diffraction studies. No differences between M–CO(trans) and M–CO(cis) distances are found from the present study.

B. (η^5-C_5H_5)Mo(CO)$_3$HgCl Molecule. Interatomic distances and angles are collected in Table IV; the molecule is depicted in Figures 5 and 6. The overall structure agrees with that reported by Oliver, Albright, and Glick,[19] but esd's are reduced to approximately 35% of their previous values, and certain bond lengths and angles are now more in line with the expected values. The following points are worthy of mention.

(1) For correct refinement of the structure, the inclusion of corrections for anomalous dispersion[22] is of great importance. With Mo Kα radiation, the appropriate values (in order of decreasing significance) are $\Delta f'(\mathrm{Hg}) = -3.084$ and $\Delta f''(\mathrm{Hg}) = 9.223$, $\Delta f'(\mathrm{Mo}) = -1.825$ and $\Delta f''(\mathrm{Mo}) = 0.688$, and $\Delta f'(\mathrm{Cl}) = 0.132$ and $\Delta f''(\mathrm{Cl}) = 0.159$ (all values in units of electrons). In the noncentrosymmetric space group $P\bar{4}2_1c$, refinement in the correct hand led to $R_F = 4.2\%$ and $R_{wF} = 3.3\%$, while refinement in the incorrect hand led to convergence with $R_F = 7.5\%$ and $R_{wF} = 9.3\%$.

(2) The revised Mo–Hg and Hg–Cl bond lengths are 2.683 (1) and 2.442 (3) Å (previously reported as 2.673 (3) and 2.437 (8) Å)[19] and the Mo–Hg–Cl angle is 160.02 (9)° (previously 160.0 (2)°). The changes here are not the most significant in the structure (see below).

(3) The Mo–C(ring) distances range from 2.257 (20) to 2.347 (23) Å, averaging 2.303 Å (previously, 2.24–2.47 Å, average = 2.36 Å);[19] the present values are totally consistent with those within the (η^5-C_5H_5)Mo(CO)$_3$Cl molecule, where the average Mo–C(ring) distance is 2.304 Å. Similarly, the Mo–centroid distance in (η^5-C_5H_5)Mo(CO)$_3$HgCl is 1.994 Å as compared with 1.992 Å in the (η^5-C_5H_5)Mo(CO)$_3$Cl molecule.

(4) The Mo(CO)$_3$Hg portion of the molecule has a geometric arrangement similar to the Mo(CO)$_3$Cl portion of the (η^5-C_5H_5)Mo(CO)$_3$Cl molecule. Trans angles are Hg–Mo–C(3) = 128.8 (5)° and C(1)–Mo–C(2) = 112.0 (7)°, whereas cis angles are Hg–Mo–C(1) = 73.1 (5)°, Hg–Mo–C(2) = 73.5 (6)°, C(1)–Mo–C(3) = 78.9 (7)°, and C(2)–Mo–C(3) = 78.8 (8)°.

(5) The Mo–C–O angles and C–O bond lengths are 173.3 (17)–177.7 (15)° and 1.136 (20)–1.155 (22) Å, respectively (previously reported as 165–171° and 1.09–1.13 Å).[19]

(6) As indicated previously,[19] the η^5-cyclopentadienyl ligand is undergoing substantial librational motion about the Mo–centroid axis, resulting in unrealistic C(ring)–C(ring) distances.

(7) There are indications of loose association of molecules about the crystallographic $\bar{4}$ axis. Thus, the mercury atom is formally two-coordinate, but there are interations with chlorine atoms of two other molecules at distances Hg···Cl $(1 - x, 1 - y, z) = 3.079$ (3) Å and Hg···Cl $(y, 1 - x, -z) = 3.078$ (4) Å.

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Registry No. (η^5-C_5H_5)W(CO)$_3$Cl, 12128-24-4; (η^5-C_5H_5)Mo(CO)$_3$Cl, 12128-23-3; (η^5-C_5H_5)Mo(CO)$_3$HgCl, 12079-83-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes for the three structural studies (23 pages). Ordering information is given on any current masthead page.

