The Crystal Structure of a Tris(ethylenediamine)–Ruthenium(III) Complex

By H. J. PERESIE and J. A. STANKO*

(*Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania* 16802)

Summary An *X*-ray crystallographic study of the tris(ethylenediamine)–ruthenium(III) complex, $Ru(en)_3^{3+}$, as the racemic chloride salt, shows the ethylenediamine rings to have the "*lel*" conformation with a significant degree of puckering.

THE long missing tris(ethylenediamine) complex of ruthenium(III), $Ru(en)_3^{3+}$, has recently been synthesized as an iodide salt by Meyer and Taube[1] and its electron-transfer reactions have been characterized. Several other interesting studies have since been reported on the tendency of the complex to form ion-pairs, its absorption and circular dichroism spectrum, and its magnetic properties.[2] However no *X*-ray structural work on the complex has appeared. Since detailed structural information should be of aid in the interpretation of previous kinetic, spectral, and magnetic data, and because of the continuing interest in the conformation of the chelate ring in these tris(ethylenediamine) complexes, we have determined the crystal structure of the chloride (and preliminarily the bromide) salt of the $Ru(en)_3^{3+}$ cation. We find the complex to be trigonally distorted with all three ethylenediamine rings in the "*lel*" conformation in the crystal, and exhibiting a high degree of puckering.

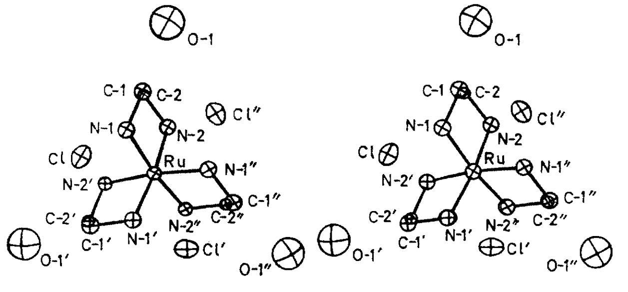

FIGURE. *Stereoscopic drawing of a* $[Ru(en)_3]Cl_3,3H_2O$ *formula unit in the unit cell, as viewed down the crystallographic three-fold axis of the* $Ru(en)_3^{3+}$ *cation. The* Δλλλ *conformer is illustrated.*

The bromide salt of the $Ru(en)_3^{3+}$ cation, $[Ru(NH_2\text{-}CH_2{\cdot}CH_2NH_2)_3]Br_3,xH_2O$, ($x \simeq 3$), was prepared from $[Ru(en)_3]ZnCl_4$[3] by oxidation with tribromide ion, Br_3^-. Crystals of this salt exhibit perfect hexagonal diffraction symmetry (*6/mmm*). However, further studies have shown that they most probably belong to the trigonal system and achieve the higher symmetry through an incoherent twinning mechanism. Hence the chloride salt, $[Ru(NH_2CH_2{\cdot}CH_2NH_2)]Cl_3,xH_2O$, ($x \simeq 4$), prepared from the bromide by ion-exchange, was investigated. This salt crystallizes from aqueous hydrochloric acid solution as almost colourless, pseudohexagonal needles with a somewhat variable hydration number. These crystals exhibited true trigonal diffraction symmetry ($\bar{3}m$), indicating the probable absence of twinning and leading us to examine their structure in detail. *Crystal data*: $a = 11{\cdot}668(6)$, $c = 15{\cdot}518(4)$ Å; $\gamma = 120°$; $D_m = 1{\cdot}77$, $D_c = 1{\cdot}64$ for $Z = 4$ and assuming $3{\cdot}5$ H_2O per formula unit (see below). Extinctions: $h0\bar{h}l$ for l odd, probable space group D_{3d}^4–$P\bar{3}c1$.

Intensity data were collected on a Syntex computer-controlled four-circle diffractometer using nickel-filtered Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). The structure was solved by standard Patterson and Fourier techniques using 507 reflections having $I > 3\,\sigma(I)$, and $2\theta \leqslant 110°$. Least-squares refinement of the structure, employing anisotropic temperature factors for the Ru and Cl atoms and isotropic temperature factors for all other atoms, has now converged to a value for the conventional R factor of 0·095. Absorption and dispersion corrections were applied to the data and scattering curves, respectively, but did not improve the agreement significantly. Hydrogen-atom contribution to the scattering was allowed for in the final refinement. The relatively high value of the R-factor at the present stage may reflect the problem of the true degree of hydration of the crystals. The *X*-ray data are consistent with a set of water molecules in the twelve-fold general positions of the space group, which would correspond to 3 H_2O per Ru atom in the cell. However on the final difference maps there were residual peaks along the c axis at 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ corresponding to occupancy of the 2-fold special positions 2a and 2b, and suggesting a formal hydration of at least 3·5 H_2O per Ru atom. Both chemical analysis and density measurements suggest a slightly greater degree of hydration and we are at present unable to explain the discrepancy. Nevertheless, the main features of the structure have been settled by the *X*-ray analysis.

