Low-temperature Neutron-diffraction Structure of $[Ru(OH_2)_6]^{3+}$ in the Caesium Sulphate Alum Lattice $CsRu[SO_4]_2{\cdot}12H_2O$

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The salt $CsRu[SO_4]_2{\cdot}12H_2O$ has been investigated by single-crystal neutron diffraction at 15 K. The crystals belong to the cubic space group $Pa\bar{3}$, $Z = 4$, with $a = 12.371(6)$ Å. The structure, which conforms to the β alum modification, was refined using 894 inequivalent reflections to give a weighted R factor of 0.026. The stereochemistry of the water co-ordination to Ru^{III} is trigonal planar, with the angle between the metal(III)–water bond and the plane of the co-ordinated water molecule being 0.8(6)°. The angle between the plane of the co-ordinated water molecule and the RuO_6 octahedron is 22.0(6)°, midway between the positions appropriate for T_h and *all-horizontal* D_{3d} symmetry of $[Ru(OH_2)_6]^{3+}$. The anisotropic thermal ellipsoids of the oxygen atom co-ordinated to Ru^{III} are large and of a shape similar to that of its co-ordinated hydrogen atoms. This observation is ascribed to a softening of the potential about the water co-ordinated to Ru^{III}. Single-crystal Raman spectra of $CsRu[SO_4]_2{\cdot}12H_2O$ exhibit features which are assigned to soft modes and which indicate that the potential softens on cooling below *ca.* 90 K. In contrast, neither the low-temperature structure nor the single-crystal Raman spectra of the isomorph $CsFe[SO_4]_2{\cdot}12H_2O$ exhibits features consistent with softening of the potential about the water co-ordinated to M^{III}. Since the sizes of the hexa-aqua cations of Ru^{III} and Fe^{III} are similar it is concluded that the electronic structure of Ru^{III} is implicated in the softening of the potential about its co-ordinated water molecule. The trigonal-field splitting of the $^2T_{2g}(O_h)$ ground term is discussed in terms of the overall stereochemistry of $[Ru(OH_2)_6]^{3+}$.

Despite their unquestionable importance, there are surprisingly few precise structural determinations of transition-metal hexa-aqua cations available in the literature (V^{II},[1] V^{III},[2] Mn^{II},[3] Fe^{II},[4] Fe^{III},[5] and Ni^{II}[6]) because neutron-diffraction techniques must be used in such studies owing to the poor X-ray scattering cross-section of hydrogen. Further, in order to reduce the effects of thermal motion of the hydrogen atoms, significant advantages accrue from the collection of such data at low temperatures. As part of our investigations into the structure and bonding of tervalent cations we report the structure of the ruthenium(III) hexa-aqua cation determined at 15.0(1) K by neutron diffraction. This represents the first precise structure determination of a second-row hexa-aqua cation to be published. In addition, the ruthenium(III) hexa-aqua cation has been the subject of magnetochemical, single-crystal e.p.r.,[7] and theoretical[8] studies in which the positions of the hydrogen atoms have been a key yet unknown parameter. The caesium sulphate alum lattice has been chosen for this low-temperature neutron structure determination for the following reasons: the caesium sulphate alum lattice is well ordered and of high symmetry, the lattice is not prone to phase transitions on cooling to liquid-helium temperatures, and an extraordinarily wide range of tervalent cations will form caesium sulphate alums.[9–12] Further these features of the lattice make it highly suitable for polarised neutron-diffraction studies of aligned paramagnetism directed towards elucidating the covalency of tervalent hexa-aqua cations. In this respect, the large trigonal splitting of the ruthenium(III) $^2T_{2g}(O_h)$ ground term in the caesium sulphate lattice, *ca.* 2 550 cm^{-1},[7] greatly simplifies the analysis of the magnetisation density.