Contribution from the School of Chemistry,
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Crystal and Molecular Structure of Racemic Tris(ethylenediamine)ruthenium(II) Tetrachlorozincate(II)

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The crystal and molecular structure of racemic $[\mathrm{Ru}(C_2H_8N_2)_3][\mathrm{ZnCl_4}]$ has been determined from X-ray data collected by counter methods. The pale yellow crystals are orthorhombic, of space group $Pna2_1$, with $a = 15.976$ (5) Å, $b = 7.683$ (4) Å, $c = 14.160$ (3) Å, $V = 1738.1$ (8) Å^3, and $Z = 4$. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares methods to a conventional R index (on F) of 0.033. The divalent ruthenium is hexacoordinated in distorted octahedral symmetry. The average N–Ru–N bite angle of the rings is 81.6 (3)°. The average dihedral angle is 55.4 (1)°. The twist angle is 52.9 (7)°. The weighted mean Ru$^{\mathrm{II}}$–N distance of 2.132 (3) Å is within experimental uncertainty identical with the Ru–N of 2.11 (2) Å in the corresponding Ru(III) complex. A Λ cation exhibits a [$\delta\delta$ (74% λ, 26% δ)] configuration. There are no strong hydrogen bonds to the complex cation. The occurrence of the $\delta\delta\lambda$ conformation is ascribed to metal–ligand distances sufficiently long to reduce the ligand–ligand interactions favoring the $\delta\delta\delta$ conformation. The role of hydrogen bonding in the structures of M(en)$_3$ complexes is discussed.

Introduction

The crystal and molecular structure of (±)-$[\mathrm{Ru}(C_2H_8N_2)_3][\mathrm{ZnCl_4}]$ has been determined for two reasons. First, in studies of electron exchange between Ru(en)$_3^{2+}$ and Ru(en)$_3^{3+}$ one needs to know the stereochemical differences between the two oxidation states in order to assess any Franck–Condon barriers to electron transfer. The difference in Ru–N bond lengths between Ru(NH$_3$)$_6^{2+}$ and Ru(NH$_3$)$_6^{3+}$ is only 4 pm,[1] so it is a reasonable inference that a similar small difference exists for the ethylenediamine complexes. However, because of the apparent very large difference in electron-transfer rates between the hexaamine and tris(ethylenediamine) complexes of cobalt(II) and cobalt(III), it seemed prudent to determine directly the structure of Ru(en)$_3^{2+}$, for comparison with the known structure of Ru(en)$_3^{3+}$.[2]

The second reason relates to clarification of earlier work on the conformations of tris(ethylenediamine)metal complexes. Calculations[3] have indicated that, because of longer metal–ligand distances, there are smaller ligand–ligand interactions

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in $Ru(en)_3^{2+}$ than in, e.g., $Co(en)_3^{3+}$. Hence the energy difference between the δ and λ ligand conformations is smaller, with the consequence that the $\delta\delta\delta$ conformation may not be the most stable configuration, as it is in $Co(en)_3^{3+}$. For an investigation of these questions, the structure of $[Ru(en)_3][ZnCl_4]$ has been determined.

Experimental Section

Crystals of the chloride salt of the $Ru(en)_3^{2+}$ cation (prepared as previously reported[4]) were grown from warm 10^{-4} M hydrochloric acid but exhibited complex multiple twinning. The tetrachlorozincate(II) salt prepared by the method of Lever and Bradford[4,5] was therefore investigated. Crystals of $[Ru(en)_3][ZnCl_4]$ grown by slow cooling from warm (45 °C) 10^{-4} M hydrochloric acid solutions were surface dried, attached to a glass fibre by means of an epoxy resin and coated with an aerosol lacquer to avoid oxidative decomposition. After many unsuccessful attempts, a nontwinned crystal suitable for X-ray examination was obtained. The space group was uniquely determined by precession photography as $Pna2_1$ from the systematic absences ($0kl$ absent for $k + l$ odd, $h0l$ absent for h odd). The crystal density was measured as 1.86 (1) g cm^{-3} by flotation in a chloroform/bromoform mixture, the corresponding value calculated for $Z = 4$ being 1.866 g cm^{-3}. The same crystal used in the preliminary work was used for automated intensity data collection. The crystal, bounded by faces $\{001\}$, $\{0\bar{1}0\}$, $\{01\bar{1}\}$, $\{\bar{2}10\}$, and $\{210\}$, was mounted on an Enraf-Nonius four-circle CAD-4/F diffractometer. Intensity data was collected with use of graphite-monochromated Mo Kα radiation [λ(Mo Kα_1) = 0.709 26 Å and λ(Mo Kα_2) = 0.713 54 Å]. The 2θ angle of the monochromator was 12.18° and the crystal-to-detector distance was 173 mm. Unit cell dimensions were obtained by least-squares refinement of 2θ values for 23 automatically centered reflections ($\theta > 19°$). The values obtained were a = 15.976 (5) Å, b = 7.683 (4) Å, c = 14.160 (3) Å, and V = 1738.1 (8) Å^3. Profile analysis of a representative reflection indicated that the conditions for the measurement of integrated intensities would be optimized by a scan purely in ω. The scan speeds were determined by a required precision, $\sigma(I) < 0.005I$, subject to a maximum scan time of 180 s. Each reflection was scanned in 96 steps. The peak count, P, was recorded over the central 64 steps with 16 steps at each end to measure the backgrounds, B_1 and B_2. The intensity, I was calculated as $I = \nu[P - 2(B_1 + B_2)]$ with standard deviation $\sigma(I) = \{\nu[P + 4(B_1 + B_2)]\}^{1/2}$, where ν is a factor to account for differences in scan speeds. Three reference reflections were measured after every 15 000 s of X-ray exposure. The orientation of the crystal was checked after every 200 reflections. No decomposition or movement of the crystal was detected. Intensities were recorded for 3683 (hkl) reflections and 474 equivalent ($h\bar{k}l$) reflections ($\theta < 30°$). The data were corrected for Lorentz and polarization factors. Absorption corrections (μ = 28.6 cm^{-1}) were applied with use of the Gaussian integration method and a 12 × 6 × 10 grid. Transmission coefficients ranged from 0.5514 to 0.7935.

