

also reflected in the larger HIO₃ unit cell. The present results on HIO₃ are in agreement with those found by Garret (1954), but at an apparent higher level of precision. However, e.s.d.'s and significance of small differences between results obtained in this study, using the Rietveld method, and those of Garret (1954), using Fourier refinements, have to be treated cautiously owing to the likely underestimate of the e.s.d.'s by the two methods. In order to further increase the precision in the structure determinations of HIO₃ and DIO₃, single-crystal neutron diffraction studies will be attempted in the near future.

Technical assistance by Mr Håkan Rundlöf, Studsvik, and financial support from the Swedish Natural Science Research Council, is gratefully acknowledged.

Acta Cryst. (1992). C48, 1574–1576

Structure of Pentaamminechlororuthenium(III) Bisulfate Tetrahydrate

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(Received 5 August 1991; accepted 31 January 1992)

Abstract. [RuCl(NH₃)₅](HSO₄)₂·4H₂O, $M_r = 487.88$, triclinic, $P\bar{1}$, $a = 10.0422$ (5), $b = 14.1044$ (7), $c = 6.3273$ (6) Å, $\alpha = 100.369$ (5), $\beta = 98.655$ (6), $\gamma = 81.354$ (4)°, $V = 864.5$ (3) Å³, $Z = 2$, $D_m = 1.86$ (1), $D_x = 1.874$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 13.3$ cm⁻¹, $F(000) = 498$, $T = 296$ (1) K, $R = 0.025$ for 4622 unique reflections with $I > 3\sigma(I)$. The structure contains (NH₃)₅RuCl²⁺ cations, bisulfate anions and solvate water molecules all linked by an extensive hydrogen-bonding network. Each Ru ion is coordinated in a distorted octahedral fashion by five ammonia molecules and a chloride ion. The Ru—Cl distance [2.3742 (5) Å] is typical for Ru^{III}—Cl linkages. The Ru—NH₃ distances span a narrow range [2.096 (2)–2.119 (2) Å] and provide no evidence for a *trans* effect.

Introduction. For some time we have been interested in the ligand to metal charge-transfer spectra of pentaammineruthenium(III)*L* complexes, where *L* = thioether (Krogh-Jespersen, Zhang, Westbrook, Fikar, Nayak, Kwik, Potenza & Schugar, 1989) or imidazole (Krogh-Jespersen, Westbrook, Potenza & Schugar, 1987). Such complexes are prepared by reaction of (NH₃)₅Ru^{II}H₂O with an excess of the appropriate ligand, followed by air oxidation to the

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Ru^{III} state. This intermediate in turn is prepared by the reduction of [(NH₃)₅RuCl]²⁺ with zinc amalgam which is accompanied by rapid aquation of the initial [(NH₃)₅RuCl]⁺ product. In an attempt to prepare the sulfate salt of (NH₃)₅Ru^{II}*L*, where *L* = 2, 4, 6-trihydroxybenzoate, by a variation of a published procedure (Stritar & Taube, 1969), the addition of saturated aqueous (NH₄)₂SO₄ to an acidic solution which contained some unreacted [(NH₃)₅RuCl]²⁺ precipitated this cation as its bisulfate salt. We report here the structure of this cation. A limited ($R_F = 0.169$, visually estimated intensities) early crystallographic study of the chloride analogue [(NH₃)₅RuCl]Cl₂ has been reported (Prout & Powell, 1962).

Experimental. The acidic reaction mixture noted above was layered over a saturated (NH₄)₂SO₄ solution in a test tube. After a week at room temperature, well formed rectangular plates showing a yellow, dark-yellow dichroism deposited. D_m was measured by flotation.

