Structure and Magnetism of Cubic Low-spin $4d^5$ $[Ru^{III}(NH_3)_6]Br[SO_4]$ †

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The structure of $[Ru(NH_3)_6]Br[SO_4]$ is reported at *ca*. 295 K. The space group is cubic $Fm\bar{3}m$ with the ruthenium atom lying at a site of O_h symmetry. There is considerable disorder, particularly involving the sulfate ion, and this implies substantial rotational–translational coupling. The Ru–N bond length is 210.7(7) and the N–H length 100(3) pm. The magnetic susceptibility is reported from 4.5 to 300 K. The ESR spectrum between 105 and 300 K showed a *g* value of 1.926(5). A simple molecular-orbital model involving the π-covalence parameter $k_{\pi,\pi}$, spin-orbit coupling for the ruthenium(III) atom and small magnetic exchange completely accounted for the susceptibility and ESR spectroscopic experiments. However, the reduction of $k_{\pi,\pi}$ from unity to 0.94 should be attributed to sources other than π covalence, given further theoretical and experimental evidence.

Understanding the ground-state electronic properties of transition-metal complexes in crystals requires a knowledge of, *inter alia*, the degree of covalence in the metal–ligand bonding and the effect of the rest of the crystal on the complex ion. Neither of these facets is as well understood in the second and third transition series as in the first, partly because relativistic effects become important, and partly because of the higher covalence and polarisabilities. There are few reliable calculations and few detailed experiments available. In the first transition series the electronic properties have been probed principally by spectroscopy of various types and by magnetic measurements, including susceptibilities, ESR spectroscopy, and more recently polarised neutron diffraction (PND). Because the greater covalence usually leads to low-energy charge-transfer bands in the spectra, spectroscopy is less useful for the second and third series, and magnetic properties remain as the main source of information. It is our intention to extend PND measurements into those series, but that requires as a preliminary sound classical magnetic information.

The two first mentioned features pose different requirements on the nature of the system to be studied. To examine covalence in transition-metal complexes one ideally should select systems with simple, orbitally non-degenerate ground states, since those are resistant to change arising from small alterations in the molecular geometry of the complex ion. The $^4A_{2g}$ state of octahedral Cr^{III} in the $[Cr(CN)_6]^{3-}$ ion[1] is a good example. Conversely, in examining crystal-environment effects one needs systems which are very sensitive to small changes in the molecular geometry. Examples of such sensitivity arise from orbitally degenerate ground terms. In the first transition series the $^2T_{2g}$ ground state of Fe^{III} in low-spin d^5 $[Fe(CN)_6]^{3-}$ [2] and the $^5T_{2g}$ ground state of Fe^{II} in high-spin d^6 $[Fe(OD_2)_6]^{2+}$ [3] show the required effects. Their ESR *g* values, magnetic susceptibilities and PND magnetisation densities are observed to be highly anisotropic due to small deviations from strictly octahedral stereochemistry. However, there is a promising area for study in the heavy transition metals based upon low-spin d^5 Ru^{III}, with the $^2T_{2g}$ ground term, for which the ESR spectra of several different complexes have been examined.[4] The *g* values observed vary dramatically, and a global explanation of this is available in terms of empirical crystal-field parameters,[5] although as yet we are not able to understand the low-symmetry effects, nor even begin to predict them qualitatively on the basis of the crystal structure.

In order to explore the area further it will be valuable to examine the same complex ion in different crystals. We have selected the hexaammineruthenium(III) ion since it is chemically very robust and many simple salts of it are known. There is also known to be the possibility of growing the large single crystals necessary for the PND experiment. Previous structural and magnetic susceptibility work on $[Ru(NH_3)_6]^{3+}$ salts is sparse.[6] The complex $[Ru(NH_3)_6][BF_4]_3$ has been shown to give rise to a cubic structure, with highly disordered BF_4^- ions.[7] The unit cell of $[Ru(NH_3)_6]Cl_3$ is known to be monoclinic with three independent ruthenium sites.[8] ESR spectra of this crystal confirm these features.[9] Bulk magnetic susceptibility measurements are available for the chloride and hydrated nitrate salts.[10,11]