An analysis of the errors was made by dividing the data for which equivalent reflections were collected into 16 ranges of $|F_{av}|$ where $|F_{av}| = \{[F(hkl) + F(h\bar{k}l)]/2\}$ and 16 ranges of $(\sin\theta)/\lambda$. Curves were fitted to plots of mean $[(\Delta F)^2 - \sigma_{STAT}{}^2(F)]$ values vs. both the mean $|F_{av}|$ and mean $(\sin\theta)/\lambda$ values (where $\Delta F = |F(hkl)| - |F(h\bar{k}l)|$ and $\sigma_{STAT}{}^2(F)$ was the statistical variance of the observed structure factor). The quantity $[(\Delta F)^2 - \sigma_{STAT}{}^2(F)]$ showed only an F dependence. The function $V_s(F) = 0.0575|F|$ representing the contributions of systematic errors to the variances[6] was fitted to the above plot. The data sets were combined, and all equivalent reflections averaged. The value of $\sigma^2(F)$ for each reflection was recalculated as the sum of $\sigma_{STAT}{}^2(F)$ and the contribution derived from the above curve.

The structure was solved for the remaining 1991 independent observed reflections with use of the X-RAY 72 program system and a CYBER72 computer. The function minimized was $\sum w(|F_o| - s|F_c|)^2$, where F_o and F_c were the observed and calculated structure amplitudes, the weights, w, were given by $1/\sigma^2(F)$, and s was the inverse of the scale factor to be applied to the $|F_o|$. Atomic scattering factors[7a] were for neutral atoms. The scattering factors for Ru, Zn, and Cl were corrected for anomalous dispersion ($\Delta f'$ and $\Delta f''$).[7b]

Solution and Refinement of Structure

The positions of the ruthenium and zinc atoms were determined from a three-dimensional Patterson function. Successive cycles of Fourier refinement with phases based initially on the two atoms found in the Patterson analysis revealed the location of the remaining 16 nonhydrogen atoms. Full-matrix least-squares refinement with isotropic thermal parameters for all nonhydrogen atoms converged at R = 0.089 and R_w = 0.091 where

$$R = (\sum||F_o| - s|F_c||)/\sum|F_o|$$

and

$$R_w = (\sum w(|F_o| - s|F_c|)^2/\sum w|F_o|^2)^{1/2}$$

Introduction of absorption corrections and anisotropic thermal parameters for all nonhydrogen atoms reduced R and R_w to 0.038 and 0.040, respectively.

Two of the carbons in one of the ethylenediamine rings displayed unusually large anisotropic thermal parameters in a direction approximately perpendicular to the plane of the Ru and coordinated nitrogen atoms. This was taken to indicate a superpositioning of both δ and λ forms of the ethylenediamine ring. A difference Fourier map showed that one of these carbons could be resolved into two positions which were subsequently separately refined. This map also revealed the positions of the 16 hydrogen atoms of the ordered ethylenediamine rings. Each of these hydrogen atoms was assigned a fixed isotropic thermal parameter which corresponded to the last isotropic value of its attached larger atom. Their positions were refined in the final refinement cycles. The other eight hydrogen atoms of the disordered ring were assigned calculated positions and populations and fixed thermal parameters, except for four fractional hydrogens of the minor δ conformer (see Table III). Refinement was terminated when the parameter shifts were less than 0.95σ. The final values for R and R_w were 0.033 and 0.035, respectively. The final nonhydrogen atomic positional and thermal parameters with esd's are listed in Table I while the atomic parameters for the hydrogen atoms are listed in Table II.

