

## Electron Transfer Behaviour of Dimeric Complexes of Cobalt and Iron with Dithiolate Ligands

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WE report the detection of an electron transfer series involving dimeric complexes derived from 1,2-dithiolate ligands.  $[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]$  is diamagnetic and dimeric in solution<sup>1</sup> and in the solid,<sup>2</sup> where discrete dimers are formed by  $\text{Co} \dots \text{S}$  interactions. We have found that the compound previously reported<sup>1</sup> as  $[\text{FeS}_6\text{C}_6(\text{CF}_3)_6]$  is actually  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$ ; it is isomorphous<sup>3</sup> and presumably isostructural with its cobalt analogue. Polarography of these two complexes in dichloromethane solution reveals two one-electron reductions. The half-wave potentials measured against a silver reference electrode described elsewhere<sup>4</sup> are +1.23, +0.62, and -0.62 v for the iron complex, and +1.24, +0.50, and -0.20 v for the cobalt analogue. We interpret these data to indicate that the dimeric unit remains intact during the first reduction to yield a species  $[\text{MS}_4\text{C}_4(\text{CF}_3)_4]_2^-$ . The second reduction produces the known species<sup>1</sup>  $[\text{MS}_4\text{C}_4(\text{CF}_3)_4]^-$ , which may be monomeric or dimeric. The final reduction produces  $[\text{MS}_4\text{C}_4(\text{CF}_3)_4]^{2-}$  which is already characterized for  $\text{M} = \text{Co}$ .<sup>1</sup> This interpretation is supported by the polarographic behaviour of

$[\text{MS}_4\text{C}_4(\text{CF}_3)_4]^-$ ,  $\text{M} = \text{Co}$  or  $\text{Fe}$ , which both exhibit two oxidative waves of equal diffusion current and a reductive wave of twice this diffusion current. The potentials for these polarographic waves agree with the values obtained from those reductions of the corresponding neutral dimeric complexes.

Two methods of preparation of the  $[\text{MS}_4\text{C}_4(\text{CF}_3)_4]_2^-$  species have been found. Oxidation of  $(\text{Et}_4\text{N})-[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]$  with one-half mole of  $[\text{NiS}_4\text{C}_4(\text{CF}_3)_4]$  yields  $(\text{Et}_4\text{N})[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$  which has a magnetic moment<sup>5</sup> of 2.14 B.M. at 298° K. Reaction of  $(\text{Et}_4\text{N})[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]$  with one-half mole of  $[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]_2$  produces  $(\text{Et}_4\text{N})[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]_2$ . The magnetic moment of 1.91 B.M. at 298° K and the single, broad e.s.r. line at  $\langle g \rangle = 2.043$  observed for this complex indicates that it is not a mixture of the diamagnetic starting materials. The polarography of these new species reveals a one-electron oxidation and a one-electron reduction followed by a two-electron reduction, all at the expected potentials.

Similar dimeric species occur with complexes of the related ligands maleonitriledithiolate ( $\text{MNT}^{2-}$ )

and toluene-3,4-dithiolate (TDT<sup>2-</sup>). Polarography in dichloromethane indicates that  $\text{Co}(\text{MNT})_2^-$  and  $\text{Fe}(\text{MNT})_2^-$  are oxidized to  $[\text{M}(\text{MNT})_2]_2^-$  at +1.08 and +1.16 v, respectively; further oxidation in these series has not been observed.  $\text{Fe}(\text{TDT})_2^-$  is oxidized polarographically to  $[\text{Fe}(\text{TDT})_2]_2^-$  and to  $[\text{Fe}(\text{TDT})_2]_2^0$  at +0.17 v and +0.48 v. Oxidation of  $(\text{Bu}_4\text{N})-[\text{Fe}(\text{TDT})_2]$  with one-quarter mole of  $\text{I}_2$  has yielded  $(\text{Bu}_4\text{N})[\text{Fe}(\text{TDT})_2]_2$  with  $\mu = 3.48$  B.M. at 298° K. These studies indicate that four-membered electron transfer series exist for cobalt and iron complexes with two dithiolate ligands. The two most oxidized members contain the dimeric unit originally found in  $[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]_2$ . With cobalt the most reduced member is a planar

monomer as evidenced by the crystal structure of  $(\text{Bu}_4\text{N})_2\text{Co}(\text{MNT})_2$ ,<sup>6</sup>  $[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]^-$  and  $\text{Fe}(\text{MNT})_2$ , which exhibit magnetic moments that are low for one unpaired electron and which decrease with decreasing temperature, must be associated to some extent in the solid state.

The magnetic properties of these unusual dimeric species are under investigation. The magnetic moments of  $(\text{Bu}_4\text{N})[\text{Fe}(\text{TDT})_2]_2$ ,  $\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$ ,  $(\text{Et}_4\text{N})[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]_2$ , and  $(\text{Et}_4\text{N})-[\text{FeS}_4\text{C}_4(\text{CF}_3)_4]$  decrease with decreasing temperature and deviate greatly from Curie-Weiss behaviour. The susceptibility of  $(\text{Et}_4\text{N})[\text{CoS}_4\text{C}_4(\text{CF}_3)_4]_2$  exhibits apparent Curie-Weiss behaviour but has a Weiss constant of  $\sim 25^\circ$ .

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<sup>1</sup> A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.

<sup>2</sup> J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, 1965, **4**, 1729.

<sup>3</sup> J. H. Enemark, Harvard University, private communication.

<sup>4</sup> F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, in the press.

<sup>5</sup> All magnetic data refer to the dimeric unit.

<sup>6</sup> J. D. Forrester, A. Zalkin, and D. Templeton, *Inorg. Chem.*, 1964, **3**, 1500.