydrogen atoms were located from subsequent difference Fourier maps. Further refinements, using anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, reduced $R$ to 0.0447 and $R_w$ to 0.0491.

The absolute configuration was checked by reversing the signs of the $\Delta f''$ terms and repeating the final refinement sequence, to give significantly larger $R$ of 0.0528 and $R_w$ of 0.0597. In Table 1 are compared the observed and calculated intensity ratios of 12 Bijvoet pairs for which the observed reflection $|F(hkl)|$ and counter-reflection $|F(\overline{hkl})|$ differed by more than 14%.

The final difference Fourier map showed no peaks higher than 0.83 e/Å$^3$.

The atomic scattering factors for non-hydrogen atoms were taken from International Tables for X-ray Crystallography[11] and those for hydrogen atoms from Stewart, Davidson, and Simpson.[12] The anomalous dispersion coefficients[11] were used for non-hydrogen atoms in structure factor calculations. The final atomic coordinates for non-hydrogen atoms are given in Table 2,[13] according to the atom labels of Fig. 2. All the computations, including ORTEP[14] drawings were carried out by a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science. The Universal Crystallographic Computation Program System, UNICS III,[15] was used.

## Results and Discussion

The crystal structure as viewed down the c axis is shown in Fig. 3. The crystal may be considered to be made up of alternate layers of complex cations and anions, both extending in the bc plane. The cation hydrogen-bonds, via N–H groups, to water oxygens (N2···Ow=2.913(6) Å and N4···Ow=3.240(7) Å) and to perchlorate oxygens (N1···O(10)=3.038(6) Å, N1···O(11)=3.399(7) Å, N6···O(10)=3.057(6) Å, and N6···O(12)=3.317(10) Å). Interatomic distances and angles are given in Table 3.

Table 1. Determination of Absolute Configuration

| $h$ | $k$ | $l$ | $\|F_o\|$ | $\|F_c\|$ | $\|F_o(\overline{hkl})\|/\|F_o(hkl)\|$ | $\|F_c(\overline{hkl})\|/\|F_c(hkl)\|$ |
|---|---|---|---|---|---|---|
| 2 | 9 | 1 | 20.90 | 20.07 | 1.24 | 1.24 |
| $\bar{2}$ | $\bar{9}$ | $\bar{1}$ | 25.95 | 24.88 | | |
| 11 | 6 | 2 | 18.41 | 17.72 | 1.16 | 1.16 |
| $\overline{11}$ | $\bar{6}$ | $\bar{2}$ | 21.40 | 20.55 | | |
| 4 | 2 | 3 | 24.29 | 26.57 | 0.85 | 0.78 |
| $\bar{4}$ | $\bar{2}$ | $\bar{3}$ | 20.66 | 20.79 | | |
| 1 | 6 | 3 | 38.30 | 38.06 | 1.14 | 1.12 |
| $\bar{1}$ | $\bar{6}$ | $\bar{3}$ | 43.69 | 42.80 | | |
| 6 | 10 | 3 | 29.72 | 29.00 | 1.14 | 1.08 |
| $\bar{6}$ | $\overline{10}$ | $\bar{3}$ | 33.86 | 31.26 | | |
| 3 | 4 | 4 | 26.06 | 25.16 | 1.14 | 1.07 |
| $\bar{3}$ | $\bar{4}$ | $\bar{4}$ | 29.77 | 27.00 | | |
| 7 | 4 | 5 | 23.09 | 23.17 | 1.14 | 1.09 |
| $\bar{7}$ | $\bar{4}$ | $\bar{5}$ | 26.25 | 25.31 | | |
| 4 | 9 | 5 | 26.96 | 26.82 | 1.15 | 1.08 |
| $\bar{4}$ | $\bar{9}$ | $\bar{5}$ | 31.04 | 28.97 | | |
| 9 | 5 | 6 | 20.02 | 21.23 | 1.14 | 1.08 |
| $\bar{9}$ | $\bar{5}$ | $\bar{6}$ | 22.74 | 22.98 | | |
| 2 | 3 | 7 | 17.82 | 18.40 | 1.28 | 1.19 |
| $\bar{2}$ | $\bar{3}$ | $\bar{7}$ | 22.73 | 21.98 | | |
| 1 | 2 | 8 | 26.75 | 26.82 | 1.14 | 1.06 |
| $\bar{1}$ | $\bar{2}$ | $\bar{8}$ | 30.42 | 28.49 | | |
| 5 | 2 | 8 | 28.61 | 28.33 | 1.16 | 1.09 |
| $\bar{5}$ | $\bar{2}$ | $\bar{8}$ | 33.19 | 30.78 | | |

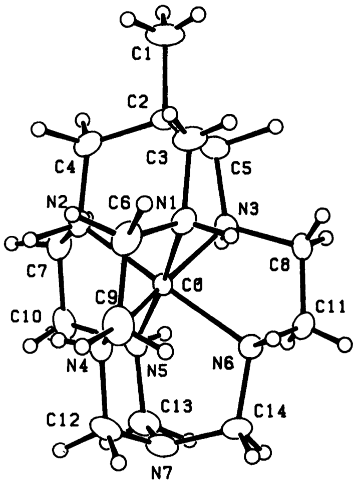

Fig. 2. Structure of the cation with atom labels. Thermal ellipsoids are drawn to include 30% of probability distribution.

