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Reconciling the Crystal Structure of [Ru(NH₃)₆]Cl₃ with its ESR Properties

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Abstract

Hexaammineruthenium(III) trichloride forms a $Z = 12$ monoclinic crystal, which is related to a simple cubic f.c.c. structure by, dominantly, a rotation of a third of the hexaammineruthenium(III) fragments. The cell contains four crystallographically inequivalent $Ru(NH_3)_6$ fragments, but two are almost identical in conformation and orientation in the crystal. In the ESR spectrum only three resolvable crystallographically different ions are thus predicted, not four. This is what is observed.

Comment

We are engaged in a study of the relation between structure and ESR properties in a series of hexaammineruthenium(III) salts containing a single crystallographically unique Ru site (Blake *et al.*, 1993; Engelhardt, Reynolds & Sobolev, 1994; Figgis, Kucharski, Reynolds & Sobolev, 1993; Reynolds *et al.*, 1992).

A detailed crystal structure is required to eliminate a possible anomaly in the case of $[Ru(NH_3)_6]Cl_3$. Four independent Ru sites are inferred from the observed unit cell of $[Ru(NH_3)_6]Cl_3$ (Trehoux, Thomas, Nowogrocki & Tridot, 1971), and four sites are inferred by NMR and X-ray diffraction in the possibly isomorphous Co^{III} salt (Kruger & Reynhardt, 1978; Reynhardt, 1977). However, Griffiths, Owen & Ward (1953) observed only three crystallographically distinct Ru sites by use of single-crystal ESR.

Stable crystals were grown by recrystallization from a solution of hexaammineruthenium(III) trichloride in dilute hydrochloric acid. However, the first growth of crystals from approximately neutral solution proved to be unstable. Unless contained, for example, in a Lindemann tube, the crystals decomposed to a white powder, possibly by reaction with atmospheric moisture. We determined the crystal structure of both forms, which proved to be identical within experimental error. We report only the results from the stable form.
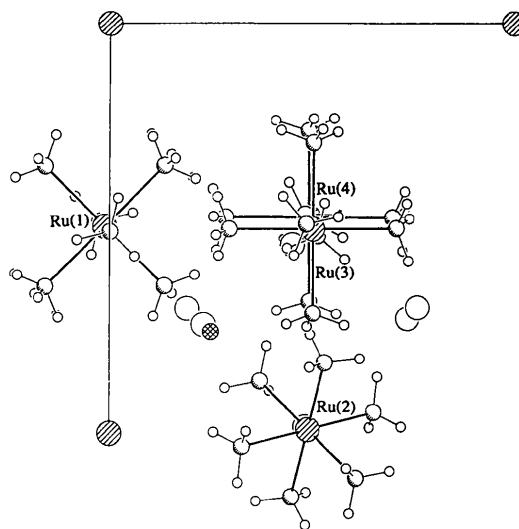

Fig. 1. The four crystallographically independent $Ru(NH_3)_6$ fragments and unique Cl and O1*w* (void site), projected down the underlying cube axis (−1/2, 0, 1/2). Underlying cube axis (−1/2, 1/3, −1/2) horizontal.

We find four independent fully occupied Ru sites: 1/6 of the total ruthenium on Ru(1), 1/6 on Ru(2), and 1/3 each on Ru(3) and Ru(4). The key to obtaining an apparently three-resonance ESR spectrum is to note that in the observed crystal structures the $Ru(3)(NH_3)_6$ and $Ru(4)(NH_3)_6$ fragments are almost superimposable with no rotation (Fig. 2). The r.m.s. deviations in N-atom positions between the two ions are 0.03 Å, and for H-atom positions 0.19 Å. This close coincidence is liable to render the ESR signals from these two ions unresolvable. Thus, although there are four independent Ru sites in the cell, we will only see three ESR signals, just as is observed.

There is an underlying cubic structure in this crystal, and in the isomorphous Co^{III} material, which is closely related to the $Fm\overline{3}m$ structure actually observed in a number of $M^{III}(NH_3)_6X_3$ crystals, *e.g.* $Co(NH_3)_6I_3$ (Wyckoff, 1981). There is an f.c.c. cubic Ru lattice of edge *ca* 10.3 Å. Approximately f.c.c. unit-cell axes are [−1/2, 0, 1/2], [1/2, 1/3, 1/2], [−1/2, 1/3, −1/2] vectors of the monoclinic cell. The Ru—N vectors
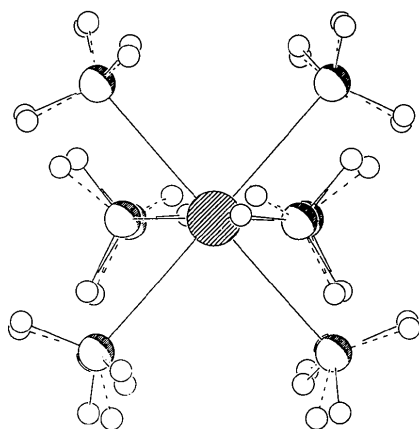
Fig. 2. The superposition, by translation, of Ru(3)(NH₃)₆ and Ru(4)(NH₃)₆: projection down **a**; **c** horizontal. N—H bonds of the Ru(4) fragment are shown dashed.

