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The interaction of ruthenium tetroxide and ammonia

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RYABOV and NIKOL'SKII(1) recently identified Ru and RuO_2 qualitatively as products of the reaction between RuO_4 and NH_3 in a bomb at 24 or 26°. They proposed reactions to account for these products and measured the corresponding heats of reaction. Since we do not contemplate further study of this reaction in the near future, we are prompted to record the results of some earlier and related experiments that were carried out under somewhat different conditions and led to results quite different from those referred to above.

Preliminary experiments showed that when gaseous NH_3 was added rapidly to RuO_4 at $-70°$ and 10^{-3} mm under strictly anhydrous conditions, the reaction mixture ignited. Very cautious initial addition of 5 ml increments of NH_3 gas to 1 g samples of RuO_4 under the above conditions permitted satisfactory control over the rate of reaction in two out of five attempts; the results of these two experiments however were in excellent agreement. These incremental additions were continued until 1 ml of liquid ammonia was condensed; thereafter an additional 9 ml was condensed rapidly.

During the initial additions of NH_3 gas the RuO_4 assumed a crimson colour;(2) subsequently this solid dissolved to form a dark red solution. As the temperature of this solution was raised from $-70°$ at the rate of 0·5°/min, evolution of N_2 began at ca. $-50°$ and the solution became red-brown. In the two successful experiments, 5·76 and 5·50 mmole of Ru as RuO_4 liberated 1·29 and 1·26 mmole of nitrogen, respectively; hence, N/Ru = 0·22 and 0·23. The solvent was removed completely at $-33{\cdot}5°$ and the residual brown solid was dried *in vacuo* for 12 hr at 25°. *Anal.* Found: Ru, 51·4; N, 19·7. Calc. for $Ru_4N_{11}O_{12}H_{33}$: Ru, 51·6; N, 19·7%.

This product failed to give an X-ray diffraction pattern; it decomposes explosively at 206°, is diamagnetic, soluble in water, but insoluble in a wide variety of organic solvents. The H^1 NMR spectrum consisted of a single rather broad peak at 4·6 ppm. The infrared spectrum showed strong broad bands at 3500 and 3200 cm^{-1}, medium bands at 1800, 1650, and 1050 cm^{-1}, strong bands at 1350 and 1320 cm^{-1} and a broad weak band at 960 cm^{-1}. Thermogravimetric analysis of an 80·5 mg sample in helium flowing at 50 ml/min and a heating rate of 3°/min resulted in a smooth weight loss of 18 mg between 45 and 202° and a more rapid loss of 7 mg between 202 and 206°. After the sample exploded at 206°, the black residual solid gave an X-ray diffraction pattern identical with that of an authentic specimen of elemental ruthenium.

Although the volume of nitrogen liberated in the reaction beginning at $-50°$ is somewhat low, the N/Ru ratio together with the diamagnetism of the solid reaction product indicates reduction to Ru^{6+}. The weight loss in the TGA experiment is entirely compatible with conversion of $Ru_4N_{11}O_{12}H_{33}$ to $RuO(NH_2)$, i.e., found: -25 mg; calc: -26 mg,

$$Ru_4N_{11}O_{12}H_{33} \rightarrow 4RuO(NH_2) + 2N_2 + 3NH_3 + 8H_2O$$

and the explosive decomposition could result from,

$$RuO(NH_2) \rightarrow RuN + H_2O$$

$$2RuN \rightarrow 2Ru + H_2$$

in a manner analogous to the known behavior of $BiO(NH_2)$ and BiN.(3)

With regard to the nature of the initial solid reaction product, all of its properties except water-solubility suggest that it may be a bridged polynuclear species similar to that resulting from the interaction of osmium tetroxide and ammonia,(4,5) i.e., $Os_3N_7O_9H_{21}$. The infrared spectrum of $Ru_4N_{11}O_{12}H_{33}$ is remarkably similar to that of $Os_3N_7O_9H_{21}$; assignments for the observed bands

(1) A. N. RYABOV and A. B. NIKOL'SKII, *Russ. J. Inorg. Chem.* **8**, 1159 (1963).