The structure of $\Delta$-[Co(azamesar)]$^{3+}$ cation, given in Fig. 2, has a pseudo-threefold axis of rotation and may be viewed as a composite of [Co(sen)]$^{3+}$ (Fig. 1) and [Co(sep)]$^{3+}$ (**I** with X=Y=N), where sep= 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane.[16] The absolute configuration of the cation that shows a positive circular dichroism peak in the first absorp-

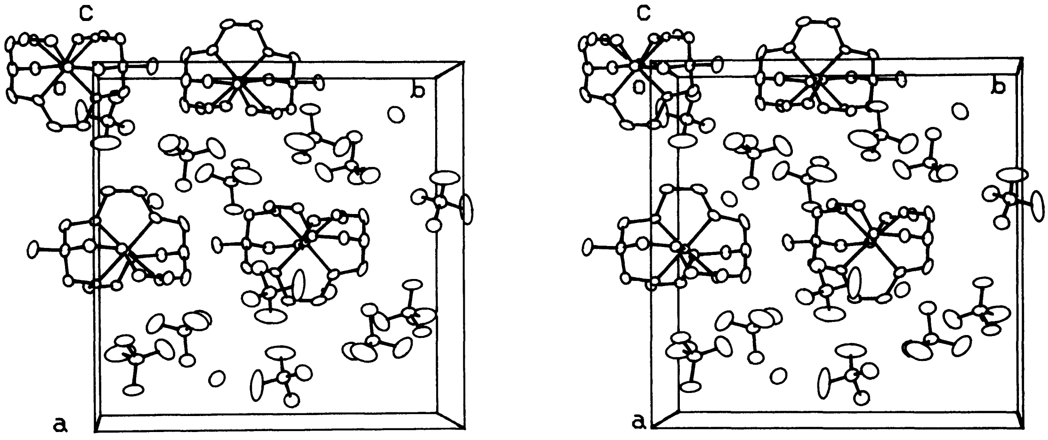

Fig. 3. Crystal packing.

Table 2. Atomic Coordinate. Positional Parameters are Multiplied by $10^5$. Thermal Parameters are Given by the Equivalent Temperature factors (Å$^2$)

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Co | 1165(3) | 41387(3) | 8080(6) | 2.0 |
| Cl(1) | 30732(7) | 38781(9) | 7801(15) | 4.4 |
| Cl(2) | 25958(8) | 74594(9) | 4443(14) | 4.5 |
| Cl(3) | −37368(8) | 47288(9) | −2234(14) | 4.3 |
| O(1) | 25364(22) | 41883(32) | −2395(43) | 6.4 |
| O(2) | 38888(22) | 39653(31) | 4098(45) | 6.8 |
| O(3) | 29296(33) | 43279(57) | 19950(55) | 13.4 |
| O(4) | 28170(41) | 31025(41) | 10621(111) | 16.0 |
| O(5) | 29093(32) | 79520(39) | 14878(58) | 9.5 |
| O(6) | 17502(26) | 75464(28) | 3917(55) | 7.2 |
| O(7) | 27970(40) | 66347(40) | 5523(89) | 12.7 |
| O(8) | 28887(36) | 77706(46) | −8199(60) | 11.3 |
| O(9) | −35784(25) | 41974(29) | 8694(45) | 6.9 |
| O(10) | −44168(25) | 44787(27) | −9787(53) | 7.0 |
| O(11) | −30743(30) | 47876(58) | −11388(58) | 13.4 |
| O(12) | −39508(61) | 55011(31) | 2552(73) | 14.1 |
| N(1) | −7223(20) | 49843(22) | 10488(36) | 2.6 |
| N(2) | 432(21) | 42385(21) | −11980(33) | 2.8 |
| N(3) | 9921(19) | 49668(19) | 8737(39) | 2.4 |
| N(4) | −7991(22) | 33444(23) | 8706(43) | 3.3 |
| N(5) | 8937(22) | 32430(21) | 4727(38) | 3.0 |
| N(6) | 2876(21) | 40335(21) | 28253(35) | 2.8 |
| N(7) | 1529(30) | 25629(22) | 23300(43) | 4.2 |
| C(1) | 536(43) | 65863(30) | −15232(59) | 5.4 |
| C(2) | 840(29) | 57587(24) | −7283(46) | 3.2 |
| C(3) | −5944(29) | 57804(30) | 3118(54) | 3.8 |
| C(4) | −401(31) | 50856(29) | −17748(46) | 3.6 |
| C(5) | 9047(29) | 56914(27) | −604(51) | 3.3 |
| C(6) | −15381(27) | 46210(31) | 7451(55) | 3.9 |
| C(7) | 7487(30) | 37844(32) | −18304(49) | 3.6 |
| C(8) | 11236(27) | 51965(27) | 23386(46) | 2.9 |
| C(9) | −15359(31) | 37841(37) | 13953(59) | 4.6 |
| C(10) | 8369(32) | 30108(30) | −10018(56) | 3.9 |
| C(11) | 10681(28) | 44332(29) | 31596(46) | 3.0 |
| C(12) | −6354(38) | 25659(32) | 16331(63) | 4.9 |
| C(13) | 8398(39) | 25209(31) | 14481(57) | 4.6 |
| C(14) | 2247(33) | 31792(28) | 33999(51) | 3.8 |
| Ow | 36636(28) | 16635(27) | 23265(50) | 7.1 |