Experimental

The caesium ruthenium sulphate alum, $CsRu[SO_4]_2{\cdot}12H_2O$, was prepared by a modified procedure to that available in the literature.[13] Ruthenium trichloride (1.1 g) was treated with sodium hydroxide (0.75 g) to yield a black precipitate. The precipitate was washed three times with distilled water then immediately dissolved in refluxing sulphuric acid (25 cm^3, 5 mol dm^{-3}). The ruthenium hydrous oxide was oxidised to ruthenium tetraoxide using potassium persulphate, $K_2S_2O_8$ (30 g, 80 °C). **CAUTION**: Ruthenium tetraoxide is toxic and explosive. It is thus necessary to take adequate precautions to protect the skin and eyes and to prevent inhalation of its vapours. All operations involving ruthenium tetraoxide must be done in a well ventilated fume-hood. All glassware and joints must be free of grease. The ruthenium tetraoxide was transferred by using a slow stream of argon to a series of three traps each containing ice-cold tetrafluoroboric acid. On completion the contents of the traps were combined and reduced overnight with lead (14 g) which had been activated for 15 min with nitric acid (30%). The unreacted lead was removed from the solution and the ruthenium(II) allowed to oxidise by exposure to air to yield a yellow solution of ruthenium(III). The lead(II) was removed from the solution by its precipitation with a minimum quantity of sodium sulphate dodecahydrate. The yellow solution was diluted and loaded onto an ion-exchange column [Dowex 50W-X8 (50—100 mesh), H^+ form], washed with dilute sulphuric acid (0.1 mol dm^{-3}), and finally eluted with sulphuric acid (0.5 mol dm^{-3}) to give a yellow solution. Since it is important that the volume of solvent be kept to a minimum, the initial and final 20 cm^3 of the yellow eluate were discarded. The remaining yellow solution was concentrated followed by the addition of an excess of caesium carbonate. On standing at 3 °C yellow crystals of octahedral form were isolated from the solution. These were recrystallised from sulphuric acid (1 mol dm^{-3}). Large single

Table 1. Atomic fractional cell co-ordinates and thermal parameters (Å^2) for $CsRu[SO_4]_2{\cdot}12H_2O$

Atom	x	y	z	B_{iso}
Cs	0.500 00	0.500 00	0.500 00	0.23(2)
Ru	0.000 00	0.000 00	0.000 00	0.25(1)
S	0.326 20(10)	0.326 20	0.326 20	0.21(3)
O(1)	0.257 05(5)	0.257 05	0.257 05	0.46(2)
O(2)	0.278 97(5)	0.333 87(5)	0.435 39(5)	
O(a)	0.053 21(5)	0.208 86(5)	0.343 08(5)	
H(a1)	0.009 07(11)	0.228 85(12)	0.281 18(11)	
H(a2)	0.126 90(11)	0.220 16(12)	0.318 35(12)	
O(b)	0.162 81(5)	−0.000 37(6)	−0.002 05(6)	
H(b1)	0.209 42(10)	−0.061 70(10)	0.022 99(11)	
H(b2)	0.205 23(11)	0.061 88(11)	−0.027 34(11)	

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
O(2)	0.59(2)	0.43(2)	0.32(2)	0.01(2)	0.14(2)	0.10(2)
O(a)	0.55(2)	0.59(2)	0.47(2)	0.00(2)	−0.01(2)	0.00(2)
H(a1)	1.51(5)	2.36(6)	1.27(5)	0.12(4)	−0.40(4)	0.20(4)
H(a2)	1.00(5)	2.36(6)	1.92(5)	−0.03(4)	0.22(4)	−0.14(4)
O(b)	0.26(2)	0.68(2)	1.28(2)	0.45(2)	0.00(2)	0.01(2)
H(b1)	1.12(4)	1.30(5)	1.94(5)	0.30(4)	−0.12(4)	1.24(3)
H(b2)	1.17(2)	1.36(2)	2.02(2)	0.38(2)	0.09(2)	−0.24(2)

crystals (*ca.* 8 mm^3) suitable for study by neutron diffraction were obtained from these solutions.

The salt $CsRu[SO_4]_2{\cdot}12H_2O$ gives crystals which conform to the space group $Pa\bar{3}$, this being retained to helium temperatures. The neutron-diffraction data were collected using the D9 diffractometer on the hot source of the reactor at the Institut Laue Langevin, Grenoble, France. The enhanced flux of higher-energy neutrons allowed us to work at a wavelength of 0.8444(3) Å, which we were subsequently able to show gave little extinction in our crystals. All measurements were made at 15.0(1) K to reduce the effects of thermal vibration.

