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Short Communications

$(NH_4)_2Ru(SO_4)_2 \cdot 6\,H_2O$ – the Ru Analog of Mohr's Salt. Preparation of this Salt and of $CsRu(SO_4)_2 \cdot 12\,H_2O$ from Ru Metal. Magnetic Properties and Ligand Field Spectra

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Hexaaqua ions of ruthenium(III) and (II) have been known since 1958[1] and 1965,[2] respectively. These ions were much later[3] isolated in solid salts (p-toluenesulfonates) and very recently[4] in the alum $Cs[Ru(H_2O)_6](SO_4)_2 \cdot 6\,H_2O$ and in the Tutton salt $Rb_2[Ru(H_2O)_6](SO_4)_2$, especially important because of their membership of the two classical inorganic series whose solid state properties (spectral and structural) compared with the spectra of their aqueous solutions gave the earliest and most prominent indication of hexaaqua ions in solution.

This communication concerns the preparation of the former of these salts and of $(NH_4)_2[Ru(H_2O)_6](SO_4)_2$ which is the Ru analogue of the famous[5] Mohr's salt which also belongs to the Tutton salts as does the mineral Schönite, $K_2[Mg(H_2O)_6](SO_4)_2$. Whereas two other elements of the second long-period are known to form alums, namely indium[6] and rhodium[7,9] (even iridium, a third long-period element forms alums[8,9]), the ruthenium Tutton salts provide the first examples of Tutton salts of a second row transition element and these salts are as yet unknown for the third row elements.

The following procedure is an elaboration and slight modification of Ref. 3 (all operations involving Ru^{II} were carried out in a CO_2 or an Ar atmosphere).

$(NH_4)_2[Ru(H_2O)_6](SO_4)_2$. **Warning:** RuO_4 is volatile and poisonous and should only be handled in a hood. It is helpful, though, that its extremely strong smell serves as a sensitive qualitative monitor. Particular protection of the eyes is required since RuO_4 is easily reduced to black solid RuO_2 which may precipitate in the cornea.

The starting material was elemental Ru (1.5 g, 15 mmol), which was heated over an open flame with Na_2O_2 (5 g, 64 mmoles) in a silver crucible. The resulting melt was heated to redness (800 °C) and stirred at this temperature for about one minute. When subsequently cooled, solidification was observed to take place while the melt was still glowing. The solid, black in appearance, was dissolved in 40 ml of water (accompanied by oxygen evolution), and the dark, orange-brown mixture was added to a distillation flask (preferably without ground glass-joints) containing 5 g of $NaIO_4$ (23 mmol). Then 80 ml of 15 M H_2SO_4 was added under cooling and stirring, changing the brown mixture into a yellow suspension of RuO_4. The RuO_4 was carried by CO_2 into a flask containing a stirred mixture of 30 g of amalgamated lead in 100 ml 1 M H_2SiF_6. At the beginning, the CO_2 stream was kept low (about 1 bubble per second) in order to avoid that RuO_4 escaped the reduction flask. When lower-valent Ru species had formed, indicated by a colour change from yellow (RuO_4) through dark brown (presumably colloidal RuO_2) to yellow or red ($Ru^{III,II}$ aqua ions), the flow was raised to 4–5 bubbles per second and continued in this way till the following day. Then, 40 g (125 mmol) of solid $Na_2SO_4 \cdot 10\,H_2O$ was added in a vigorous counterstream of CO_2 and, after filtration, the red solution was diluted with 200 ml of deaerated water, loaded onto a column (35 g DOWEX 50W–X8 50–100 mesh), washed with 200 ml of 0.05 M H_2SO_4, and eluted with 0.5 M H_2SO_4. *Ca.* 600 ml of pink solution were collected, 8.2 g (105 mmoles) of ammonium carbamate were added and the solution was evaporated at 35 °C under vacuum. When precipitation began, the evaporation was stopped and the flask, still rotating, was cooled slowly to 0 °C. When crystallization was complete, and the filtrate was almost colourless, the well-shaped,

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red crystals were filtered off and washed successively with a saturated ammonium sulfate solution, 50 ml 50 vol-% ethanol (twice) and 96 % ethanol, followed by airdrying. Yield: 4,1 g (9.4 mmol, 63 % based on Ru metal).