A stereoscopic view of the formula unit, $[Ru(en)_3]Cl_3,3H_2O$, viewed down the crystallographic threefold axis of the complex is shown in the Figure. The overall structure of the ruthenium salt is very similar to that of the cobalt analogue, $[Co(en)_3]Cl_3,3H_2O$.[4] The cell contains the $Ru(en)_3^{3+}$ complex in both enantiomeric forms. For the Δ-isomer (right-handed chirality) shown in the Figure, each of the three ethylenediamine rings is in the λ conformation, *i.e.*, with its C–C bond direction nearly parallel to the C_3 (threefold) axis of the complex—conventionally the "*lel*" conformation. This is the conformation observed for the cobalt analogue in a structurally similar crystalline solid, and serves to support the view advanced by Raymond, Corfield, and Ibers[5] that the solid-state ring conformation is principally determined by the available hydrogen bonding for the amine hydrogens. There are, however, some significant structural differences between the $Ru(en)_3^{3+}$ complex and the cobalt or other tris(ethylenediamine) metal complexes with regard to the puckering of the chelate ring.

A summary of selected bond distances and angles for the $Ru(en)_3^{3+}$ cation is given in the Table. The ruthenium–nitrogen distances of 2·10(2) and 2·12(2) Å are typical of those reported for Ru^{II} and Ru^{III} ammine complexes,[6] namely $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_4Cl(SO_2)]Cl$, $[Ru(NH_3)_5N_2]Cl_2$, and $[Ru(NH_3)_5(N_2)Ru(NH_3)_5](BF_4)_2,2H_2O$, although no published values for ethylenediamine complexes are available for comparison. The extent of the trigonal distortion of the complex from octahedral coordination can be gauged by the N(1)–Ru–N(2) intra-ring angle of 81·6(7)°, which is among the more contracted reported for similar complexes. The extent of the puckering of the chelate ring can most readily be judged by the magnitudes of the dihedral angles, β, between the nitrogen atoms when the ring is viewed down the carbon–carbon bond, and α, between the planes defined by the metal and ring atoms N(1), Ru, N(2) and C(1), Ru, C(2). In the ruthenium complex the angle β is 58·3 (1·9)°, the largest yet observed in a tris(ethylenediamine) complex. Values for this angle in other metal complexes have ranged between 38 and 57·5°.[5,7] Similarly the value of α in the ruthenium complex is 30·4(1·9)° while for other complexes the magnitude of this angle has ranged between 18·9 and 28·9°. We feel these large values for the ring dihedral angles in the ruthenium complex reflect the influence of a larger second-row transition-metal ion on the puckering of the chelate ring, and indeed among the first-row complexes whose structures have been determined, the ruthenium(III) values are most similar to those of copper(II)[7]—an ion with an anomalously large effective radius for trigonal coordination.

TABLE

Distance (Å)		Angle (degrees)	
Ru–N(1)	2·102 ± 0·018	N(1)–Ru–N(2)	81·63 ± 0·68
Ru–N(2)	2·117 ± 0·018	N(1)–Ru–N(2′)	91·56 ± 0·68
C(1)–N(1)	1·466 ± 0·029	N(1)–Ru–N(2″)	173·19 ± 0·69
C(2)–N(2)	1·520 ± 0·030	N(1)–Ru–N(1′)	93·63 ± 0·65
C(1)–C(2)	1·599 ± 0·030	Ru–N(1)–C(1)	111·45 ± 1·32
N(1)–N(2)	2·758 ± 0·024	Ru–N(2)–C(2)	107·79 ± 1·15
		N(1)–C(1)–C(2)	103·10 ± 1·66
		N(2)–C(2)–C(1)	106·95 ± 1·50

We thank the College of Science of the Pennsylvania State University for the allocation of computer time for this work.

(*Received, October 5th*, 1970; *Com.* 1707.)

---

[1] T. J. Meyer and H. Taube, *Inorg. Chem.*, 1968, **7**, 2369.

[2] H. Elsbernd and J. K. Beattie, *Inorg. Chem.*, 1968, **7**, 2468; 1969, **8**, 893; G. W. Watt and C. V. Senoff, *Canad. J. Chem.*, 1969, **47**, 359.

[3] F. M. Lever and R. Bradford, *Platinum Metal Rev.*, 1964, 106.

[4] K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1956, **29**, 428.

[5] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 843; and references therein.

[6] C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 1962, 137; L. H. Vogt, J. L. Katz, and S. E. Wiberly, *Inorg. Chem.*, 1965, **4**, 1157; F. Bottomley and S. C. Nyburg, *Acta Cryst.*, 1968, **B24**, 1289; I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, *J. Amer. Chem. Soc.*, 1969, **91**, 6512.

[7] D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, 1970, **9**, 1858.