A crystal (31 mg) of truncated-octahedral form was wrapped in greased aluminium foil before mounting in the two-stage Displex refrigerator of the four-circle diffractometer, which is now equipped with a small position-sensitive helium-3 gas detector having 32 × 32 pixels at 2-mm spacing and a detection efficiency of 75% at 0.8 Å.[14] Its particular virtue for the present study is that it enables more accurate estimates to be made of the intensities of weak peaks than does a conventional detector.

After cooling to 15 K, centring, and determining the crystal orientation matrix, integrated intensity measurement was carried out in two stages. Following a preliminary check that good equivalence could be obtained for groups of five out of six of a number of axial reflections, the integrated intensities of a set of reflections with $(\sin\theta)/\lambda < 0.6$ Å^{-1} in one octant of reciprocal space were measured with a standard reflection being monitored every 50 reflections. These data, totalling 914 reflections, were reduced using the program RETREAT in which the shape of strong reflections is used to improve the estimate of weak peak intensities.[15] A refinement of the structure was then carried out and the resulting parameters used to predict which reflections in the range $0.6 < (\sin\theta)/\lambda < 0.8$ Å^{-1} would have structure factors greater than 1×10^{-12} cm. These were then measured in the same octant as for the low-angle data, to give a total of 2 705 reflections which reduced to 894 independent moduli of structure factors. The merging χ^2 and R on F^2 for equivalent reflections were 2.08 and 0.049 respectively. No reflections were rejected and these moduli were used in a weighted ($1/\sigma^2$) least-squares refinement (Cambridge Crystallographic Subroutine Library, CSSL[16]) to derive the 71 independent variables of the atomic positional and thermal parameters and a scale factor in the Becker–Coppens Lorentzian form of extinction correction.[17] The domain radius was fixed at a large value (100 μm) and the refined value for the mosaic spread of $0.53(3) \times 10^{-4}$ rad^{-1} showed that the extinction was small, amounting to some 30% in intensity for the worst case. Isotropic thermal parameters were used for Cs, Ru, S, and O(1). The final R factor was 0.035 with a χ^2 of 1.64. The weighted R factor (sum of squares of weighted differences/sum of weighted observed structure factors) was 0.026. Table 1 contains the refined values for the crystallographic parameters together with their standard deviations.

Raman spectra were collected using a Spex 14018 double monochromator in conjunction with an Hamamatsu R943-02 photomultiplier tube and single-photon counting. Samples were excited using Coherent Radiation I 70 argon-ion or CR 3000 K krypton-ion lasers and were maintained at low temperature in an Oxford Instruments DM4 cryostat with helium used as an exchange gas.

Results and Discussion

Selected bond lengths and angles for $CsRu[SO_4]_2{\cdot}12H_2O$ are given in Table 2. In general they are in good agreement with those obtained from a room-temperature *X*-ray study,[18] with the main structural difference being the co-ordination sphere about caesium where the Cs–O(a) bond length is 0.034(6) Å shorter in the low-temperature neutron structure. This difference is related to the different unit-cell dimensions at room temperature [12.441(4) Å] and at 15.0(1) K [12.371(6) Å] and suggests that the co-ordination sphere about caesium is determined primarily by the hydrogen bonding of the lattice rather than by caesium–oxygen interactions. Similar reductions of the Cs–O(a) bond length are observed on cooling the caesium iron sulphate and selenate alums from room temperature to 15 K.

The structure of $CsRu[SO_4]_2{\cdot}12H_2O$ is in all respects typical of the β alum modification. The twelve oxygens about the caesium cation define a cuboctahedron with the O(a)–Cs–O(a) angle being 60.0(1)°, the $[Ru(OH_2)_6]^{3+}$ is aligned with the unit-cell axes, and the ratio *r*[Cs–O(2)/*r*Cs–O(a)] is 1.064(1), *i.e.* close to the 1.050(1):1 found for $CsFe[SO_4]_2{\cdot}12H_2O$.[5] The hydrogen-bonding network through the crystal is remarkably similar for the caesium sulphate β alums of ruthenium and iron as evidenced by comparison of the bond lengths and angles in the two salts. Consistent with this the co-ordination sphere

Table 2. Bond lengths (Å) and angles (°) which define the co-ordination environments within $CsRu[SO_4]_2{\cdot}12H_2O$*