A listing of $|F_o|$ and $|F_c|$ values is available (supplementary material).

Even though the crystal contains a racemic mixture of both Λ and Δ cations, the crystal belongs to a polar space group. The hkl and $hk\bar{l}$ data are not equivalent since the $\Delta f''$ do not contribute equally to F_{hkl} and $F_{hk\bar{l}}$. This leads to (anomalous scatterer)–(other atom) distances which are systematically in error due to a phase shift along the polar axis if the data are assigned to the incorrect chirality.[8] For a determination that the x, y, z refinement used represents the correct chirality of the crystal, the structure was refined to convergence for x, y, $-z$ in an identical manner to the x, y, z refinement. The final values of R and R_w of 0.036 and 0.038 are slightly larger, indicating that the x, y, z assignment represents the correct chirality.

Results

The structure determination establishes the presence of $Ru(en)_3^{2+}$, $ZnCl_4^{2-}$, and the absence of water of crystallization. The average ethylenediamine chelate bite distance of 2.784 (9) Å effects a distortion from regular octahedral geometry of RuN_6 by compressing the N–Ru–N angle of each ligand to 81.6 ± 0.3°. This distorted octahedron is actually a trigonal antiprism in which the average twist angle between the trigonal planes defined by N1–N4–N6 and N2–N3–N5 is 52.9 (7)°. The puckering of the chelate ring can be judged by the magnitude of the dihedral angle, ω, between the nitrogen atoms when the ring is viewed down the carbon–carbon bond. The average dihedral angle of 55.4 (1)° indicates a more puckered ring than in $Co(en)_3Cl_3\cdot3H_2O$ (ω = 50.8°).

In the Λ isomer of $Ru(en)_3^{2+}$, two ethylenediamine rings are in the δ conformation, with their C–C bond directions nearly parallel to the threefold axis of the $\Lambda(\delta\delta\delta)$ conformer. The other ethylenediamine ring is disordered. The carbon atom C4 has been resolved into two positions; one for the δ conformation (population 26 (3)%) and one for the λ conformation (population 74 (3)%). The carbon atom C3 could

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Table I. Final Atomic Positional and Thermal Parameters of the Nonhydrogen Atoms for Racemic $[Ru(en)_3][ZnCl_4]$[a, b]

atom	10^4x	10^4y	10^4z	10^3U_{11} or U_{ISO}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Ru	1229.9 (3)	2038.1 (6)	0	27.9 (2)	41.7 (2)	30.7 (2)	0.9 (2)	−1.3 (2)	0.0 (2)
Zn	1291.4 (5)	1243.2 (10)	4044.6 (6)	37.6 (4)	50.3 (4)	42.1 (4)	2.1 (3)	2.0 (4)	−1.2 (4)
Cl(1)	1073.0 (14)	8839 (3)	3148.7 (15)	71 (1)	68 (1)	48.8 (9)	−10 (1)	12.1 (9)	−17.2 (9)
Cl(2)	2335.8 (12)	2779 (3)	3350.6 (14)	51.1 (9)	68 (1)	46.4 (9)	−15.4 (9)	−3.8 (8)	6.8 (8)
Cl(3)	3367.2 (12)	5187 (3)	498.7 (13)	58 (1)	61 (1)	40.7 (8)	3.1 (8)	3.0 (8)	0.2 (8)
Cl(4)	121.3 (14)	2880 (3)	4178 (2)	53 (1)	58 (1)	120 (2)	17 (1)	13 (1)	6 (1)
N(1)	−34 (3)	2912 (8)	167 (5)	37 (3)	51 (3)	58 (4)	1 (3)	−3 (3)	−9 (3)
N(2)	1395 (4)	3511 (10)	1257 (4)	51 (4)	74 (5)	39 (3)	9 (3)	−9 (3)	−115 (3)
N(3)	1496 (4)	4169 (8)	−889 (5)	42 (3)	53 (3)	55 (3)	−5 (3)	−4 (3)	6 (3)
N(4)	1044 (4)	810 (9)	−1344 (4)	39 (3)	64 (4)	39 (3)	3 (3)	−2 (2)	−11 (3)
N(5)	249 (3)	1127 (7)	−8 (5)	37 (2)	51 (3)	53 (3)	8 (2)	−3 (3)	−8 (4)
N(6)	1042 (4)	−263 (8)	799 (4)	53 (4)	54 (3)	42 (3)	3 (3)	7 (3)	6 (3)
C(1)	−122 (5)	3495 (14)	1177 (6)	48 (4)	94 (7)	54 (5)	7 (4)	13 (3)	−13 (5)
C(2)	632 (5)	4527 (13)	1443 (6)	58 (5)	78 (6)	54 (5)	16 (4)	−9 (4)	−31 (4)
C(3)	1298 (10)	3726 (15)	−1860 (7)	167 (13)	69 (5)	46 (4)	−20 (7)	5 (6)	14 (4)
C(4A)	1432 (10)	1375 (20)	−2075 (9)	57 restricted					
C(4B)	1001 (20)	2397 (36)	−2087 (19)	57 restricted					
C(5)	2568 (5)	−136 (11)	779 (6)	55 (4)	62 (5)	52 (4)	18 (4)	−14 (4)	−5 (4)
C(6)	1815 (5)	−1329 (10)	775 (6)	68 (5)	55 (4)	47 (4)	11 (4)	1 (4)	5 (4)

