known, but it is seen that the number of attachments, bipodal, tripodal, etc., largely determines the ring type within the limits imposed by the molecular formula.

[11] Invited Professor at the University of Geneva.

**R. M. Moriarty,[11] C.-L. Yeh, K.-N. Chen, E. L. Yeh**
*Department of Chemistry, University of Illinois, Chicago Circle*
*Chicago, Illinois 606080*

**K. C. Ramey**
*ARCO Chemical Company*
*Glenolden, Pennsylvania 19036*

**C. W. Jefford***
*Department of Chemistry, University of Geneva*
*1211 Geneva 4, Switzerland*

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## Disulfur Binuclear Ruthenium Ammines

*Sir:*

In the course of earlier work[1] with sulfur-containing ligands (*e.g.*, thiophene, thiosulfate) reacting with ruthenium ammines, a green color was frequently observed, but the species responsible for the color was not identified. We have now established the stoichiometry and some features of the structure of a green cation containing ruthenium, sulfur, and ammonia. The species we have characterized is remarkably stable and can be produced in a variety of ways. The ion, which we take to be $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ (I) represents a novel bonding mode for sulfur to metal ions,[2] and because of the simplicity of its composition and presumably of its structure, the chemistry of I and of related species offers an opportunity for improving the basic understanding of sulfur as a ligand.

The green ion has been produced in three different ways: (1) by the action of the sulfurizing agents $C_2H_4S$ and COS on $(NH_3)_5RuH_2O^{2+}$, (2) by reducing $(NH_3)_5RuSO_2{}^{2+}$ with amalgamated zinc, (3) by oxidizing a mixture of $(NH_3)_5RuH_2O^{2+}$ and $H_2S$. It is of interest to note that oxidation of $(NH_3)_5RuSR_2{}^{2+}$ or $(NH_3)_5RuSHR^{2+}$ does not produce the green ion, except for trace amounts in the second case.

Typical preparative procedures following methods 1 and 2 are herewith described.

In method 1, the preparation of $[(NH_3)_5RuS]_2Br_4$ (II), a slurry of 0.3 g of $[(NH_3)_5RuCl]Cl_2$ in 18 ml of $H_2O$ was reduced with amalgamated zinc under argon for about 45 min. The solution containing $[(NH_3)_5RuOH_2]^{2+}$ was then transferred under Ar into a vessel with 25 ml of methanol and 2 ml of ethylene sulfide. The reaction mixture was kept under argon for about 30 min. Methanol and excess of episulfide were removed by vacuum distillation. The solution was filtered from polymerization products of episulfide and 3 ml of saturated $NH_4Br$ solution was added. After the solution was cooled, a precipitate of dark fine needles was collected. This product usually was contaminated by organic impurities and was recrystallized three times. *Anal.* Calcd for $[(NH_3)_5RuS]_2Br_4 \cdot 2H_2O$: Ru, 25.5; N, 17.7; H, 4.3; S, 8.1; Br, 40.3. Found: Ru, 24.9; N, 17.8; H, 4.1; S, 8.4; Br, 39.6 (analysis for Ru by residue; values obtained in this way are somewhat inaccurate). The chloride salt can be prepared by a similar method.

In method 2, the preparation of *trans*-$[Cl(NH_3)_4RuS]_2Cl_2$ (III), an amount (150 mg) of *trans*-$[(NH_3)_4RuSO_2Cl]Cl$ was dissolved in 10 ml of 0.05 *M* HCl. The solution was cooled in ice, and several pieces of amalgamated zinc were added to it. As the solution was stirred in air, it gradually turned green and after 15–20 min it was filtered and charged onto a cation exchange column (Bio-Rad AG 50W-X2 200–400 mesh, hydrogen ion form). The resin was eluted first with 0.25 *M* NaCl which carried along a species resembling the starting material. After this stage, the column was washed with 0.05 *M* HCl. These treatments left a dark green band at the top of the column which moved slowly with 0.9 *M* HCl and more rapidly with 1.6 *M* HCl. The green solution was collected and concentrated by rotary evaporation. After cooling overnight at $-5°$, a black-green solid formed. This was collected, washed with ethanol and diethyl ether, then dried in a vacuum desiccator. More of the product was obtained by treating the first eluent as has been described, total yield 60 mg. *Anal.* Calcd for $[Cl(NH_3)_4RuS]_2Cl_2 \cdot 1.5H_2O$: S, 11.21; H, 4.72; N, 19.61; Cl, 24.87; Ru, 35.4. Found: S, 11.18; H, 4.25; N, 19.69; Cl, 25.05; Ru, 35.3 by atomic absorption, 33.35 by residue (the compound is hydroscopic). The positions trans to the disulfur group appear to be fairly labile; taking advantage of this fact, the compound [isonicotinamide-$(NH_3)_4RuS]_2Br_4$ (IV) was prepared. *Anal.* Calcd for the dihydrate: Ru, 20.2; C, 14.4; N, 16.8; H, 4.0. Found: Ru, 20.0; C, 13.82; N, 16.4; H, 3.58.