(*i*) SO_4^{2-}					
S–O(1)	1.482(2)	[1.477(3)]	O(1)–S–O(2)	109.7(1)	[110.1(2)]
S–O(2)	1.475(2)	[1.470(4)]	O(2)–S–O(2)	109.2(1)	[108.9(2)]
(*ii*) $[Ru(OH_2)_6]^{3+}$					
Ru–O(b)	2.014 3(7)	[2.010(4)]	O(b)–Ru–O(b)	90.85(3)	[90.5(2)]
(*iii*) Cs^+					
Cs–O(2)	3.512 7(6)	[3.521(4)]	Cs–O(a)	3.298 2(6)	[3.332(5)]
O(2)–Cs–O(2′)	40.0(1)	[39.7(1)]	O(2)–Cs–O(a′)	77.3(1)	[76.3(1)]
O(a)–Cs–O(a)	60.0(1)	[60.0(1)]	O(2)–Cs–O(a″)	80.3(1)	[80.3(1)]
O(2)–Cs–O(a)	66.6(1)	[67.5(1)]			
(*iv*) Water molecules					
O(a)–H(a1)	0.972(2)		O(b)–H(b1)	1.002(2)	
O(a)–H(a2)	0.972(2)		O(b)–H(b2)	0.983(2)	
H(a1)–O(a)–H(a2)	104.0(2)		H(b1)–O(b)–H(b2)	112.6(2)	
(*v*) Hydrogen bonds					
H(a1) ··· O(2)	1.800(2)		H(b1) ··· O(a)	1.597(2)	
H(a2) ··· O(1)	1.837(2)		H(b2) ··· O(2)	1.646(2)	
O(a)–H(a1) ··· O(2)	173.9(3)		O(b)–H(b1) ··· O(a)	174.5(3)	
O(a)–H(a2) ··· O(1)	171.1(3)		O(b)–H(b2) ··· O(2)	177.5(3)	

* The values in square brackets were obtained from a room-temperature *X*-ray study of $CsRu[SO_4]_2{\cdot}12H_2O$.[18]

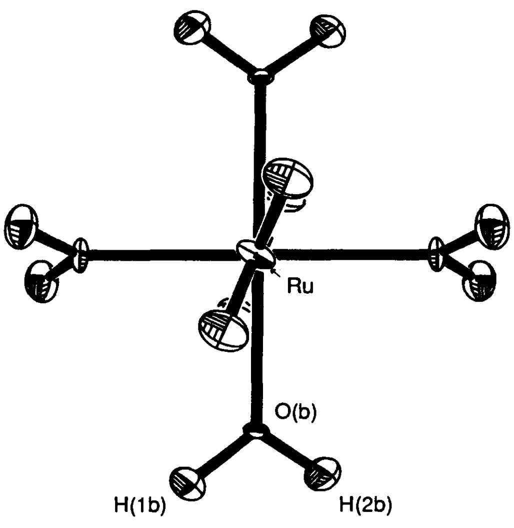

Figure 1. The ruthenium(III) hexa-aqua cation as viewed along the unit-cell axes

about caesium, including hydrogen atoms, is almost identical in the $CsRu[SO_4]_2{\cdot}12H_2O$ and $CsFe[SO_4]_2{\cdot}12H_2O$ alums.

The ruthenium(III) hexa-aqua cation is regular (Figure 1) with a O(b)–Ru–O(b) angle of 90.85(3)°; the water molecules are co-ordinated in a trigonal planar arrangement with the angle between the Ru–O(b) bond vector and the plane of the co-ordinated water molecule being 0.8(6)°. The angle between the RuO_6 framework and the plane of the water molecule is 22.0(6)°, *i.e.* close to that found for the iron(III) hexa-aqua cation in its corresponding alum [19.4(6)°]. It is interesting that the $(t_{2g})^5$ tervalent hexa-aqua ion yields the largest splitting of its $^3T_{1g}$ (O_h) ground term with the water molecules twisted about the metal–oxygen bond by 45° so as to give *all-horizontal* D_{3d} symmetry and thus the slightly larger twist of the water molecule relative to the $M^{III}O_6$ framework for ruthenium may be due to electronic considerations. If this is so, we should expect that a study of the corresponding vanadium and chromium (or molybdenum) alums would show that they have different twist angles: for $(t_{2g})^3$ cations there is no change of the electronic stabilisation energy with twist angle and this should be similar to that for iron, whereas for $(t_{2g})^2$ cations the electronic energy will be minimised by a larger twist angle.