ideally coincide with the f.c.c. cube axes; Cl(3) and Cl(6) occupy the octahedral holes at (1/2, 0, 0) (f.c.c.) and the remaining atoms Cl(1), Cl(2), Cl(4) and Cl(5) occupy the tetrahedral holes at (1/4, 1/4, 1/4) in the f.c.c. lattice. This ideally gives six RuCl distances of $10.3/2 = 5.15$ Å along the f.c.c. cube axes, and eight of $10.3\sqrt{3}/4 = 4.46$ Å along the cube diagonals. This arrangement of Ru and Cl atoms is clearly visible in the observed monoclinic structure, e.g. for Ru(3) and Ru(4) we see two sets of six f.c.c. cube-axis Ru···Cl contacts of 5.17–5.54 Å, and two sets of eight diagonals of 4.29–4.46 Å. The Cl-atom environments of Ru(1) and Ru(2) are more distorted, but still clearly recognizable as 6 + 8 distorted rhombic dodecahedral environments, with two sets of six cube axes of 4.10–6.63 Å and two sets of eight diagonals of 4.38–5.36 Å. This extra distortion around Ru(1) and Ru(2) reflects the fact that the vectors of Ru(3) and Ru(4) to N atoms remain almost parallel to the cube axes (Fig. 1), while those involving Ru(1) and Ru(2) are rotated by ca 45°. Thus, the major deviations from an ideal f.c.c. lattice are a rotation of one third of the Ru(NH₃)₆ units in the cell by ca 45°, and ordering of all the H-atom positions [except those attached to N(13)], which are disordered in an ideal $Fm\bar{3}m$ lattice. A consequence of these distortions is the opening of a void at (0, 0, 1/2). The nearest other atoms are four neighbours at 2.02 Å [H(311)] and two neighbours at 2.43 Å [Cl(1)]. In the stable form we also refined an O-atom population here of 0.00 (3), eliminating the possibility of the crystal being a hydrate.

Experimental

Crystal data

[Ru(NH₃)₆]Cl₃
$M_r = 309.6$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$C2/m$
$a = 12.705$ (4) Å
$b = 21.680$ (6) Å
$c = 13.013$ (4) Å
$\beta = 113.10$ (2)°
$V = 3297$ (2) Å³
$Z = 12$
$D_x = 1.87$ Mg m⁻³
$D_m = 1.85$ (1) Mg m⁻³
D_m measured by flotation

Cell parameters from 12 reflections
$\theta = 16–19°$
$\mu = 2.096$ mm⁻¹
$T = 293$ (2) K
Block
0.35 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.48$, $T_{max} = 0.59$
3154 measured reflections
3154 independent reflections
2658 observed reflections
$[I > 2\sigma(I)]$

$\theta_{max} = 25.05°$
$h = -15 \rightarrow 13$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 100 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0271$
$wR(F^2) = 0.0695$
$S = 1.179$
2658 reflections
152 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0297)^2 + 7.1533P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.460$ e Å⁻³
$\Delta\rho_{min} = -0.417$ e Å⁻³
Extinction correction: secondary, $F_c^* = kF_c(1 + 0.001\chi F_c^2\lambda^3/\sin 2\theta)^{1/4}$
Extinction coefficient: $\chi = 0.00038$ (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru(1)	0	0	0	0.0217 (1)
Ru(2)	1/2	0	1/2	0.0208 (1)
Ru(3)	0	0.16567 (1)	1/2	0.0216 (1)
Ru(4)	1/2	0.17170 (2)	0	0.0230 (1)
Cl(1)	0.0993 (1)	0	0.3745 (1)	0.0400 (3)
Cl(2)	0.3625 (1)	0	0.0541 (1)	0.0434 (3)
Cl(3)	0.6918 (1)	0	0.3094 (1)	0.0377 (3)
Cl(4)	0.62819 (8)	0.18792 (5)	0.35736 (8)	0.0460 (2)
Cl(5)	0.86846 (9)	0.17109 (5)	0.13694 (9)	0.0530 (3)
Cl(6)	0.25903 (8)	0.13608 (5)	0.24876 (7)	0.0473 (2)
N(11)	-0.0888 (4)	0	0.1064 (4)	0.050 (1)
N(12)	0.1537 (3)	0	0.1407 (3)	0.052 (1)
N(13)	0	0.0964 (2)	0	0.075 (2)
N(21)	0.4410 (3)	0	0.3256 (3)	0.045 (1)
N(22)	0.3790 (3)	0.0670 (1)	0.4939 (3)	0.045 (1)
N(31)	0.0959 (3)	0.0975 (2)	0.6103 (3)	0.057 (1)
N(32)	0.0973 (3)	0.2346 (2)	0.6091 (3)	0.053 (1)
N(33)	0.1152 (3)	0.1641 (1)	0.4206 (3)	0.046 (1)
N(41)	0.5990 (4)	0.1044 (2)	0.1095 (3)	0.065 (1)
N(42)	0.3922 (3)	0.1711 (2)	0.0861 (4)	0.079 (1)
N(43)	0.6002 (3)	0.2395 (2)	0.1089 (3)	0.061 (1)