The ion exchange behavior of a solution of II, comparing the elutability with ions of known 4+ charge, indicates that the cation contained in II also carries a 4+ charge. Measurements of the magnetic susceptibility of II show it to have a small positive value, corresponding to 0.45 BM per dimer at 25°, but independent of temperature over the range 25 to $-100°$. For III, the magnetic susceptibility at room temperature (22–24°) corresponds to 1.1 BM per dimer. A solution of III in $D_2O$ (0.1 *M* DCl) shows a single proton nmr signal, at 3.10 ppm referred to trimethylsilyl propionate, having within 10% the intensity expected for the octaammine formulation. No esr signal was observed for III dissolved (0.01 *M*) in water even on cooling to liquid nitrogen temperatures. The Raman spectrum of II dissolved in $H_2O$, taken with a Spex 1401 spectrometer using 488 nm as the exciting line, shows a band at $519 \pm 2$ cm$^{-1}$. This can be compared to the S–S stretching frequency in $H_2S_2$, dialkyl disulfides, and disulfur halides at 509, 495–520, and 510–540 cm$^{-1}$, respectively. The band at 519 cm$^{-1}$ is absent from the ir spectrum and is unshifted on deuteration of the complex. The diaquooctaammine, dichlorooctaammine, and the diisonicotinamideoctaammine ions show Raman bands at $515 \pm 3$, $520 \pm 3$, and $526 \pm 3$ cm$^{-1}$.

The results quoted support structure I for the green ion present in II. The cations present in III and IV are taken to have molecules of $Cl^-$ or isonicotinamide occupying coordination positions on Ru, trans to sulfur.

The spectrum of a solution of II is shown in Figure 1.

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[1] J. N. Armor and H. Taube, unpublished observations.

[2] Other examples of the disulfur group bridging metal atoms have been reported: *cf.* C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965); D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3727 (1967); G. T. Kubas, T. G. Spiro, and A. Tirzes, *ibid.*, **95**, 273 (1973). In all of these cases, the metal centers are connected by other bonds as well.

Table I. Band Maxima (nm) and (Extinction Coefficients, $M^{-1}$ cm$^{-1}$) for Disulfur Bridged Ruthenium Ammines, *trans*-$[L(NH_3)_4RuS]_2^{n+}$

| | | | | | |
|---|---|---|---|---|---|
| $H_2O$ | 704 (1.46 × $10^4$) | 412 (1.35 × $10^3$) | 285 (5.11 × $10^3$) | 221 (1.98 × $10^4$) | |
| $NH_3$ | 720 (1.73 × $10^4$) | 390 (1.18 × $10^3$) | 284 (5.40 × $10^3$) | 235 (2.23 × $10^4$) | 215 (2.03 × $10^4$) |
| $Cl^-$ [a] | 723 (1.43 × $10^4$) | 428 (1.53 × $10^3$) | 292 (4.63 × $10^3$) | 238 (2.39 × $10^4$) | |
| $Br^-$ | 732 | 440 | 344 | *b* | |
| $I^-$ | 740 | 440 (sh) | 350 | *b* | |
| ISN | 755 | 370 | 350 | 237 | |

[a] The dichloro compound was dissolved in 1 *M* HCl to get the chloro and in 1 *M* trifluoromethylsulfonic acid to get the aquo ion. [b] Experiments done in excess halide ion; the short wavelength band may have been masked by the halide charge transfer absorption. Extinction coefficients were comparable with the chloro and the aquo compounds.

The band maxima and extinction coefficients for the solutions of several related ions are summarized in Table I.

Of special interest are the redox properties of the species. On reducing a solution containing I, 4 equiv of $Eu^{2+}$ is consumed, producing Ru(II) + $H_2S$ (or the complex of $H_2S$ with Ru(II)) but with no detectable formation of intermediate oxidation states. Reduction with amalgamated zinc under certain conditions (for instance, when the concentration of complex is high, say 0.1 *M*) can lead to a red product, which is assumed by analogy to the spectral properties of other compounds synthesized in our laboratories to be a sulfide complex of Ru(III). This decomposes to a black-brown precipitate. The red colored product was also observed when species I was synthesized by method 3 and oxidation was carried out slowly with air.