The major difference between the structure of $CsRu[SO_4]_2{\cdot}12H_2O$ and that of $CsFe[SO_4]_2{\cdot}12H_2O$ is the thermal parameters of the water molecule co-ordinated to ruthenium(III) (Table 1). The motion of the water molecule is normal to its molecular plane [Figure 2(*a*)]. This observation may be explained in terms of a small disorder of the atomic positions or a larger thermal amplitude of motion due to a softening of the potential about the water molecule. Although we note that in the room-temperature structure of the toluene-*p*-sulphonate salt, $[Ru(OH_2)_6][C_7H_7SO_3]_3{\cdot}3H_2O$, there is a disorder of two of the three symmetry-inequivalent water molecules co-ordinated to ruthenium(III),[13] we consider that in $CsRu[SO_4]_2{\cdot}12H_2O$ the latter alternative is more probable. It seems unlikely that there could be disorder of a water molecule whose hydrogen-bond partners O(3) and O(2), which are also contained within the plane of the water molecule, do not exhibit unusual thermal parameters [Figure 2(*b*)]. This argument is strengthened by the fact that these hydrogen bonds are the strongest in the structure. It is unclear what is responsible for the softening of the potential, although it is likely to be associated with the metal(III)–ligand interaction since no similar behaviour is seen for the corresponding iron(III) alum despite the two hexa-aqua ions being similar in size [2.014 3(7), Ru; 1.994(1) Å, Fe]. However the behaviour may be related to the softening of certain modes which are observed in the single-crystal Raman spectrum. In particular, on cooling the crystal from 110(5) to 55(5) K a mode at 30 cm^{-1} moves to 21 cm^{-1} (Figure 3), other bands at higher wavenumber also broaden and shift to lower wavenumber. No similar behaviour is observed in the single-crystal Raman

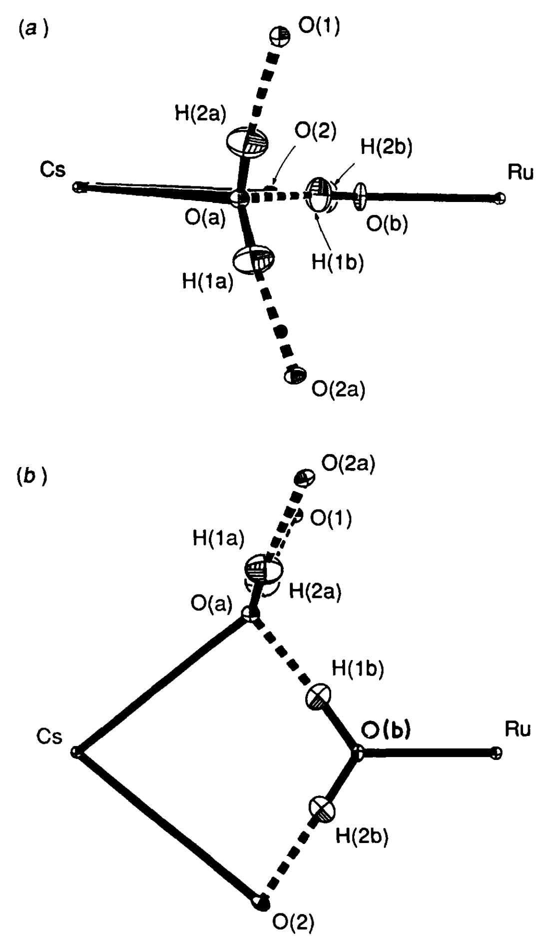

Figure 2. The co-ordination geometry about the two water molecules in the asymmetric unit of $CsRu[SO_4]_2{\cdot}12H_2O$ viewed (*a*) in the plane of the water molecule co-ordinated to ruthenium(III) and (*b*) normal to that plane