A yellow plate 0.15 × 0.30 × 0.32 mm crystal was mounted in a capillary and data collected using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo *K*α radiation and θ -2 θ scans. No systematic absences were observed. Cell con-

stants were determined from setting angles of 25 reflections with $21.67 < \theta < 27.82^\circ$. Data were corrected for Lorentz, polarization and absorption (empirical correction; ψ scan; transmission coefficient range 0.95–1.00) effects. Variation in intensity of three standard reflections was $\pm 0.1\%$. 5009 unique reflections were measured with $4 < 2\theta < 60^\circ$; 4662 with $I > 3\sigma(I)$ were used in refinement. Data were collected for h 0 to 14, k -19 to 19 and l -8 to 8. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques. H atoms were located from difference maps or placed in calculated positions; bisulfate H atoms were not located; B_H was set to $1.1 B_N$ before the final refinement cycles; H-atom positional parameters were refined. Full-matrix refinement was based on F with all non-H atoms anisotropic; $w = 4F_o^2/[\sigma(F_o^2) + 0.0016F_o^4]$. Final $R = 0.025$, $wR = 0.038$, $S = 1.59$, $(\Delta/\sigma) < 0.05$; $\Delta\rho_{\max} = 0.58$, $\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$. Scattering factors were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs used were from the Enraf–Nonius (1985) *SDP* system.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the asymmetric unit, showing the atom-numbering scheme, is given in Fig. 1. Selected bond distances and angles are listed in Table 2.

The structure contains discrete $[(\text{NH}_3)_5\text{RuCl}]^{2+}$ cations, bisulfate anions and lattice water molecules. Each Ru ion is coordinated in an approximately octahedral fashion by a chloride ion and five ammonia molecules. Bond distances and angles within the cation are unexceptional. The Ru—Cl distance [2.3742 (5) Å] lies within the range reported for other Ru^{III} complexes including $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [2.34 (5) Å] (Prout & Powell, 1962), *cis*- $[\text{Ru}(\text{cyclam})\text{Cl}_2]\text{Cl}$ [2.373 (1), 2.369 (1) Å] (Che, Kwong, Poon, Lai & Mak, 1985) and *cis*- $[\text{Ru}(\text{en})_2\text{Cl}(\text{OH}_2)](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ [2.323 (1) Å] (Hambley & Lawrance, 1984). The Ru—Cl bond(s) is *trans* to an ammine ligand for these last two approximately octahedral Ru complexes. The Ru—Cl distance reported for the centrosymmetric *trans*- $[\text{Ru}(\text{cyclam})\text{Cl}_2]\text{Br}$ complex is 2.343 (1) Å (Walker & Taube, 1981). The average Ru—NH₃ distance [2.106 (9) Å] in the title complex compares well with the value of 2.104 (4) Å reported for $[\text{Ru}(\text{NH}_3)_6](\text{BF}_4)_3$ (Stynes & Ibers, 1971). The Ru—N bond distances in the title complex show

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

$$B_{\text{eq}} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)].$$

	x	y	z	B_{eq}
Ru	0.49236 (1)	0.23642 (1)	0.08119 (2)	1.462 (2)
Cl	0.42704 (5)	0.16031 (4)	0.34828 (8)	2.564 (8)
S(1)	0.74820 (4)	0.50234 (3)	0.26578 (7)	1.781 (7)
S(2)	0.09984 (5)	0.84746 (3)	0.25229 (7)	2.078 (8)
O(1)	0.7065 (2)	0.4476 (1)	0.4175 (2)	2.76 (3)
O(2)	0.7281 (2)	0.6072 (1)	0.3540 (3)	2.97 (3)
O(3)	0.6670 (2)	0.4839 (1)	0.0534 (3)	3.81 (4)
O(4)	0.8919 (2)	0.4717 (1)	0.2416 (4)	3.81 (4)
O(5)	0.0438 (2)	0.7961 (1)	0.3938 (3)	3.50 (3)
O(6)	0.2307 (2)	0.8773 (2)	0.3582 (3)	3.95 (4)
O(7)	0.0062 (2)	0.9336 (1)	0.2073 (4)	4.85 (5)
O(8)	0.1207 (2)	0.7820 (2)	0.0504 (3)	4.34 (4)
O(9)	0.7338 (2)	0.9840 (1)	0.2538 (3)	3.88 (4)
O(10)	0.0887 (2)	0.5930 (1)	0.2409 (3)	3.64 (4)
O(11)	0.1180 (2)	0.3249 (2)	0.2536 (4)	4.33 (4)
O(12)	0.0974 (2)	0.1171 (2)	0.2696 (3)	4.24 (4)
N(1)	0.6886 (2)	0.2381 (1)	0.2506 (3)	2.18 (3)
N(2)	0.5538 (2)	0.3034 (1)	-0.1517 (3)	2.11 (3)
N(3)	0.4350 (2)	0.3764 (1)	0.2477 (3)	2.13 (3)
N(4)	0.5560 (2)	0.0987 (1)	-0.0949 (3)	2.49 (3)
N(5)	0.2946 (2)	0.2379 (1)	-0.0897 (3)	2.38 (3)