Table 2. *Selected geometric parameters* (Å, °)

Ru(1)—N(11)	2.102 (4)	Ru(3)—N(32)	2.097 (3)
Ru(1)—N(12)	2.088 (4)	Ru(3)—N(33)	2.097 (3)
Ru(1)—N(13)	2.089 (5)	Ru(4)—N(41)	2.082 (3)
Ru(2)—N(21)	2.092 (4)	Ru(4)—N(42)	2.081 (4)
Ru(2)—N(22)	2.093 (3)	Ru(4)—N(43)	2.092 (3)
Ru(3)—N(31)	2.087 (3)		
N(11)—Ru(1)—N(12)	88.9 (2)	N(32)—Ru(3)—N(33^{ii})	91.0 (1)
N(21)—Ru(2)—N(22)	90.8 (1)	N(41)—Ru(4)—N(42)	88.6 (2)
N(22)—Ru(2)—N(22^i)	87.8 (2)	N(41)—Ru(4)—N(43)	89.2 (2)
N(31)—Ru(3)—N(32)	90.5 (2)	N(42)—Ru(4)—N(43)	89.7 (2)
N(31)—Ru(3)—N(33)	89.7 (1)	N(41)—Ru(4)—N(41^{iii})	91.0 (2)
N(32)—Ru(3)—N(33)	90.3 (1)	N(42)—Ru(4)—N(41^{iii})	90.9 (2)
N(31)—Ru(3)—N(31^{ii})	89.9 (2)	N(42)—Ru(4)—N(42^{iii})	179.3 (3)
N(33)—Ru(3)—N(31^{ii})	89.0 (1)	N(43)—Ru(4)—N(41^{iii})	179.4 (2)
N(33)—Ru(3)—N(33^{ii})	178.1 (2)	N(43)—Ru(4)—N(42^{iii})	90.8 (2)
N(32)—Ru(3)—N(31^{ii})	179.2 (1)		

Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, 1 - z$; (iii) $1 - x, y, -z$.

Data collection, reduction and cell refinement programs: *SHELXS*86 (Robinson & Sheldrick, 1988) was used by direct methods for crystal structure solution and *SHELXL*93 (Sheldrick, 1993) for structure refinement. Molecular graphics: *SHELXTL* (Sheldrick, 1991).

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Nickel Ultraphosphate, NiP4O11

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Abstract

The structure of NiP4O11 is built of layers of cations and layers of corner-sharing PO4 tetrahedra. These crystals display a new connectivity scheme. Layers of rings containing 6 or 14 PO4 tetrahedra were observed.
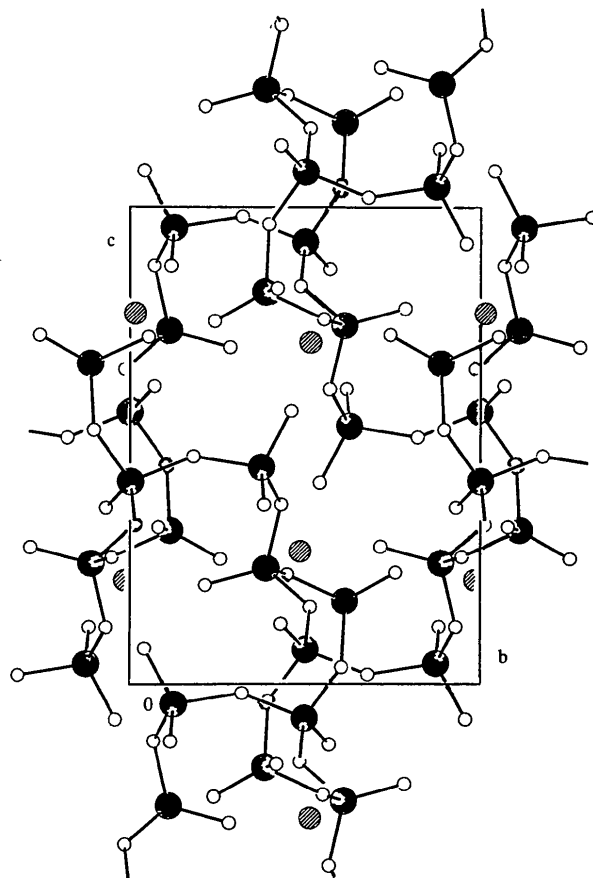

Fig. 1. *PLUTON*93 (Spek, 1993) view along the [100] direction. All atoms are drawn as circles of arbitrary radii: Ni hatched, P filled and O open.