In this paper we present structural, magnetic susceptibility and ESR data on the salt $[Ru(NH_3)_6]Br[SO_4]$. The choice of this salt was suggested by the octahedral morphology observed by Gleu *et al.*[12] in their preparative study of a number of ruthenium(III) hexaammine salts. We found a cubic structure and the ruthenium atom occupying a site of O_h symmetry. We show that a simple covalent model explains the magnetic data, and thus that we are justified in further experimentation on salts with lower symmetry in which magnetic behaviour may be strongly perturbed by low-symmetry effects.

Experimental

(*a*) *Preparation*.—The salt $[Ru(NH_3)_6]Br[SO_4]$ was crystallised by evaporation from an aqueous solution of $[Ru(NH_3)_6]Cl_3$ to which excess K_2SO_4 and KBr had been added in equal stoichiometric amounts (Found: Br, 21.30; N, 22.20; S, 8.20. Calc.: Br, 21.05; N, 22.15; S, 8.45%). The clear transparent octahedral crystals showed no optical extinction.

(*b*) *Crystal Structure Determination*.—$H_{18}BrN_6O_4RuS$, M = 379.2, cubic, space group $Fm\bar{3}m$, a = 1.0615(3) nm, U = 1.196(1) nm^3, Z = 4, D_c = 2.11 Mg m^{-3}, D_m = 2.13(1) Mg

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† *Supplementary data available* (No. SUP 56884, 3 pp.): magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Atomic fractional coordinates ($\times 10^3$), populations and equivalent isotropic thermal parameters for $[Ru(NH_3)_6]Br[SO_4]$ [$\bar{U} = (U_{11} + U_{22} + U_{33})/3$ pm^2]. Constrained and symmetry-restricted values have no errors noted

Atom	*x*	*y*	*z*	Population	$\bar{U}$
Ru	0	0	0	1.0	258
N	199(1)	0	0	1.0	340
H	248(3)	58(2)	58	1.15(19)	340
H′	248	0	82	−0.40	340
S	258(1)	258	258	−0.095	280
S′	258	258	258	0.22(3)	1500
O	291(1)	291	362(2)	0.1667	1200
Br	258	258	258	0.125	280

Table 2 Bond lengths (pm) and angles (°) in $[Ru(NH_3)_6]Br[SO_4]$

Ru–N	210.7(7)
N–H	100(3)
S–O	143(2), 133(2), 122(2)
Ru–N–H	122(2)

m^{-3}, *F*(000) = 741.5, μ(Mo) = 4.99 mm^{-1}. The specimen studied showed octahedral faces, (111), from 0.024 to 0.039 mm from the centre. A hemisphere of data was measured at *ca.* 295 K using an Enraf–Nonius CAD-4 diffractometer in conventional ω–2θ scan mode. Monochromatic Mo-K$\bar{\alpha}$ radiation was employed (λ = 71.069 pm); $2\theta_{max}$ was 80°, 3874 reflections were measured.

After a Gaussian absorption correction (maximum transmission 0.31, minimum 0.21) the equivalent reflections were averaged to give 232 unique data. The agreement factor between equivalent intensities was $R(I) = 0.055$, which was improved from 0.095 before the absorption correction. For the resultant data $\Sigma\sigma(I)/\Sigma I = 0.02$. There was no pattern to the disagreement of equivalents. Super-cell formation is common amongst hexaammineruthenium(III) salts, but long-exposure Weissenberg photographs showed no trace of it, leading us to conclude the cell is genuinely *F*-centred cubic. Neutral-atom complex scattering factors[13] were employed, and the data processing and refinement used the XTAL program system.[14]