Table 2. *Selected bond lengths (Å) and angles (°)*

Ru—Cl	2.3742 (5)	S(1)—O(2)	1.478 (2)
Ru—N(1)	2.098 (2)	S(1)—O(3)	1.465 (2)
Ru—N(2)	2.096 (2)	S(1)—O(4)	1.466 (2)
Ru—N(3)	2.106 (2)	S(2)—O(5)	1.467 (2)
Ru—N(4)	2.119 (2)	S(2)—O(6)	1.467 (2)
Ru—N(5)	2.113 (2)	S(2)—O(7)	1.464 (2)
S(1)—O(1)	1.475 (2)	S(2)—O(8)	1.458 (2)
Cl—Ru—N(1)	90.24 (5)	N(4)—Ru—N(5)	91.58 (8)
Cl—Ru—N(2)	178.93 (6)	O(1)—S(1)—O(2)	108.8 (1)
Cl—Ru—N(3)	92.40 (5)	O(1)—S(1)—O(3)	110.1 (1)
Cl—Ru—N(4)	90.30 (6)	O(1)—S(1)—O(4)	109.5 (1)
Cl—Ru—N(5)	90.51 (6)	O(2)—S(1)—O(3)	109.8 (1)
N(1)—Ru—N(2)	88.69 (8)	O(2)—S(1)—O(4)	109.5 (1)
N(1)—Ru—N(3)	89.80 (8)	O(3)—S(1)—O(4)	109.1 (1)
N(1)—Ru—N(4)	89.32 (8)	O(5)—S(2)—O(6)	109.7 (1)
N(1)—Ru—N(5)	178.83 (6)	O(5)—S(2)—O(7)	110.1 (1)
N(2)—Ru—N(3)	87.70 (8)	O(5)—S(2)—O(8)	108.8 (1)
N(2)—Ru—N(4)	89.58 (8)	O(6)—S(2)—O(7)	109.3 (1)
N(2)—Ru—N(5)	90.55 (8)	O(6)—S(2)—O(8)	109.1 (1)
N(3)—Ru—N(4)	177.16 (7)	O(7)—S(2)—O(8)	109.9 (1)
N(3)—Ru—N(5)	89.27 (8)		

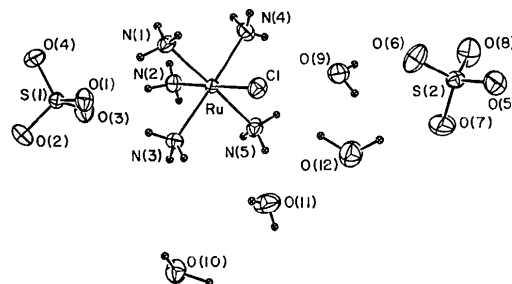


Fig. 1. View (ORTEP; Johnson, 1976) of the asymmetric unit of the title complex showing the atom-numbering scheme. Bisulfate H atoms were not located. Thermal ellipsoids are drawn at the 50% probability level; thermal parameters for H atoms are shown arbitrarily small for clarity.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55120 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0193]

only small differences (0.002–0.023 Å) for the amines that are *cis* and *trans* to the chloride ligand, *i.e.* there is little if any of a *trans* effect for chloride as a ligand.

Table 3. Hydrogen-bond parameters (Å, °)