tion band ($\Delta\varepsilon_{463}=+3.10$) has been determined to be $\Delta$ (see Table 1). This assignment is consistent with the deduction[16)] made from the comparison of circular dichroism spectra of related complexes such as [Co(en)$_3$]$^{3+}$, [Co(sen)]$^{3+}$, and [Co(sep)]$^{3+}$.

Table 3. Bond Distances ($l$/Å) and Angles ($\phi$/°) with E.S.D.'s

| | | | |
|---|---|---|---|
| Co–N1 | 1.965(4) | Co–N2 | 1.967(3) |
| Co–N3 | 1.976(3) | Co–N4 | 1.987(4) |
| Co–N5 | 1.970(4) | Co–N6 | 1.995(4) |
| C1–C2 | 1.562(7) | C2–C3 | 1.505(7) |
| C2–C4 | 1.518(7) | C2–C5 | 1.497(7) |
| C6–C9 | 1.510(8) | C7–C10 | 1.510(8) |
| C8–C11 | 1.491(7) | N1–C3 | 1.505(7) |
| N1–C6 | 1.494(6) | N2–C4 | 1.505(6) |
| N2–C7 | 1.507(6) | N3–C5 | 1.504(6) |
| N3–C8 | 1.493(6) | N4–C9 | 1.496(7) |
| N4–C12 | 1.502(7) | N5–C10 | 1.490(7) |
| N5–C13 | 1.522(7) | N6–C11 | 1.473(6) |
| N6–C14 | 1.510(6) | N7–C12 | 1.463(8) |
| N7–C13 | 1.416(8) | N7–C14 | 1.457(7) |
| | | | |
| N1–Co–N4 | 86.0(2) | N1–Co–N5 | 175.3(2) |
| N2–Co–N5 | 86.3(2) | N2–Co–N6 | 175.4(2) |
| N3–Co–N6 | 85.8(2) | N3–Co–N4 | 175.7(2) |
| C1–C2–C3 | 106.8(4) | C2–C3–N1 | 113.8(4) |
| C1–C2–C4 | 107.1(4) | C2–C4–N2 | 114.0(4) |
| C1–C2–C5 | 107.9(4) | C2–C5–N3 | 114.0(4) |
| C3–N1–C6 | 112.0(4) | N1–C6–C9 | 106.0(4) |
| C4–N2–C7 | 111.8(4) | N2–C7–C10 | 105.5(4) |
| C5–N3–C8 | 113.3(3) | N3–C8–C11 | 107.0(4) |
| C9–N4–C12 | 112.6(4) | C12–N7–C14 | 113.7(4) |
| C10–N5–C13 | 113.7(4) | C13–N7–C14 | 113.9(5) |
| C11–N6–C14 | 112.8(4) | C12–N7–C13 | 114.8(5) |
| Co–N1–C3 | 117.3(3) | Co–N1–C6 | 108.7(3) |
| Co–N2–C4 | 117.0(3) | Co–N2–C7 | 108.7(3) |
| Co–N3–C5 | 117.0(3) | Co–N3–C8 | 108.0(3) |
| Co–N4–C9 | 107.7(3) | Co–N4–C12 | 116.0(3) |
| Co–N5–C10 | 108.1(3) | Co–N5–C13 | 116.0(3) |
| Co–N6–C11 | 107.6(3) | Co–N6–C14 | 112.5(4) |

The coordination geometry around Co(III) appears to be typical for this type of complexes. The Co–N bond length and N–Co–N bond angle averaged over $C_3$ equivalents are 1.977(12) Å and 86.0(3)°. The corresponding values in [Co(sen)]$^{3+}$ are 1.971(6) Å and 86.1(2)°, respectively.[10)] Further, other bond lengths and angles of the "[Co(sen)]$^{3+}$" moiety of [Co(azamesar)]$^{3+}$ are slso very similar to those of [Co(sen)]$^{3+}$. Thus, it may be concluded that the $N(CH_2-)_3$ capping takes place without affecting significantly the geometry of [Co(sen)]$^{3+}$.