[a] Anisotropic thermal parameters ($Å^2 \times 10^3$) are defined by the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}hlb^*c^*)]$. [b] Isotropic temperature factors are of the form $\exp[-8\pi^2 U((\sin\theta)/\lambda)^2]$. Estimated standard deviations are given in parentheses.

Table II. Final Atomic Positional Parameters for Racemic $[Ru(en)_3][ZnCl_4]$ Hydrogen Atoms

atom[a, b]	population	10^4x	10^4y	10^4z
H1N1	1	−132	3755	−205
H2N1	1	−372	2085	53
H1N2	1	1487	2827	1717
H2N2	1	1808	4197	1191
H1N5	1	2599	632	−531
H2N5	1	2826	1972	75
H1N6	1	936	0	1370
H2N6	1	634	836	570
H1C1	1	−608	4197	1241
H2C1	1	−167	2508	1577
H1C2	1	607	4807	2096
H2C2	1	647	5569	1083
H1C5	1	3066	−799	705
H2C5	1	2585	467	1364
H1C6	1	1834	−2097	1281
H2C6	1	1820	−1986	187
H1N3	0.74	1214	5060	−709
H2N3	0.74	2018	4427	−849
H1N4	0.74	1251	−224	−1334
H2N4	0.74	519	720	−1459
H1C3	0.74	710	3994	−1969
H2C3	0.74	1615	4451	−2279
H1C4	0.74	1226	1548	−2686
H2C4	0.74	2037	1617	−2084
H3N4	0.26	1450	136	−1473
H4N4	0.26	590	235	−1348
H3C4	0.26	979	1875	−2702
H4C4	0.26	580	3095	−1955

[a] The notation H1N1 refers to atom H1 bound to atom N1. In the disordered ring hydrogen atoms labeled 1 or 2 refer to the H atom positions of the major population conformation while those labeled 3 or 4 refer to the minor population conformation. [b] The positions of atoms H3N3, H4N3, H3C3, and H4C3 could not be assigned.

not be resolved but was characterized by a very large anisotropic thermal vibration encompassing what would be the δ and λ positions. Interatomic distances and angles are listed in Table III. Stereoscopic views of the unit cell with $Ru(en)_3^{2+}$ in the predominant $\Lambda(\delta\delta\lambda)$ and $\Delta(\lambda\lambda\delta)$ conformations and of the assymmetric unit with atom numbering are shown in Figures 1 and 2.

Two N–Cl distances indicate weak hydrogen bonding interactions. The N(2)–Cl(2) and N(6)–Cl(1) distances are 3.367 (7) and 3.398 (7) Å with N(2)–H(21)···Cl(2) and N(6)–H(61)···Cl(1) angles of 142 (8) and 145 (8)°, respectively. These can be compared, for example, with the strong hydrogen bonds reported in $[(+)_D\text{-}Co(en)_3]Cl_3 \cdot H_2O$,[9] namely, N–Cl distances of 3.120 (7) and 3.250 (6) Å with angles of 160 and 165°.

