Tris(dithiocarbamato)metal(IV) Complexes

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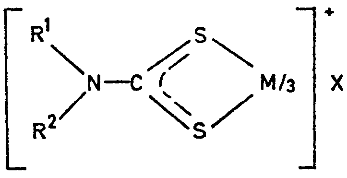
Summary Some diamagnetic tris(dithiocarbamato)metal(IV) tetrafluoroborates (M = Co, Rh, Ru) have been synthesised by the oxidation of the corresponding metal(III) compounds with boron trifluoride; the diamagnetism is probably due to the existence of associated species which are detected by osmometric molecular weight determinations on chloroform solutions of the complexes.

THERE is much interest in the synthesis and properties of the tris-(*NN'*-substituted-dithiocarbamato)metal(IV) species (**1**; R = Me *etc.*). The preparation of a series of Fe^{IV} compounds of type (**1**) (X = BF_4) has recently been reported.[1] I.r. and Mössbauer spectra and magnetic measurements indicate that the compounds have octahedral stereochemistry and contain low-spin Fe^{IV}.

Oxidation of tris(dithiocarbamato)iron(III) complexes with $FeCl_3$ (benzene–ether solution) or $Fe(ClO_4)_3,6H_2O$ (acetone or alcohol) has been shown to give the corresponding Fe^{IV} species ($X = FeCl_4, ClO_4$).[2]



(1)

The large isotropic shifts present in these paramagnetic low-spin Fe^{IV} complexes facilitate the study of structural rearrangements in solution and for (**1**) (M= Fe; R^1 = Me, $R^2 = CH_2Ph$; $X = BF_4$) both geometrical (*cis* ⇌ *trans*) isomerism and inversion of the dissymmetric metal centre is found to be slow on the ^{1}H n.m.r. time-scale at −110°.[3]

We report the isolation of several second-row transition metal(IV) species (M = Rh, Ru) together with some unexpected structural properties which these compounds and the corresponding cobalt(IV) complexes display.

Oxidation of the appropriate tris(dithiocarbamato)metal(III) complex with boron trifluoride in dry toluene or benzene using the previously reported method[1] gives oily products which may be crystallized from suitable organic solvents. The following compounds of type (**1**) ($X = BF_4$) have been characterized: (**1a**) M = Rh; R^1,R^2 = Et, (**1b**) M = Ru; R^1,R^2 = Et, (**1c**) M = Co; R^1,R^2 = Me, (**1d**) M = Co; R^1,R^2 = Et, (**1e**) M = Co; R^1,R^2 = Pr^i, (**1f**) M = Co; R^1,R^2 = cyclohexyl. All compounds show the characteristic shift of ν(C=N) to higher frequency in the i.r. spectrum near 1500 cm^{-1} previously observed in the iron(IV) complexes.[1]

The one-electron oxidation ($E_{\frac{1}{2}}$) values for a series of first-row transition-metal dithiocarbamates have recently been measured in acetone and the results indicate that the electron transfer primarily depends on the metal species and that unusually high oxidation states of these metals, when complexed with the dithiocarbamate ligand, are readily accessible.[4] Another investigation[5] has established that in dimethylformamide with 0·10M-tetraethylammonium perchlorate as supporting electrolyte, tris-(*NN*-diethyldithiocarbamato)metal(III) complexes (M = Co, Ru) undergo one-electron oxidations to the corresponding metal(IV) compounds at +0·949 and +0·382 V, respectively, *vs.* a standard calomel electrode using platinum working electrodes. In the present study we find values of 0·82 and 0·32 V for the corresponding compounds in acetonitrile with 0·1M-sodium perchlorate supporting electrolyte. In addition, the rhodium(III) complex undergoes oxidation ($E_{\frac{1}{2}}$ = 1·06 V) under similar conditions.[6]

Compounds (**1a**—**f**) are all diamagnetic in the solid state.[7] In the absence of spin-exchange the rhodium(IV) complex (d^5 configuration) should be paramagnetic and have one unpaired electron in either a trigonal antiprismatic or trigonal prismatic stereochemical arrangement of the ligands. The iso-electronic cobalt(IV) species might also be expected to be paramagnetic with either one or five unpaired electrons.[3]

Osmometric molecular weight determinations of chloroform solutions of the complexes where ion-pair formation is strongly favoured, show that compounds (**1a**—**f**) are associated over a wide concentration range and the apparent association factor $\bar{n}$ (osmometric mol. wt./mol. wt. of monomer) for (**1a**—**f**) at 3×10^{-2}M stoicheiometric concentration is 3·7, 2·6, 2·6, 2·4, 3·7, and 2·4, respectively. A detailed computer-assisted study[8] of the association of (**1d**) in chloroform indicates that the tetrameric unit is the limiting case. This is strong evidence that the diamagnetism of the compounds is due to the existence of associated species which lead to the pairing of electron spins present in the monomeric units.

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[7] Sufficient amounts for the determination of the solid magnetic moment of (**1b**) by the Gouy method have not yet been obtained, but the compound is found to be diamagnetic in $CHCl_3$ solution using the n.m.r. method for determination of susceptibilities: D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

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