The C1–C2 bond length (1.562(7) Å) appears to be somewhat longer than normal. However, this may not be physically significant, because no such trend was observed in our previous structural studies on cobalt(III) complexes with ligands containing the $CH_3C(CH_2-)_3$ capping group, such as Δ-[Co(sen)]Cl·*d*-tart·$6H_2O$,[10] [Co(L)(en)]$(ClO_4)_3$,[4] and [Co(stn)]$Cl_3\cdot 3.5H_2O$,[5] where tart=tartrate ion, L=6-methyl-6-(4-amino-2-azabutyl)-1,4-diazacycloheptane, and stn=1,1,1-tris(5-amino-2-azapentyl)ethane (see Fig. 1).

The C–N bond lengths alternate along the ligand strand from the capping nitrogen N7 to the first carbon atom of the "en" moiety; for example, the C–N bond lengths vary from 1.457(7) Å to 1.510(6) Å to 1.473(6) Å along the chain N7–C14–N6–C11, in this order. Concomitantly with the bond length alternation of this type, C(cap)–N(cap)–C(cap) angles open (the cap flattens) up to an average value of 114.1(6)°. Both of these tendencies are observed in other aza-capped complexes like $[Co(sep)]^{3+}$ and $[Co(azacapten)]^{3+}$ (azacapten=8-methyl-6,10,19-trithia-1,3,13,16-tetraazabicyclo[6.6.6]icosane; see Fig. 1),[16,17] and considered to be responsible for very reduced proton affinity of the capping nitrogens.[8]

The "en" rings of the cation adopt the $(lel)_3$ conformation. This is most clearly seen in Fig. 4. This $(lel)_3$ conformation has also been reported for Δ-[Co(sen)]Cl·*d*-tart·$6H_2O$[10] and Δ-[Co(sep)]$Cl_3\cdot H_2O$.[16] In this conformation, all the N–H hydrogens point approximately to the $C_3$ equatorial direction and therefore are more suitable for double hydrogen bonding proposed previously (between two N–H hydrogens of the cation and oxygen atoms of the associating anion) than in the $(ob)_3$ one. The energy difference between the $(lel)_3$ and $(ob)_3$ conformations in the cage complexes of cobalt(III) is estimated to be rather small.[2] Thus, it is probable that the $(lel)_3$ conformation may be stabilized by such double hydrogen bonding in aqueous solution; multiple hydrogen bonding is known to be capable of stabilizing one conformation selectively over the other.[18]

Deviations from the tetrahedral value are observed in C–C–N, C–N–C, and Co–N–C angles, as well as the previously noted C(cap)–N(cap)–C(cap) angles. The angles averaged over $C_3$ equivalents are, along the ligand strand from C2, C2–C(cap)–N(en)=113.9(1)°, C(cap)–N(en)–C(en)=112.4(8)°, C(en)–N(en)–C(cap)=113.0(6)°, and N(en)–C(cap)–N(cap)=112.8(7)°. The Co–N(en)–C(cap) angles similarly averaged are 115.9(22)° near the $CH_3C(CH_2-)_3$ cap and 116.0(1)° near the $N(CH_2-)_3$ cap. The torsional angles averaged similarly are, along the ligand strand from C1 to C2 to C(cap) and so on, C1–C2–C(cap)–N(en)=173.7(12)°, C2–C(cap)–N(en)–C(en)=116.0(5)°, C(cap)–N(en)–C(en)–C(en)=171.8(8)°, N(en)–C(en)–C(en)–N(en)=53.4(5)°, C(en)–C(en)–N(en)–C(cap)=169.8(5)°, and C(en)–N(en)–C(cap)–N7=117.8(7)°. All these angles do not differ significantly from the corresponding angles of $[Co(sen)]^{2+}$ and $[Co(sep)]^{3+}$, suggesting that the ligand strand does not differ significantly.

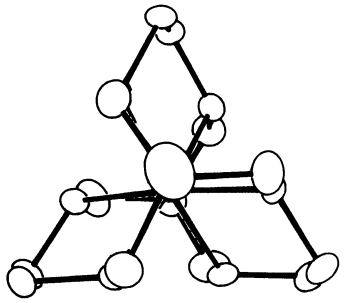

Fig. 4. Projection down the pseudo-threefold axis of rotation of the cation. Ellipsoids enclose 30% probabilities.

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