Table III. Bond Lengths (Å) and Angles (Deg) for Racemic $[Ru(en)_3][ZnCl_4]$[a]

		Coordination Sphere			
Ru–N(1)	2.143 (6)	Ru–N(4)	2.145 (6)		
Ru–N(2)	2.137 (7)	Ru–N(5)	2.134 (5)		
Ru–N(3)	2.110 (7)	Ru–N(6)	2.119 (7)		
N(1)–Ru–N(2)	81.8 (3)	N(3)–Ru–N(4)	80.9 (3)	N(5)–Ru–N(6)	82.1 (3)
N(1)–Ru–N(3)	90.7 (3)	N(1)–Ru–N(4)	96.1 (3)	N(4)–Ru–N(6)	94.9 (3)
N(1)–Ru–N(6)	94.1 (3)	N(2)–Ru–N(3)	93.6 (3)	N(2)–Ru–N(6)	90.7 (3)
		Chelate Rings			
N(1)–C(1)	1.507 (12)	N(5)–C(5)	1.477 (12)		
N(2)–C(2)	1.472 (12)	N(6)–C(6)	1.482 (12)		
N(3)–C(3)	1.455 (13)	C(1)–C(2)	1.497 (13)		
N(4)–C(4A)	1.465 (14)	C(5)–C(6)	1.520 (13)		
N(4)–C(4B)	1.60 (4)	C(3)–C(4A)	1.496 (17)		
		Tetrachlorozincate			
Zn–Cl(1)	2.268 (3)	Zn–Cl(3)	2.279 (2)		
Zn–Cl(2)	2.267 (2)	Zn–Cl(4)	2.260 (3)		
Cl(1)–Zn–Cl(2)	107.2 (1)	Cl(2)–Zn–Cl(3)	113.6 (1)		
Cl(1)–Zn–Cl(3)	104.7 (1)	Cl(2)–Zn–Cl(4)	110.8 (1)		
Cl(1)–Zn–Cl(4)	111.9 (1)	Cl(3)–Zn–Cl(4)	108.6 (1)		

[a] The figures in parentheses are the esd's in the least significant figure shown.

Discussion

The Ru^{II}–N distance of 2.132 (3) Å found in $Ru(en)_3^{2+}$ is within experimental uncertainty identical with that of 2.11 (2) Å reported[2] for $Ru(en)_3^{3+}$. Hence there is no significant inner-sphere reorganizational energy barrier to electron transfer between these two oxidation states. The Ru^{II}–N distance is within two standard deviations of that of 2.144 (4) found[1] in $Ru(NH_3)_6^{2+}$, indicating that there is no important bond length difference between ammonia and ethylenediamine ligands σ bonded to Ru(II).

The Ru^{II}–N distance of 2.056 (6) Å recently reported[10] for $Ru(bpy)_3^{2+}$ is ~0.08 Å shorter than in $Ru(en)_3^{2+}$.

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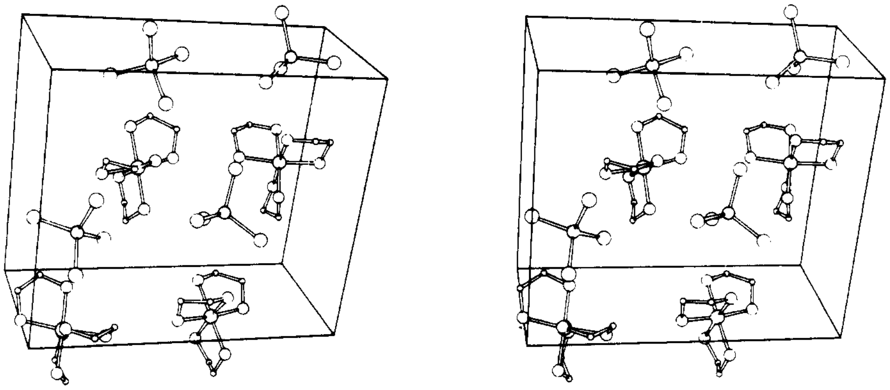

Figure 1. Stereoscopic view of the unit cell with the *a* axis horizontal and *c* axis vertical illustrating the predominant Λ(δδλ) configuration.