D—H...A	D—H...A	D...A	H...A	D—H
N(1)—H(N11)...O(8 ^b)	170 (3)	2.849 (3)	2.04 (3)	0.82 (3)
N(1)—H(N12)...O(1)	167 (3)	2.977 (3)	2.10 (3)	0.89 (3)
N(1)—H(N13)...O(6 ^b)	166 (3)	3.143 (3)	2.30 (3)	0.86 (3)
N(2)—H(N21)...O(3)	173 (3)	2.949 (3)	2.14 (3)	0.81 (3)
N(2)—H(N22)...O(2)	154 (2)	3.108 (3)	2.33 (3)	0.84 (3)
N(3)—H(N31)...O(3 ^b)	169 (2)	2.952 (3)	2.02 (3)	0.94 (3)
N(3)—H(N32)...O(1)	172 (3)	3.026 (3)	2.20 (3)	0.84 (3)
N(3)—H(N33)...O(2 ^b)	169 (3)	3.163 (3)	2.36 (3)	0.81 (3)
N(4)—H(N41)...O(6 ^b)	161 (3)	2.995 (3)	2.13 (3)	0.90 (3)
N(4)—H(N43)...O(9 ^b)	171 (3)	3.148 (3)	2.30 (3)	0.86 (3)
N(5)—H(N51)...O(11)	160 (2)	2.985 (3)	2.10 (3)	0.92 (3)
N(5)—H(N52)...O(2 ^b)	167 (3)	2.946 (2)	2.16 (3)	0.80 (3)
N(5)—H(N53)...O(9 ^b)	173 (2)	3.156 (3)	2.31 (3)	0.85 (3)
O(10)—H(O101)...O(1 ^h)	176 (3)	2.825 (3)	1.77 (3)	1.06 (3)
O(9)—H(O91)...O(7 ^h)	164 (3)	2.768 (3)	1.98 (4)	0.81 (3)
O(12)—H(O121)...Cl	172 (3)	3.403 (2)	2.35 (4)	1.06 (4)
O(10)—H(O102)...O(4 ^a)	165 (3)	2.803 (3)	1.77 (3)	1.05 (3)
O(11)—H(O111)...O(4 ^a)	151 (4)	2.834 (3)	2.16 (4)	0.75 (4)
O(12)—H(O122)...O(7 ^h)	150 (3)	2.815 (3)	1.88 (4)	1.02 (4)
O(9)—H(O92)...O(6 ^a)	160 (4)	2.863 (3)	2.21 (4)	0.68 (3)
O(11)—H(O112)...O(2 ^h)	170 (5)	2.812 (3)	2.19 (4)	0.63 (4)

Symmetry code: (i) 1 - x, 1 - y, -z; (ii) 1 - x, 1 - y, 1 - z; (iii) x, y - 1, z; (iv) x + 1, y, z; (v) x - 1, y, z; (vi) 1 - x, 2 - y, 1 - z.

The (NH₃)₅RuCl²⁺ cations, bisulfate counterions and lattice water molecules are linked by an extensive hydrogen-bonding network involving the chloride ion, the five ammine N atoms, the four water O atoms and seven of the eight bisulfate O atoms. Details of the hydrogen-bonding network are given in Table 3. In addition to these parameters, there are several other short non-bonding contacts in the structure involving the bisulfate O atoms, one or more of which could correspond to hydrogen bonds involving the bisulfate H atoms which were not located. The small but significant differences in

Ru—N bond lengths in the title complex do not depend in any obvious way on the number or strength of the hydrogen bonds associated with a given ammonia ligand.

We thank the National Science Foundation for support of research (Grant CHE 8919120) and the National Institutes of Health for an instrumentation grant (Grant 1510 RRO 1486 O1A1).

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Acta Cryst. (1992). **C48**, 1576–1578

A New Type of Borate Double Salt: Structure of LiBa₂B₅O₁₀

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(Received 23 September 1991; accepted 13 November 1991)

Abstract. Dibarium lithium pentaborate, LiBa₂B₅O₁₀, *M_r* = 495.67, monoclinic, *P*2₁/*m*, *a* = 4.413 (2), *b* = 14.585 (9), *c* = 6.700 (4) Å, β = 104.30 (4)°, *V* = 417.9 (7) Å³, *Z* = 2, *D_m* = 3.90 (by specific gravity bottle in toluene), *D_x* = 3.94 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 94.1 cm⁻¹, *F*(000) = 440, *T* = 296 K. Full-matrix least-squares refinement

gave a final *R* of 0.018 and *wR* of 0.022, for 1015 [*I* ≥ 8σ(*I*)] observed reflections. The structure contains a new type of [B₅O₁₀]⁵⁻ moiety composed of three BO₃ triangles and two BO₄ tetrahedra.

Introduction. The relationship between crystal structure and optical properties of nonlinear optical