The structure solution was based on packing and symmetry considerations and involved placing the $[Ru(NH_3)_6]^{3+}$ ion at (0,0,0), using the geometry of Stynes and Ibers,[7] and S at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. The remaining atoms were located, and the model improved, by successive full-matrix least-squares refinement on F_{obs} with observed statistical weights for all data, followed by examination of the residual-density map. The Br atom was readily located on the tetrahedral site at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ disordered 1 : 1 with the sulfate group and does not occupy the octahedral site. In order to flatten the difference-density map an extra diffuse sulfur atom at the tetrahedral site, a small shift of (S + Br) along (111) and anisotropic thermal motion for N and O were introduced. Appropriate population, coordinate and thermal-motion constraints were applied. Hydrogen atoms were modelled at (*x*,*y*,*y*) and $(x,0,\sqrt{2}y)$ with the refineable, constrained populations and with their thermal parameter constrained to that of the nitrogen atom. The validity of these various parameters will be discussed later.

A large peak of height *ca.* 7000 e nm^{-3} remained at $(\frac{1}{2},0,0)$ in the difference map. It could be removed by postulating a change in chemical composition, but that is ruled out by the measured density, the unit-cell size, and the chemical analysis. The introduction of stacking faults is an alternative preferred explanation. Disorder of the hexammineruthenium(III) ion over the sites (0,0,0) and $(\frac{1}{2},0,0)$ was refined, and that removed the peak completely. This stacking fault does not disorder the site $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. We obtained a value of 5.2(3)% of the ruthenium complex ion on $(\frac{1}{2},0,0)$. This stacking disorder pertains to the particular crystal studied. We have not carried out the complete structure determinations of crystals from the same and other batches which would be required to establish its generality. Disorder is known to affect extinction. Separate extinction parameters were refined for the (*h*,*k*,*l*)-odd reflections which are affected by this disorder and the (*h*,*k*,*l*)-even reflections which are not. The value of the refined extinction parameter for the (*h*,*k*,*l*)-odd reflections gave only small corrections (< 5%) while the parameter for the (*h*,*k*,*l*)-even case gave a larger maximum reduction in intensity of 26%. This provided a further small improvement in final agreement factors, whose values were $R = 0.037$ and $R' = 0.037$ for the model with 19 parameters. The final residual-electron-density map showed extrema of −600 and +600 e nm^{-3}. Atomic coordinates and isotropic thermal parameters from the final refinement are given in Table 1 and bond lengths and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises anisotropic thermal parameters.

(*c*) *Magnetic Measurements*.—The magnetic susceptibility of a powder specimen of the substance was measured at a magnetic field of 1.0 T from 4.5 to 300 K using a Quantum Design SQUID magnetometer.[15] After correction for the container and the diamagnetism of the compound (-219×10^{-6} cm^3 mol^{-1}) the molar susceptibility was obtained, and values at 62 temperatures are given in the Supplementary material (SUP 56884). Errors were estimated to be 1% of the susceptibility value. The magnetic moments at 300 and 4.5 K are 2.12 and 1.65 respectively, showing the substantial change expected for the $^2T_{2g}$ term in the presence of spin-orbit coupling.[11,16] Since the crystal is cubic the susceptibility is isotropic rendering single-crystal experiments superfluous.

(*d*) *ESR Spectroscopic Measurements*.—A Bruker ER100 spectrometer with a cold-nitrogen-gas flow low-temperature attachment was employed. The undiluted crystals gave a single broad symmetrical absorption, with a *g* value of 1.926(5) which was independent of temperature between 105 and 300 K. A ruthenium-doped (*ca.* 1%) crystal of the isomorphous hexaaminecobalt(III) salt gave a temperature independent *g* value of 1.915(5), indicating that the magnetic exchange present in the pure substance does not in this case affect the *g* value.