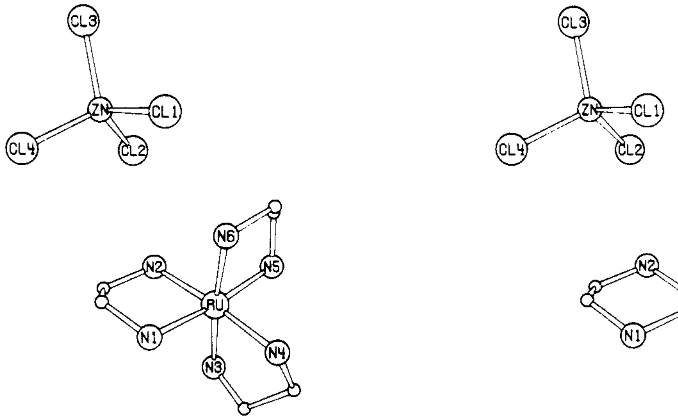

Figure 2. Stereoscopic view of the asymmetric unit illustrating the predominant Λ(δδλ) configuration and the atom numbering scheme.

For Ni(II), the distance of 2.13 (1) in Ni(en)$_3^{2+}$ [11-15] is only 0.03 Å longer than that of 2.10 (1) in Ni(bpy)$_3^{2+}$.[16,17] This is consistent with the idea that Ru(II) is a better π donor than Ni(II), resulting in shorter bonds to π-acceptor ligands.

The occurrence of the Λ(δδλ) configuration in [Ru(en)$_3$][ZnCl$_4$] is consistent with conformational energy calculations[3] which indicate that this configuration is ~0.15 kcal mol^{-1} lower in free energy than the δδδ configuration. These calculations indicate that at M–N distances greater than about 2.07 Å the mixed-ligand configuration is more stable due to its 3:1 statistical entropy advantage, which outweighs the lesser ligand–ligand repulsions of the λ conformation. This mixed δδλ configuration is also observed in [Ni(en)$_3$][B(Ph)$_4$]·3Me$_2$SO[11] and [Ni(en)$_3$](ClO$_4$)$_2$·H$_2$O,[12] which possess similar M–N bond lengths. In all of these structures the H bonds to the cation are extremely weak.

In other structures with similar bond lengths, however, namely, [Ru(en)$_3$]Cl$_3$·3H$_2$O,[2] [Ni(en)$_3$](CH$_3$CO$_2$)$_2$·2H$_2$O,[13] [Ni(en)$_3$](NO$_3$)$_2$,[14] and [Ni(en)$_3$]SO$_4$,[15] the δδδ configuration is observed, together with *stronger* hydrogen bonding.

A role of hydrogen bonding in determining the relative conformational energies of M(en)$_3$ complexes in the solid state was described by Raymond, Corfield, and Ibers,[18] who suggested that strong hydrogen bonding lowers the energy of the λ conformer. This hypothesis was subsequently elaborated[15,19] to account for the particular geometric requirements of some hydrogen-bond acceptors. Recently, Cramer and Huneke[11] proposed that the separation between the acceptor sites determines the configuration. This proposal is contradicted, however, by comparison of the structures of [Cr(en)$_3$][Co(CN)$_6$]·6H$_2$O[20] and [Co(en)$_3$][Fe(CN)$_6$]·2H$_2$O.[21] In both cases the distances between the acceptor sites on the anions is nearly the same. In the hexahydrate structure the λλλ configuration is found together with extensive, strong hydrogen bonding. In the dihydrate structure, however, the δδδ configuration occurs in connection with weak hydrogen bonds. These hexacyanide structures are thus consistent with the original Raymond, Corfield, and Ibers[18] hypothesis that strong hydrogen bonding can lower the energy of the λ conformers.

Strong hydrogen bonding is also present, however, in structures with the δδδ configuration. These include salts of Ni(en)$_3^{2+}$ with the anions NO$_3^-$,[14] SO$_4^{2-}$,[15] and CH$_3$CO$_2^-$ [13] and also a series of halide salts (±)-[M(en)$_3$]Cl$_3$·3H$_2$O, where M = Cr,[22] Co[22,23] Ru,[2] and Rh.[24] In this isomorphous series each cation is equatorially surrounded by three anions which each form two nearly linear N–H···X hydrogen bonds with amine protons. At the same time these anions participate in weaker interactions along the threefold axes of adjacent complexes. The strength of this hydrogen bond network is indicated by its persistence in a variety of structures. As the metal–nitrogen distance increases from Co through Cr and

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Table IV. Selected Data for the Isomorphous Series of Salts (±)-$[M(en)_3]Cl_3 \cdot 3H_2O$

