Dimeric Dithio-carbamato Cationic Complexes

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Summary Novel dimers of cobalt(III) with dithiocarbamate ligands $[Co_2(R_2dtc)_5]X$ are described and their properties suggest that the previously reported cobalt(IV) species $[Co(R_2dtc)_3]^+$ may require reformulation.

Recent studies of dithiocarbamates (R_2dtc) have revealed that this ligand is capable of stabilising metal ions in unusually high oxidation states including Cu^{III}, Ni^{IV}, Mn^{IV}, and Fe^{IV}.[1-5] An extension of these reactions to cobalt has led to two reports of a Co^{IV} complex, $Co(R_2dtc)_3BF_4$,[2,6] with unusual properties. We have found that this type of reaction leads to a novel dimer of Co^{III}. The properties previously reported[2,6] for the "$Co(R_2dtc)_3BF_4$" compounds suggest they should be reformulated as the new dimer.

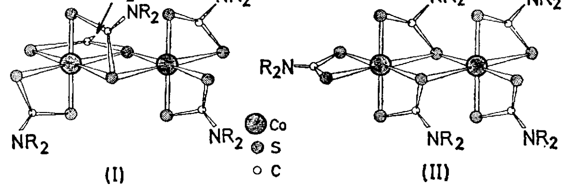
Reaction of benzene solutions of tris-(dithiocarbamato)-cobalt(III) compounds with Et_2OBF_3 in the presence of air or oxygen affords green-brown crystalline complexes which analyse as $[Co_2(R_2dtc)_5]^+BF_4^-$. For five substituent groups: $R_2 = Me_2$; Et_2; pyrrolidyl; Me,Bu^n, and benzyl$_2$; complete analytical data for all elements confirm the basic formulation as $Co(R_2dtc)_{2\cdot5}(BF_4)_{0\cdot5}$, *i.e.*, $Co_2(R_2dtc)_5BF_4$ rather than $Co(R_2dtc)_3BF_4$. Anion exchange by admixture of $NaBPh_4$ and $Co_2(Bu^n,Medtc)_5{}^+BF_4^-$ in ethanol affords the corresponding tetraphenylboron complex, $Co_2(Bu^n,Medtc)_5BPh_4$.

Conductance measurements (nitromethane, 25·0 °C, *ca.* 10^{-3}M) yield the following molar conductance values ($cm^2 M^{-1} ohm^{-1}$) for the complexes $Co_2(R_2dtc)_5BF_4$; $R_2 = Me_2$ (89); Et_2 (85); pyrrolidyl (78); $MeBu^n$ (71); being in accord with the values expected for a 1 : 1 electrolyte in this solvent.[7]

The i.r. spectra (KBr disc, 1600—300 cm^{-1}) of the new compounds are very similar to those of their monomeric precursors. Additional sharp bands at 521 and 532 cm^{-1} and a broad complex band centred at 1070 cm^{-1} confirm the presence of BF_4^-.[8] The only band to show a significant shift in energy is the ν(C–N) band which moves 15—19 cm^{-1} to higher energies in the dimers. Such a shift is generally observed on increasing the oxidation state of the metal (*i.e.* increasing the positive charge shared by a set number of ligands) but in the present example, this shift is ascribed to the decrease in the number of ligands which share the same positive charge. However, the presence of bridging ligands in the dimer may also modify the ν(C–N) frequency.

Electronic spectra (CH_2Cl_2 solutions) show only slight changes in intensities and peak positions in the region 700—320 nm on forming the dimer; *cf.*, $Co(Me_2dtc)_3$ λ (nm), log ε; 641(2·69), 476(2·83), 386(3·92) and $Co_2(Me_2dtc)_5BF_4$, 622(3·09), *ca.* 516(sh), 412(4·14) suggesting that the new compound contains Co^{III} in a similar environment to the tris-(dithiocarbamato)cobalt(III) parent.

The compounds are substantially ion paired in approximately 10^{-3}M solutions of CH_2Cl_2 as determined by vapour pressure osmometry at 25 °C, with $Co_2(Me_2dtc)_5BF_4$ giving a molecular weight of 760, (fully ion-paired, 806; dissociated 403). In contrast, the concentration dependence of the conductance in nitromethane (25·0 °C) between *ca.* 10^{-4} and 2×10^{-2}M shows little evidence of ion-pairing. The experimental molecular weight of this complex in nitromethane (37 °C) is 433 at 0·0179 M. N.m.r. spectra ($CDCl_3$ solutions) of the dimeric cobalt(III) dithiocarbamates, whilst confirming the diamagnetism of the species, are quite complex, and we are unable to distinguish between the possible structures (I) and (II). An *X*-ray crystallographic study of the diethyldithiocarbamate dimer is in progress to resolve this problem.[9] Dithiocarbamate bridged oligomers are to be expected with metals other than cobalt. Thus the rhodium and ruthenium compounds reported by Gahan and O'Connor[6] may also be of the present type.



(I) (II)

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[1] H. C. Brinkhoff, *Rec. Trav. chim.*, 1971, **90**, 377.
[2] E. A. Pasek, and D. K. Straub, *Inorg. Chem.*, 1972, **11**, 259.
[3] R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Austral. J. Chem.*, 1973, **26**, 2533.
[4] A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, 1974, **13**, 1933.
[5] R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Austral. J. Chem.*, 1972, **25**, 2567, and refs. therein.
[6] L. R. Gahan, and M. J. O'Connor, *J.C.S. Chem. Comm.*, 1974, 68.
[7] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.
[8] N. N. Greenwood, *J. Chem. Soc.*, 1959, 3811.
[9] D. Taylor, personal communication.