Results and Discussion

(*a*) *Structure*.—The structure of the $[Ru(NH_3)_6]Br[SO_4]$ salt is highly disordered. Apart from the 5.2(3)% of stacking faults, we see substantial rotational disorder. In the hexaammineruthenium(III) ion, the RuN_6 unit, on rigid-body analysis of the thermal motion, gives an r.m.s. translational amplitude of 18 pm and an r.m.s. librational amplitude of 6.9°. The Ru–N bond length of 210.7(7) pm agrees with that for the BF_4^- salt [210.4(4) pm],[7] given that in neither case has a correction for the large thermal motion been made. The hydrogen atom density apparently peaks at the (*x*,*y*,*y*) position with a minimum at $(x,0,\sqrt{2}y)$. That is, it is not a free rotor. Since the NH_3 unit has three-fold symmetry, and the symmetry around (*x*,0,0) is four-fold, we expect to find a free rotor if rotation only is involved. To produce four peaks around (*x*,0,0) we must invoke substantial correlated motion of the nitrogen with the hydrogen atoms. This involves nitrogen rotation about the ruthenium centre, since the RuN_6 thermal motions are well fitted by a rigid-body model, indicating that the Ru–N stretch motion is small.

In the vicinity of $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ the (SO_4 + Br) units do not fit a simple model of localised S and Br atoms with tetrahedrally located, harmonically moving, O atoms along $(\frac{1}{4} + x, \frac{1}{4} + x, \frac{1}{4} + x)$. Rather, the oxygen atoms prefer to disorder over the 12 sites $(\frac{1}{4} + x, \frac{1}{4} + x, \frac{1}{4} + z)$, where *x* [0.041(1)] and *z* [0.112(2)] differ substantially. It is not possible to locate simultaneously all four sulfate oxygen atoms on four of these sites; the best that can be done is to place three of them there. This implies that the sulfur atoms must be displaced from ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$) and that there must again be substantial translational–rotational coupling. The distance from the O site to ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$) is only 134(2) pm, substantially shortened from typical sulfate S–O bond lengths of *ca.* 143 pm. The sulfur atom shows a large diffuse component and a smaller sharp negative component in the difference-density map, indicating that it gives a complex distribution resembling a hollow sphere around ($\frac{1}{4},\frac{1}{4},\frac{1}{4}$). Both of these effects are just those expected from strong translational–rotational coupling as outlined above. By contrast, the Br atom is well localised. An alternative model in which the S atom is well localised and the Br atom distribution is allowed to be more complicated gives a poorer fit. Although our model provides a reasonable explanation of the total charge density in the (SO_4 + Br) region we cannot be confident that it is unique, since we require 10 parameters to produce a featureless difference density map in this region.

We summarise the structure as being a relatively well localised array of Ru and Br atoms, the latter occupying 50% of the tetrahedral sites in the face-centred-cubic lattice. Distributed around these are NH_3 and SO_4 units with large rotational disorder, and in which the orientation and centre of mass are highly correlated. The ammonium and sulfate ions are certainly hydrogen bonded, and this must be responsible in part for the correlation between them. However, our experiment does not allow us to comment usefully on this aspect of the structure. Because of the disorder at the O and H sites, O–S–O and H–N–H bond angles are not available to be quoted in Table 2.

(*b*) *Magnetism.*—The magnetic properties of this compound are largely determined by the spin-orbit splitting of the $^2T_{2g}$ ground term of the ruthenium(III) ion. The rigorous time-averaged O_h site symmetry for the ruthenium atom precludes a low-symmetry component in the ligand field relevant for the magnetic susceptibility and ESR spectroscopic experiments, whose time-scale is long. To fit the magnetic-susceptibility data which we report, we use the free-ion theory of Kotani[16] modified for π covalence[17] and for magnetic exchange in the molecular-field approximation.[18]

Consider expression (1) and hence expression (2), which can be modified by exchange, giving expression (3), where ξ is the

$$x = \xi/kT \tag{1}$$

$$\chi_{Ru} = \left(\frac{N\mu_B{}^2}{3kT}\right)[3(k_{\pi,\pi} - 1)^2x + 8(k_{\pi,\pi} + 2)^2 + \{3(2k_{\pi,\pi} + 1)^2x - 8(k_{\pi,\pi} + 2)^2\}\exp(-\tfrac{3}{2}x)/9x[2 + \exp(-\tfrac{3}{2}x)] \tag{2}$$