M	M–N,[a] Å	*a*, Å	*c*, Å	*V*, Å^3	twist angle, deg	ring pucker angle (ω), deg	bite angle, deg	av N–Cl dist,[b] Å	av N–H···Cl bond angles,[b] deg	ref
(±)Co	1.953 (4) 1.958 (4) 1.956 (mean)	11.457 (3)	15.482 (6)	1760	55.5	50.6	85.3 (3)	N1 3.297 N2 3.380	N1Cl 154 N2Cl 141	22, 23
(±)Rh	2.067 (6) 2.056 (7) 2.061 (mean)	11.614 (2)	15.492 (4)	1810 (1)	55.3	55.8	83.6 (2)	N1 3.300 N2 3.390	N1Cl 154 N2Cl 140	24
(±)Cr	2.075 (3) 2.084 (3) 2.079 (mean)	11.591 (4)	15.472 (6)	1800	53.5	54.8	82.5 (3)	N1 3.317 N2 3.378	N1Cl 154 N2Cl 140	22
(±)Ru	2.102 (18) 2.117 (18) 2.110 (mean)	11.668 (6)	15.518 (4)	1830	51.9	58.3 (1.9)	81.6 (7)	N1[c] N2[c]	N1Cl[c] N2Cl[c]	2
(+)Co, (−)Cr		11.524 (3)	15.484 (6)	1781						
(+)Co	2.028 (5) 1.965 (6)				55.2	51.3	84.2 (2)	N1 3.304 N2 2.282		25
(−)Cr	1.958 (8) 2.066 (5)				54.6	52.1	84.7 (3)	N1 3.312 N2 3.378		
(+)Cr, (+)Rh		11.587 (3)	15.522 (6)	1805						
(+)Cr	2.081 (7) 2.076 (7)				53.6		82.9 (3)	N1 3.322 N2 3.390		26
(+)Rh	2.054 (8) 2.072 (7)				54.3		83.4 (3)	N1 3.306 N2 3.393		

[a] The bond lengths given are for the two crystallographically distinct nitrogen atoms. A mean M–N distance for the nonactive racemate structures is given. [b] Interactions considered H bonds by the original authors[22,24] have been used. [c] Not given.

Rh to Ru (Table IV) the unit cell expands predominantly along the *a* axis, remaining nearly constant along the *c* axis, parallel to the threefold axis. The increase in the M–N distance is accompanied by a contraction in the chelate bite angle, with the result that the hydrogen bond lengths to the two crystallographically independent nitrogen atoms remain almost constant. Even more striking is a comparison of the isomorphous active racemate $(+)_D$-$[Co(en)_3]$-$(-)_D$-$[Cr(en)_3]Cl_6 \cdot 6H_2O$[25] with the preceding racemic structures. The volume of the active racemate (1781 Å^3) is intermediate between the structures of the racemic cobalt complex (1760 Å^3) and the racemic chromium complex (1800 Å^3), again the consequence of expansion along the *a* axis with the *c* axis remaining invariant. Remarkably, however, in the active racemate one set of three crystallographically distinct Co–N bonds appears to have lengthened toward the usual Cr–N distance and one set of three Cr–N bonds shortened to the Co–N distance, presumably to maintain the optimum hydrogen bonding in the lattice.

These examples illustrate the fact that hydrogen bonding forces are far stronger than those generated by conformational energy differences in $M(en)_3$ complexes. A final example is that of $[Cd(en)_3]S_2O_3$[27] with a Cd–N bond length of 2.45 Å. Calculations[3] indicate no energy difference between the *δδδ* and λλλ configurations. Hence the *δδ*λ and *δ*λλ configurations are favored on statistical ground by 0.65 kcal mol^{-1}. The observed structure contains the *δδδ* configuration with strong hydrogen bonding along the threefold axis. Hence, while hydrogen bonding is clearly an important determinant of the observed conformations, its presence or absence cannot be used to predict which configurations will be observed. The original Raymond, Corfield, and Ibers[18] hypothesis is limited to rationalizing the occurrence of the higher energy λ conformers which are stabilized by hydrogen bonding.

Finally, it should be emphasised that other factors such as packing arrangements or dispersion forces can affect lattice arrangements and hence conformational stabilities. In the structure of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$[28] the *δ*λλ configuration is not stabilized by strong hydrogen bonding. It may result from the packing of the nonspherical $Cu_2Cl_8^{4-}$ anions along the threefold axis of the cation, resulting in a compression of $Co(en)_3^{3+}$ from its usual *δδδ* configuration to one less extended along the threefold axis.

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Supplementary Material Available: A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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