

A RUTHENIUM CHLORO NITROSYL DERIVATIVE OF DITHIOACETYLACETONE

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Abstract

The novel dithioacetylacetonato complex $[\text{Ru}(\text{C}_5\text{H}_7\text{S}_2)_2(\text{NO})\text{Cl}]$ has been characterized by analytical and spectral methods. A *trans* configuration is suggested. The electronic spectrum is consistent with the oxidation state II for the coordinated metal ion.

An attempted routine preparation of tris(dithioacetylacetonato)ruthenium(III), $[\text{Ru}(\text{SacSac})_3]$ where $\text{SacSac}^- = \text{C}_5\text{H}_7\text{S}_2^-$, yielded instead a nitrosyl derivative analytically consistent with the formulation $[\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}]$. Checking revealed that the original starting material, commercial ruthenium trichloride, contained coordinated nitric oxide. The compound has been reprepared from authentic $\text{Ru}(\text{NO})\text{Cl}_3 \cdot \text{H}_2\text{O}$. We have since confirmed that NO-free commercial trichloride reliably leads to $[\text{Ru}(\text{SacSac})_3]$.¹

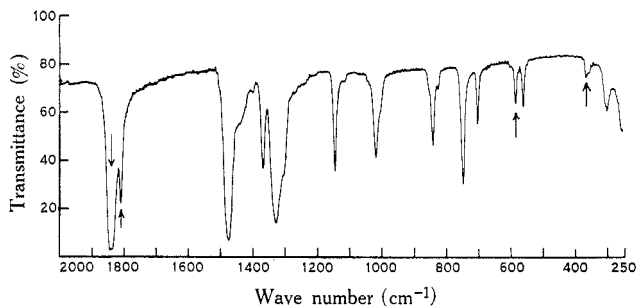


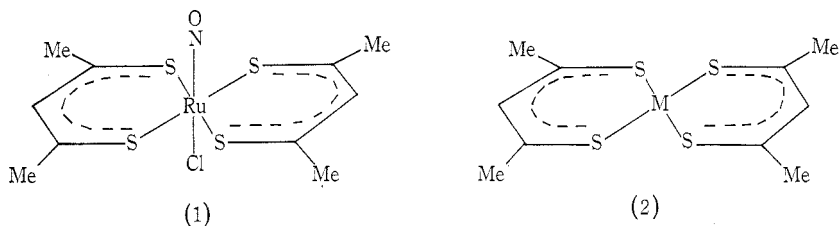
Fig. 1.—Infrared spectrum in KBr disk. Arrows point to peaks not in spectrum of $[\text{Ru}(\text{SacSac})_3]$.

The new diamagnetic complex is a red-brown crystalline material, yielding rose-red solutions in organic solvents. Comparison of the infrared (Fig. 1) and p.m.r. (Fig. 2) spectra with those of well-characterized dithioacetylacetonato complexes confirms that the organic ligand is intact and is chelated in the usual way. The presence of NO is established by a strong new band in the infrared spectrum at 1840 cm^{-1} , which is due to the N-O stretching vibration. The splitting of this band when the compound is supported in a potassium halide disk (either KCl or KBr) is ascribed to a lattice effect. Solution spectra exhibit a single symmetric band at 1840 cm^{-1} yet, if the sample is recovered by evaporation and re-examined in disk form, the splitting returns. Two further new bands, at 580 cm^{-1} and 300 cm^{-1} , were

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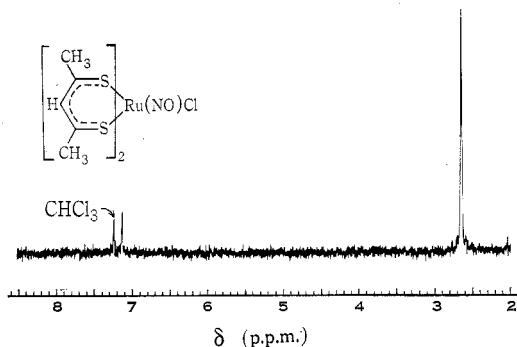
¹ Heath, G. A., and Martin, R. L., *Aust. J. Chem.*, 1970, **23**, 1721.

tentatively assigned as Ru-N and Ru-Cl stretching vibrations, respectively. These three absorptions were also observed in the infrared spectrum of $\text{Ru}(\text{NO})\text{Cl}_3 \cdot \text{H}_2\text{O}$.



The p.m.r. spectrum reveals only two resonances in the intensity ratio 1 : 6, corresponding to the ring proton and methyl protons respectively. No inequivalence of the methyl groups is evident, an observation which accords with the *trans* formulation (1). In the six-coordinate mixed complexes such as $[\text{Co}(\text{SacSac})_2(\text{dpt})]$ (where dptH = diphenyltriazene) the non-equivalence of the SacSac^- methyl groups is clearly displayed in the p.m.r. spectrum.²

Fig. 2.—P.m.r. spectrum in deuteriochloroform. (δ from TMS).