(2) M. L. HAIR and P. L. ROBINSON, *J. Chem. Soc.* 2775 (1960).

(3) G. W. WATT and W. C. FERNELIUS, *J. Amer. Chem. Soc.* **61**, 1692 (1939).

(4) G. W. WATT and E. M. POTRAFKE, *J. Inorg. Nucl. Chem.* **17**, 248 (1961).

(5) G. W. WATT and W. C. MCMORDIE, In press.

will be reported elsewhere.[5] The single broad NMR peak suggests rapid and essentially complete exchange with the D_2O solvent.

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Thiourea complexes of cobalt(II) sulphate

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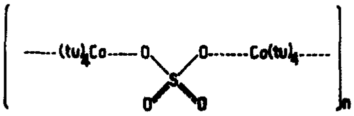
It has been recently reported by Cotton *et al.*[1] that cobalt(II) sulphate reacts with thiourea (tu) in methanol to give the blue tetrahedral complex $Co(tu)_3SO_4$. They also described the occasional formation of a green solid which turned blue upon heating or prolonged standing. During the course of an investigation of the thiourea complexes of cobalt(II) we have isolated the green product and we conclude that it has the formula $Co(tu)_4SO_4{\cdot}2H_2O$, involving the tetrahedral cation tetrakis-thiourea-cobalt(II). This suggestion is based upon the following evidence: (a) The infrared spectrum of the solid has a strong-broad band at about 1100 cm^{-1} and very weak bands at ca., 1015 and 975 cm^{-1} in the S–O stretching region, as expected for a sulphate ion of T_d symmetry slightly perturbed by the crystal field.[2] (b) Its diffuse reflectance spectrum in the visible region is very similar to that of $Co(tu)_4(ClO_4)_2$,[1] which is believed to contain the same tetrahedral cation. This partial evidence however, is rather inconclusive since it has been shown by Cotton *et al.*[1] that the formally analogous complex $Co(tu)_4(NO_3)_2$ is very probably octahedral as inferred from the magnitude of its magnetic moment, although the electronic spectrum of the solid is typical of a tetrahedral cobalt(II) complex. (c) The observed magnetic moment (4·45 B.M. at 16°C) is strongly indicative of tetrahedral coordination of the cobalt(II) ion.[3]

Furthermore, we have found that the change in colour from green to blue is associated with the reaction

$$Co(tu)_4SO_4{\cdot}2H_2O \rightarrow Co(tu)_3SO_4 + tu + 2H_2O$$

which occurs spontaneously in the solid state even at room temperature.

Figure 1 illustrates the change in the S–O region due to concomitant lowering of symmetry of the sulphate group in passing from $Co(tu)_4SO_4{\cdot}2H_2O$ to $Co(tu)_3SO_4$ and free thiourea. It can be noted that the typical spectrum of a partially transformed sample is markedly different from those of the initial and final products. It shows four bands at about 1160, 1090, 1020 and 990 cm^{-1}, which can be assigned to bidentate sulphato groups of C_{2v} symmetry. Absence of a band at about 1220 cm^{-1} suggests that the sulphato group is a bridging rather than a chelating group.[2,4] Hence, it seems reasonable to assume that the conversion of $Co(tu)_4SO_4{\cdot}2H_2O$ to $Co(tu)_3SO_4$ involves the formation of an octahedral intermediate (I)



I

Attempted isolation of this intermediate resulted in the immediate formation of $Co(tu)_3SO_4$ with concurrent separation of thiourea.

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[1] F. A. Cotton, O. D. Faut and J. T. Mague, *Inorg. Chem.* 3, 17 (1964).
[2] K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, *J. Amer. Chem. Soc.* 79, 4904 (1957).
[3] F. A. Cotton, D. M. L. Goodgame and M. Goodgame, *J. Amer. Chem. Soc.* 83, 4690 (1961).
[4] C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.* 1993 (1961).