X-Ray Structure and Characterization of a Novel Dithiocarbamato-complex of Ruthenium(III) Containing a Metal–Metal Bond

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Summary Reaction of tris-(*NN*-diethyldithiocarbamato)-ruthenium(III) [Ru(Et_2dtc)$_3$] with boron trifluoride in benzene solution open to the air gives a dark red benzene-insoluble compound which has been found by *X*-ray crystallography to be $[Ru_2(Et_2dtc)_5]^+BF_4^-$ with two types of bridging dithiocarbamato-ligands.

Recently it has been shown that the *NN*-disubstituted dithiocarbamato-ligand, R_2dtc, can stabilize metals in unusually high oxidation states.[1-5] For example, the reaction of [Fe(R_2dtc)$_3$] complexes, where R = alkyl or aryl, with oxidizing agents such as $Fe(ClO_4)_3{\cdot}6H_2O$ or BF_3 open to the air gives stable cationic complexes of iron(IV)[1,2,4,6] $[Fe(R_2dtc)_3]^+X^-$ where X = ClO_4^- or BF_4^-. These complexes have been characterized by *X*-ray crystallography[2,3] and shown to be monomeric with no indication of ligand oxidation to disulphide species.

The analogous oxidation using boron trifluoride with [M(R_2dtc)$_3$] complexes of cobalt(III), rhodium(III), and ruthenium(III) to give diamagnetic products has been reported.[5] Monomeric tris-chelate complexes of cobalt(IV) (d^5) and ruthenium(IV) (d^4) should be paramagnetic. Osmometric molecular weight determinations on chloroform solutions indicated strong association, up to the tetrameric unit.[5] In addition, a recent polarographic study[7] showed that the one-electron oxidations $[M(Et_2dtc)_3 \rightarrow M(Et_2dtc)_3^+]$ in dimethylformamide of the iron(III) and ruthenium(III) complexes occur at +0·423 and +0·382 V, respectively, *vs.* a saturated calomel electrode. In view of the similarity of these oxidation potentials and the proposed difference in structure of the oxidation products (monomer *vs.* tetramer, respectively), we undertook an *X*-ray investigation of the 'ruthenium(IV)' oxidation product.

BF_3 gas was slowly bubbled through a solution of [Ru(Et_2dtc)$_3$] (*ca.* 0·5 g) in benzene (*ca.* 50 ml), open to the air, for *ca.* 20 s. The dark red oil which separated was washed with benzene and crystallized by slow evaporation from acetone–Et_2O. The dark red crystals of $[Ru_2(Et_2dtc)_5]BF_4$-

C_3H_6O are orthorhombic, space group $Pna2_1$, $a = 18{\cdot}31$, $b = 20{\cdot}68$, $c = 12{\cdot}41$ Å, $D_m = 1{\cdot}55$, $D_c = 1{\cdot}54$ g cm^{-3} for $Z = 4$. 2100 unique non-zero reflections were recorded on a four-circle Hilger and Watts automatic diffractometer using Zr-filtered Mo-K_α radiation. The structure was solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares using absorption-corrected data (μ 10·98 cm^{-1}) to a current R value of 0·089. The acetone of crystallization is disordered and several of the terminal Et_2dtc methyl carbons have large anisotropic thermal motion preventing a good fit to the data.

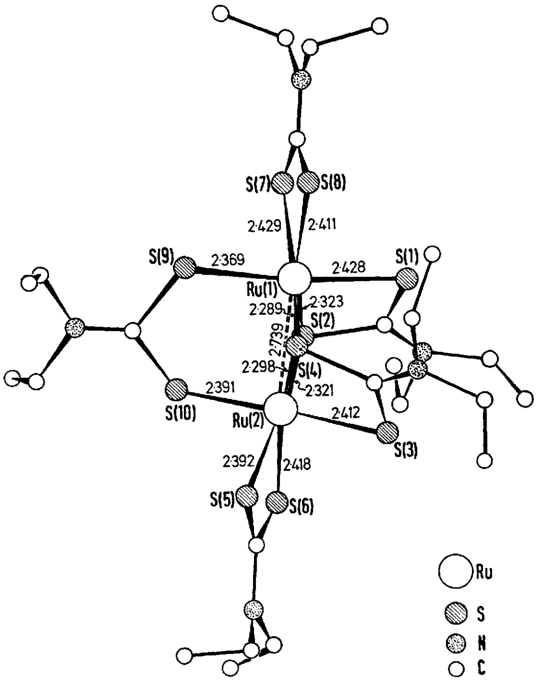

FIGURE. Molecular structure of $[Ru_2(Et_2dtc)_5]^+$. Selected bond lengths are shown in Å and important bond angles (°) are S(1)-Ru(1)-S(2), 73·0; S(7)-Ru(1)-S(8), 72·4; S(3)-Ru(2)-S(4), 74·0; S(5)-Ru(2)-S(6), 72·7.

The molecular structure of the cation is shown in the Figure with selected bond distances and angles. The stoicheiometry and charge of the cation, $[Ru_2(Et_2dtc)_5]^+$, indicate ruthenium in the +3 oxidation state and not Ru(IV) as originally expected. The relatively short Ru–Ru bond (2·74 compared to 2·65 Å in elemental ruthenium) accounts for the diamagnetism of the compound (in $CHCl_3$ solution). The nature of the bridging dithiocarbamato-ligands is novel as no other structures reported to date contain either type of bridging dtc group. However, thioxanthato-ligands are known to bridge isoelectronic iron-(III) atoms[8] in a manner similar to the S(9)–S(10) dtc ligand. The Ru–S distances except those involving S(2) and S(4) are similar to those found in $[Ru(Et_2dtc)]$ [2·38(1)].[9] Those involving S(2) and S(4) are short, with an average value of 2·308 Å.

Conductivity measurements in nitromethane and chloroform and osmometric molecular weight measurements in chloroform (conc. range $2{\cdot}0 \times 10^{-4}$ to $1{\cdot}6 \times 10^{-3}$ M) indicate a one-to-one electrolyte with a molecular weight consistent with the solid state molecular unit (only slight ionic dissociation is observed in chloroform solution by the conductivity results).† These results suggest that the molecular unit in the Figure is maintained in solution.

The formation of the $[Ru^{III}_2\,(dtc)_5]BF_4$ complex rather than $[Ru^{IV}\,(dtc)_3]BF_4$ monomers is surprising. The by-product of the reaction appears to be thiuramdisulphide which is the two-electron oxidation product of two dtc^- ligands.

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† Molecular weight results indicate some molecular association at concentrations greater than 1×10^{-3} M. This has also been observed by Gahan and O'Connor.[5]

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