$$\chi_{Ru}{}^{(corr)} = \chi_{Ru}/[1 - 2zJ\chi_{Ru}/(Ng^2\mu_B{}^2)] \tag{3}$$

spin-orbit coupling for the Ru^{III} ion in the complex, $k_{\pi,\pi}$ is the π-covalence parameter, defined in terms of the mixing parameter λ_π in the normalised wavefunction describing covalence in the $Ru^{III}(NH_3)_6$ complex, z is the number of nearest magnetic neighbours and J the magnetic-exchange constant. Together with expression (4), where L_p is an appropriate set of symmetry-adapted ligand p orbitals, expressions (5)–(7) are implied. This

$$|\Psi_{xz}> = N_\pi(|4d_{xz}> - \lambda_\pi|L_p>) \tag{4}$$

$$k_{\pi,\pi} = 1 - N_\pi{}^2\lambda_\pi{}^2/2 \tag{5}$$

$$\zeta = N_\pi{}^2(\zeta_{4d} - \lambda_\pi{}^2\xi_{lig}/2) \tag{6}$$

$$g = \tfrac{2}{3}(1 + 2k_{\pi,\pi}) \tag{7}$$

theory gives an excellent fit to the magnetic-susceptibility data minimising $(\chi_{obs} - \chi_{cal})^2\sigma(\chi_{obs})^{-2}$ with $R = 0.002$, $R' = 0.005$, goodness of fit 0.07 with $\zeta = -894(10)$ cm^{-1} and $k_{\pi,\pi} = 0.924(8)$, $zJ = 0.16(6)$ cm^{-1} and $\sigma(\chi_{obs}) = 10^{-2}\ \chi_{obs}$. The value of g calculated is 1.922(11), which agrees well with that measured by ESR spectroscopy, 1.926(5).

The use of equation (6) to obtain the free-ion spin-orbit coupling constant then yields $\zeta_{4d} = 940(60)$ cm^{-1}. This compares as well as can be expected with the value 1250 cm^{-1} for the free Ru^{3+} ion obtained from spectroscopy, given the sensitivity of ζ_{4d} to charge, and the expected charge reduction by covalence of the ruthenium centre in the complex.

The magnetic properties and the ESR spectrum of $[Ru(NH_3)_6]Br[SO_4]$ are thus consistent with a rather simple cubic covalent model which formally corresponds to π spin delocalisation of 0.34(9) spins onto the ligand ammonia molecules. However, the conventional picture of bonding in complexes involving ammine ligands holds that the π contribution to the M–N bond is absent because the N atom is sp^3 hydridised, leaving no orbital free for π interactions. Earlier *ab initio* calculations on the $[Co(NH_3)_6]^{3+}$ ion[19–21] and our own local-density-approximation[22] (DV-Xα) calculations on that ion and on the $[Ru(NH_3)_6]^{3+}$ ion confirm that picture: there is no molecular orbital of π symmetry involving more than *ca.* 1% of M–N mixing density. Thus, our model is merely a parameterisation of the magnetic properties of the $[Ru(NH_3)_6]^{3+}$ ion, and the physical interpretation of the quantity $k_{\pi,\pi}$ must lie elsewhere than in π covalence of the Ru–N bond. A simple-minded interpretation of our calculation on the $[Ru(NH_3)_6]^{3+}$ ion is that the reduction of $k_{\pi,\pi}$ from 1.00 occurs because the unpaired electron does not occupy a 'pure' 4d-orbital set on the Ru^{3+} ion, but rather, because of a combination of spin polarisation and σ-covalence effects, has populations of *ca.* + 3% in Ru 5s orbitals and a net − 7% in N and H σ orbitals. In addition, the contribution of $t_{2g}{}^4e_g{}^1$ ionic configurations can affect $k_{\pi,\pi}$ to a significant extent.[17] This area has been discussed in some depth previously[17,23] and we do not repeat it here.

Given this satisfactory outcome we intend to use the parameters derived and the same theory in dealing with the magnetic properties of less symmetric hexaammineruthenium(III) complexes to try to correlate low-symmetry magnetic effects with observed structures. These salts are likely to be good candidates for a PND experiment, but in fact, because of the extensive structural disorder present, this present bromo-sulfate salt will not be useful.

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