Iron and Cobalt Nitrosyl 1,2-Dithiolenes

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MCDONALD and his co-workers[1] have presented e.s.r. evidence for the existence of $[Fe(NO)S_4C_4(CN)_4]^{2-}$ and $[Fe(NO)(S_2C_6H_4)_2]^{2-}$ in solution but did not isolate the solid complexes. We have now obtained these as crystalline tetra-alkylammonium or tetra-arylphosphonium salts and have confirmed their formulation. However, during our studies of these dianions, we discovered a new series of mononitrosyls which are related by one-electron transfer reactions.

In general, iron 1,2-dithiolene[2] systems, $[FeS_4C_4R_4]_2^z$,[3] where $z = 0$ and R = Ph or CF_3, or $z = -2$ and R = CN or CF_3, and $[Fe(TDT)_2]_2^{2-}$,[4] readily absorb NO in solution, and crystalline solids can be isolated on precipitation with heavy organic cations (where appropriate).[5] The complexes most easily obtained are diamagnetic *monoanions* which have the simplified empirical formula $[Fe(NO)S_4]^-$. Polarographic studies[7] show that these can be reduced (some reversibly) to the

TABLE

NO *Stretching frequencies in iron and cobalt* 1,2-*dithiolenes*

Complex	Cation	ν_{NO} (cm.$^{-1}$)	Solvent
$[Fe(NO)S_4C_4(CN)_4]^{2-}$	Et_4N^+	1650	CH_2Cl_2
$[Fe(NO)S_4C_4(CN)_4]^-$	Et_4N^+	1837	CH_2Cl_2
$[Fe(NO)S_4C_4Ph_4]^{2-}$	Et_4N^+	1620	HCBD
$[Fe(NO)S_4C_4Ph_4]^-$	Et_4N^+	1770	CH_2Cl_2
$[Fe(NO)S_4C_4Ph_4]^0$		1805	$CHCl_3$
$[Fe(NO)(TDT)_2]^{2-}$	Ph_4P^+	1620	KBr
$[Fe(NO)(TDT)_2]^-$	Ph_4P^+	1790	KBr
$[Fe(NO)S_4C_4(CF_3)_4]^-$	Ph_4P^+	1820	$CHCl_3$
$[Fe(NO)S_2C_2Ph_2]_2^-$	Et_4N^+	1713, 1743	KBr
$[Fe(NO)S_2C_2Ph_2]_2^0$		1775, 1820	$CHCl_3$
$[Co(NO)S_4C_4(CN)_4]^{2-}$	Ph_4P^+	1607	$CHCl_3$
$[Co(NO)S_4C_4(CN)_4]^-$	Ph_4P^+	1692	KBr
$[Co(NO)S_4C_4(CF_3)_4]^-$	Ph_4P^+	1630	Nujol

dianions, $[Fe(NO)S_4-]^{2-}$ and, in some cases, reversibly oxidised to $[Fe(NO)S_4-]^0$.

The *dianions*, $[Fe(NO)S_4C_4R_4]^{2-}$, where R = CN and Ph, and $[Fe(NO)(TDT)_2]^{2-}$, are paramagnetic as expected[1] (one unpaired electron) and, except when R = CN, are extremely unstable towards air in solution, being reoxidised to the monoanions. Their e.s.r. spectra are very similar to each other (a triplet due to ^{14}N hyperfine interaction), and to the results obtained by McDonald *et al.*[1]

Chemical oxidation of $[Fe(NO)S_4C_4Ph_4]^-$, or treatment of $[FeS_4C_4Ph_4]_n^0$ with NO in dichloromethane, affords the *neutral* complex $[Fe(NO)S_4C_4Ph_4]^0$. This compound is paramagnetic (one unpaired electron) and exhibits a single line in its e.s.r. spectrum; ^{14}N hyperfine interactions were not observed in solution or glass spectra. Chemical reduction to the monoanion is easily achieved. A further compound, $[Fe(NO)S_2C_2Ph_2]_2$, possibly similar to $[Fe(NO)S_2C_2(CF_3)_2]_2$ reported by King,[7] is obtained from the reaction between NO and $[FeS_4C_4Ph_4]_n^0$. Reduction (irreversible) of this results in the formation of a dimeric monoanion, $[Fe(NO)S_2C_2Ph_2]_2^-$, which also is paramagnetic (one unpaired electron).

Dicyano- and bisperfluoromethyl-1,2-dithiolene complexes of cobalt absorb NO forming mononitrosyls, $[Co(NO)S_4C_4R_4]^z$, where $z = -1$ when R = CN or CF_3, and $z = -2$ when R = CN. It is clear from polarographic studies that these complexes behave similarly to their iron analogues. The cobalt *monoanions* are paramagnetic (one unpaired electron) and are unstable in solution, gradually losing NO. However, they exhibit eight-line e.s.r. spectra (^{59}Co, $I = 7/2$) at room temperature but ^{14}N hyperfine interactions were not observed, even in glass spectra at ~100°K. The *dianion* (R = CN) is diamagnetic.

The "monoanionic" complexes $[Bu_4^nN]$ $[MS_4C_4(CN)_4]$, where M = Fe or Co, and $[Bu_4^nN]$ $[Fe(TDT)_2]$ are dimeric,[8] containing two sulphur-bonded five-co-ordinate metal atoms. Preliminary physical measurements in solution indicate that the nitrosyl monoanions and $[Fe(NO)S_4C_4Ph_4]^0$ are probably dimeric, with NO acting as the sixth ligand on each metal atom.

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[1] C. C. McDonald, W. D. Phillips, and H. F. Mower, *J. Amer. Chem. Soc.*, 1965, **87**, 3319.

[2] We prefer the general name "1,2-dithiolene" for ligands of the type $(S_2C_2R_2)$ described in this Communication since it does not imply a particular ligand structure or valence formalism.

[3] It is not known whether $[FeS_4C_4Ph_4]^0$ is a dimer or polymer.

[4] TDT = toluene-3,4-dithiol.

[5] All compounds analyse satisfactorily for C, H, N, and S. Conductivities were measured in nitromethane, nitrobenzene, or acetone and molecular weights were obtained either osmometrically or cryoscopically.

[6] In DMF using a dropping-mercury electrode.

[7] R. B. King, *Inorg. Chem.*, 1963, **2**, 1275.

[8] A. Davison and R. H. Holm, personal communication; I. Bernal, personal communication.