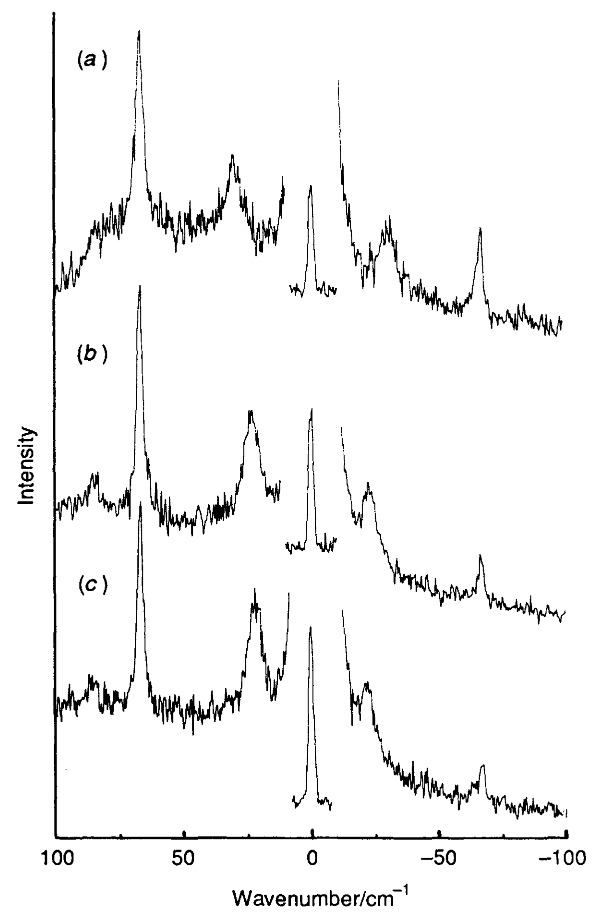

Figure 3. Single-crystal Raman spectra of $CsRu[SO_4]_2{\cdot}12H_2O$; polarisation = $X'[Y'(X' + Y')]Z$, where X', Y', Z are related to X, Y, Z by a rotation about Z by $\pi/4$ rads; 20 mW of 514.5-nm radiation at the sample, spectral bandpass = 1.8 cm^{-1}, integration time = 2 s, temperature = 110 (*a*), 75 (*b*), and 55 (*c*) K

spectra of the corresponding iron alum at temperatures down to 80 K. A more detailed examination of the low-wavenumber Raman spectrum is in progress.

The electronic structure of $[Ru(OH_2)_6]^{3+}$ has attracted considerable attention, including single-crystal e.p.r. and magnetochemical studies.[7] From an analysis of the single-crystal e.p.r. results[8] the trigonal-field splitting of the orbital-triplet ground term has been estimated to be 2 550 cm^{-1}. An Xα calculation of the e_π parameter and application of the angular-overlap model[19] leads to an expression from which the twist of the plane of the water molecule with respect to the RuO_6 octahedron can be evaluated. Unfortunately these authors[8] erroneously used C_3 as the site symmetry of Ru^{III}, and accordingly two twist angles for the co-ordinated water molecules are necessary to define the hexa-aqua ion. Clearly, two twist angles cannot be unambiguously determined from the magnitude of the trigonal-field splitting. Using the correct S_6 symmetry of the cation site there is only one twist angle needed to define the $[Ru(OH)_2)_6]^{3+}$ cation and this can be calculated from the magnitude of the trigonal-field splitting as 15.7°, well below that obtained in this study, 22.0(6)°. This implies either that the estimation of the trigonal splitting is too small or that the value calculated for e_π is too large. In an attempt to resolve this ambiguity we have extended our single-crystal Raman investigation to the high-wavenumber region in order to observe an electronic Raman band due to the transition between the trigonally split components of the ground term. In this preliminary study we were unable to observe any features assignable to such a transition.

Conclusion

The acquisition of high-quality neutron data on $CsRu[SO_4]_2{\cdot}12H_2O$ has enabled us fully to characterise the $[Ru(OH_2)_6]^{3+}$ cation. The cation has site-imposed S_6 symmetry with an approximately O_h RuO_6 framework with trigonal-planar co-ordination of the water molecules. The twist of the water molecules is 22.0(6)° with respect to the RuO_6 framework and is midway between T_h and *all-horizontal* D_{3d} symmetry. This arrangement is imposed on the cation by the hydrogen bonding within the lattice, although the slightly larger twist of the plane of the co-ordinated water molecule found for ruthenium compared to iron is in the direction expected based on the electronic structure of the ruthenium(III) cation. The twist angle is significantly larger (33%) than that calculated from estimates of e_π and the trigonal field splitting. We defer commenting upon the covalency of $[Ru(OH_2)_6]^{3+}$ at this time but note that we plan to collect polarised neutron data from this salt.

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