Anal., N: 6.42 %, H: 4.50 %, S: 13.96 %, Ru: 22.93 %.

Calcd., N: 6.41 %, H: 4.58 %, S: 14.65 %, Ru: 23.11 %.

The product was reprecipitated in about 80 % yield by dissolution of 1 g in 12 ml of 0.05 M H_2SO_4, dropwise addition of 2 ml of a saturated ammonium sulfate solution, and treatment of the precipitated solid as described above.

$Cs[Ru(H_2O)_6](SO_4)_2 \cdot 6\ H_2O$. The procedure was analogous to that for the preparation of the Tutton salt, and differed from this only in that 5 ml (40 mmoles) of a saturated Cs_2CO_3 solution was added instead of ammonium carbamate, whereupon the red solution was oxidized by the addition of 7.5 ml of 1 M H_2O_2 (Ref. 3 uses air as an oxidant). A colour change to yellow, which took place within a few minutes, indicated the formation of $[Ru(H_2O)_6]^{3+}$. The solution was then evaporated as described above, this time to a volume of about 100 ml when it was cooled in ice-water. Crystallization sometimes had to be provoked by scratching with a glass rod. The filtered crystals were washed with small portions of ice-water, then with 96 % ethanol, and finally airdried. Yield: *ca.* 4.8 g (7.4 mmol, 50 %) of tiny yellow crystals, which were recrystallized by dissolution in 0.1 M H_2SO_4 (*ca.* 10 ml per g) at 45 °C, filtration, and cooling to 0 °C. Total yield: *ca.* 38 % based on Ru metal.

Anal., H: 3.73 %, S: 9.61 %, Ru: 15.66 %.

Calcd., H: 3.77 %, S: 9.98 %, Ru: 15.74 %.

The compounds were further characterized by their X-ray powder diagrams, from which unit cell dimensions were obtained. These were for the Tutton salt (monoclinic, $P2_1/c$):a=9.15 Å, b=12.48 Å, c=6.26 Å, β=107.0°, and for the alum (cubic, $Pa3$): a=12.45 Å. (Close agreement with Ref. 4). Absorption spectra were recorded in 0.1 M (Tutton salt) and 1 M (alum) CF_3SO_3H and agreed with the data given by Kallen and Earley,[10] except that, for the Tutton salt, somewhat greater intensities were observed: $[\lambda_{1,max}(^1A_{1g} \rightarrow {}^1T_{1g});\ \varepsilon_{1,max}]$ = (535; 11.5), $[\lambda_{2,max}(^1A_{1g} \rightarrow {}^1T_{2g});\ \varepsilon_{2,max}]$ = (393; 13.5). Δ and B for $[Ru(H_2O)_6]^{2+}$ were calculated as 20050 and 490 cm^{-1}, respectively, using the full d^6 energy matrices.[11] For the alum, the magnetic susceptibility was measured from 6 to 300 K. With a diamagnetic correction of -2.90×10^{-4} cgs mol^{-1} and a temperature-independent paramagnetism of 0.00 cgs mol^{-1}, the effective magnetic moment obeyed the linear equation, $\mu_{eff}=2.012+6.92\times10^{-4}$ T, in the T-interval from 25 to 300 K. Similar measurements made on the diamagnetic crude Tutton salt showed this to contain up to 4 % Ru^{III}. After being reprecipitated once, the Ru^{III}-content dropped to less than 1 %. Crystals of both compounds are air stable, as we can confirm for the corresponding *p*-toluenesulfonates,[3] and do not lose or take up water within reasonable humidity limits. Approximate solubilities at 25 °C were 0.26 and 0.09 moles per liter for the Tutton salt and the alum using as solvents 0.01 M and 0.1 M H_2SO_4, respectively.

Ru analyses were carried out essentially as described by Woodhead and Fletcher:[12] the compounds (~40 mg) were oxidized at 0 °C with $K_2S_2O_8$ (0.80 g) in 2 M KOH (100 ml), resulting in complete conversion into ruthenate within less than ten minutes. Absorbance was measured at 465 nm, using ε_{465}=1710.[12]

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Note added in proof. For a more thorough magnetic study, see Bernhard, P., Stebler, A. and Ludi, A. *Inorg. Chem. 23* (1984) 2151.

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