The suggested coplanar disposition of the chelate rings is known to be stable in the related $[\text{M}(\text{SacSac})_2]$ complexes (2) where $\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Pd}^{\text{II}}, \text{or Pt}^{\text{II}}$.^{3,4} In contrast, an X-ray study shows that $[\text{Ru}(\text{NO})(\text{Et}_2\text{NCS}_2)_3]$ contains two bidentate dithiocarbamate ligands and one monodentate dithiocarbamate ligand *cis* to the nitrosyl group, giving an octahedral structure.⁵

The parent ion $[\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}]^+$ and the molecular ions $[\text{Ru}(\text{SacSac})_2\text{Cl}]^+$ and $[\text{Ru}(\text{SacSac})_2]^+$ are the three heaviest species evident in the mass spectrum; $[\text{Ru}(\text{SacSac})_2(\text{NO})]^+$ is not observed. The spectrum is characterized by a strong peak at m/e 30 (NO^+), whereas there is no ion of this m/e value in the fragmentation pattern of the ordinary dithioacetylacetone complexes.

We have previously observed a striking difference in the electronic spectra of the low-spin $[\text{M}(\text{SacSac})_3]$ chelates of the iron(III), ruthenium(III), and osmium(III) (t_{2g}^5)

² Heath, G. A., and Martin, R. L., unpublished data.

³ Barraclough, C. G., Martin, R. L., and Stewart, I. M., *Aust. J. Chem.*, 1969, **22**, 891.

⁴ Beckett, R., and Hoskins, B. F., *Chem. Commun.*, 1967, 909.

⁵ Domenicano, A., Vacicgo, A., Zambonelli, L., Loader, P. L., and Venanzi, L. M., *Chem. Commun.*, 1966, 476.

and cobalt(III), rhodium(III), and iridium(III) (t_{2g}^6) metal ions.^{1,6} Intense low energy electronic transitions occurring only for the former class were ascribed to charge transfer to the hole in the stabilized metal t_{2g} subshell. Interestingly, these absorptions are absent in the present nitrosyl ruthenium compound (Fig. 3). This supports the

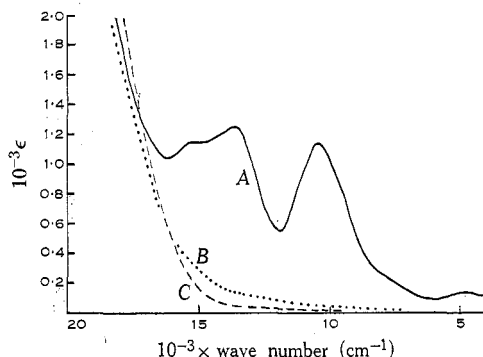


Fig. 3.—Visible and near-infrared spectra in benzene.
A, $[\text{Ru}(\text{SacSac})_3]$;
B, $[\text{Rh}(\text{SacSac})_3]$;
C, $[\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}]$.

generally accepted contention that nitric oxide may function as a "three-electron donor". We regard $[\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}]$ as formally containing the nitrosonium ion coordinated to ruthenium(II) which has a complete t_{2g}^6 subshell. The observed N–O stretching frequency is well within the range recognized for coordinated NO^+ .⁷

Polarographic studies on $[\text{Ru}(\text{SacSac})_2(\text{NO})\text{Cl}]$ in acetone/ Et_4NClO_4 reveal two reversible one-electron reductions at the dropping mercury electrode, at -0.27 V and -1.44 V relative to $\text{Ag}|\text{AgCl}|0.1\text{M LiCl}$ (acetone). In comparison, $[\text{Ru}(\text{SacSac})_3]$ undergoes a one-electron reduction at $+0.04$ V and $[\text{Rh}(\text{SacSac})_3]$ undergoes a two-electron reduction at -1.05 V, both relative to $\text{Ag}|\text{AgCl}$ in acetone.⁸

EXPERIMENTAL

Synthesis

(A) Commercial ruthenium trichloride (1 g, B.D.H., batch No. 008030) and acetylacetone (1.5 ml) were dissolved in ethanol (35 ml) and the resulting crimson solution was added to saturated HCl – EtOH solution (20 ml). Hydrogen sulphide was passed in for 20 min at 0° , then the reaction vessel was left loosely sealed in an ice-bath. After a day, the crude crystalline product (0.6 g) was collected, washed with ethanol, and dried by suction. The compound was recrystallized by addition of ethanol to a hot saturated chloroform solution (Found: C, 27.9; H, 3.6; Cl, 7.4; N, 3.2; Ru, 23.8; S, 29.1. Calc. for $\text{C}_{10}\text{H}_{14}\text{ClNORuS}_4$: C, 28.0; H, 3.3; Cl, 8.3; N, 3.3; Ru, 23.6; S, 29.9%).

An infrared spectrum of the original commercial ruthenium trichloride indicated the presence of some form of coordinated nitric oxide. This problem has been encountered previously, elsewhere.⁹

(B) The preparation was repeated exactly as before using authentic $\text{Ru}(\text{NO})\text{Cl}_3 \cdot \text{H}_2\text{O}$ (1.2 g). The same product was obtained in smaller yield (0.1 g).

⁶ Heath, G. A., and Martin, R. L., *Chem. Commun.*, 1969, 951.

⁷ Johnson, B. F. G., and McCleverty, J. A., *Prog. inorg. Chem.*, 1966, 7, 277.

⁸ Bond, A. M., Heath, G. A., and Martin, R. L., "Polarography in Acetone of Tris(dithioacetylacetonato)-Complexes of Iron(III), Ruthenium(III), Osmium(III), and Rhodium(III)." *J. electrochem. Soc.*, in press.

⁹ Chatt, J., and Shaw, B. L., *J. chem. Soc. (A)*, 1966, 1811.