Cyclic voltammetric measurements done on an aqueous solution of II (in 0.1 *M* sodium tosylate with a Pt button as electrode) show a reduction wave at about −0.49 V referred to nhe, and, if the potential sweep is not carried much beyond this value, a corresponding oxidation peak at −0.40 V. Since the latter peak is small compared with the former, we infer that the substance produced on reduction undergoes a rapid decomposition. If the sweep is continued to more negative values, a second reduction peak occurs, but no corresponding peak is observed in the oxidation phase of the cycle. Oxidation of the ion occurs at *ca.* 1.0 V, producing a number of new peaks in the reduction cycle. In dry acetone using tetraethylammonium perchlorate as supporting electrolyte, a reversible peak is observed at 1.04 V if the species is subjected to an oxidizing current and reversible peak at −0.43 V if it is first subjected to a reducing current. The diisonicotinamideoctaammine ion shows a reversible peak in water at −0.22 ± 0.01 V (0.1 *M* sodium tosylate with a hanging mercury drop electrode).

Cation I reacts readily with $CN^-$ to produce an intermediate species which we take to be $(NH_3)_5RuSCN^+$. On acidification and exposure to the air, the spectrum of the product solution shows a band maximum at 487 mμ which gradually shifts to 500 mμ and increases in intensity. The final spectrum agrees rather well with that reported[3,4] for $(NH_3)_5RuNCS^{2+}$ (N bound) with as much as 80% of the ruthenium appearing in this form. Thus, the stoichiometry of the reaction of $CN^-$ with I approaches that expressed by

$$[(NH_3)_5RuSSRu(NH_3)_5]^{4+} + 2CN^- \longrightarrow 2(NH_3)_5RuSCN^+$$

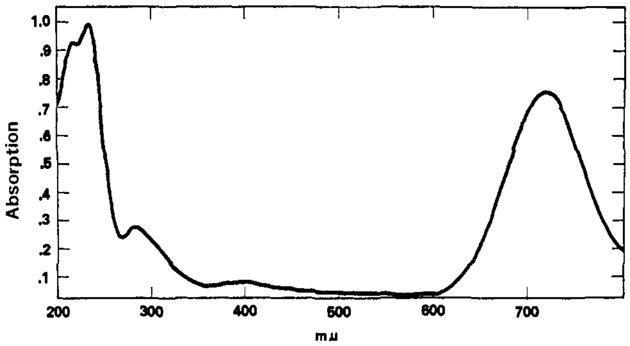

Figure 1. Absorption spectrum of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4$ in aqueous solution (4.6 × $10^{-5}$ *M*, 1-cm cell).

When I is treated with bisulfite ion the solution shows light absorption characteristic[5,6] of $(NH_3)_5RuSSO_3^+$ ($\lambda_{max}$ 488 mμ).

The fact that the S–S stretching frequency lies close to that observed for species regarded as featuring S–S single bonds suggests that the ion is to be formulated as Ru(III) bridged to Ru(III) by $S_2^{2-}$. To account for the fact that unpaired electrons are not present, at least a small degree of coupling between the metal atoms through the $S_2^{2-}$ bridge must be invoked. Alternatively, it might be argued that the metal atoms are in the 2+ state, but bridged by singlet disulfur, and now ascribing the "weak" S–S bond to back-donation. Experiments in progress[7] with $R_2S$ and $RS^-$ as ligands on Ru(II) and Ru(III) should help to decide whether either formal description is appropriate for the ion and may provide some indication of how strongly the properties of the two metal centers are modified by combining them in the same molecule.

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**Christa R. Brulet, Stephan S. Isied, Henry Taube***
*Department of Chemistry, Stanford University*
*Stanford, California 94305*

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(3) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 11, 1460 (1972).

(4) Unpublished experiments by J. N. Armor, measuring the affinity of $Hg^{2+}$ for $(NH_3)_5RuNCS^{2+}$ and comparing it with those measured for the species $(H_2O)_5CrNCS^{2+}$ and $(NH_3)_5CrNCS^{2+}$, confirm the conclusions reached by Lim, *et al.*,[3] on the structure of the thiocyanate complex of ruthenium.

(5) J. N. Armor, Ph.D. Thesis, Stanford, 1970.

(6) F. M. Lever and A. R. Powell, *J. Chem. Soc. A*, 1477 (1969).

(7) C. Kuehn, research in progress.