Dinuclear Iron Nitrosyl Diphenyl-dithiolenes

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IN the reaction between $[FeS_4C_4Ph_4]_2^0$ and NO in cold chloroform, two compounds are formed: the well-characterised brown paramagnetic monomer $[Fe(NO)S_4C_4Ph_4]^0$,[1,2] and a purple diamagnetic crystalline compound, (I). We previously[1] formulated (I) as $[Fe_2(NO)_2S_4C_4Ph_4]^0$ on the basis of (incomplete) elemental analyses, molecular weight data obtained osmometrically in dichloromethane, and by analogy with $[Fe_2(NO)_2S_4C_4(CF_3)_4]^0$.[3] In a similar reaction between $[FeS_4C_4Ph_4]_2^0$ and NO in benzene, Schrauzer and his colleagues[4] reported the formation of the five-co-ordinate monomer and a violet species, (II), described as $[Fe_3(NO)_2S_6C_6Ph_6],C_6H_6,C_6H_{12}$.† In view of the apparent similarity between the preparations of (I) and (II), and because $[Fe_2(NO)_2S_4C_4(CF_3)_4]^0$ was reformulated[5] as a mixture, one component of which was $[Fe_3(NO)_3S_6C_6(CF_3)_6]^0$, we have re-examined (I)

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† The cyclohexane was used in chromatography of the reaction product obtained from benzene.

and (II) in order to establish their relationship to one another and whether they are di- or tri-nuclear iron species.

On the basis of an *X*-ray molecular weight determination and total elemental analyses, we find that (I) is a dinuclear iron complex, $[Fe_2(NO)_2S_6C_6Ph_6],CHCl_3$.‡ A repetition of the reaction reported to give (II) afforded, in our hands, a complex having an identical infrared spectrum to (I), although the compound clearly contained hydrocarbon solvent of crystallisation. We conclude from the analyses, electronic and infrared spectral data that (I) and (II) are dinuclear iron complexes which are identical but for the solvent of crystallisation. Voltammetric reduction of (I)§ revealed the existence of two well-defined one-electron reduction waves presumably corresponding to the generation of $[I]^{-1}$ and $[I]^{-2}$. Borohydride reduction of (I) in acetone afforded a green paramagnetic ion (one unpaired electron), previously described as $[Fe_2(NO)_2S_4C_4Ph_4]^{-1}$ but which now must be formulated as $[Fe_2(NO)_2S_6C_6Ph_6]^{-1}$; analytical, voltammetric, and spectral data are consistent with this formulation. Full details of these compounds, and of other unusual nitrosyl dithiolenes obtained from them, will be presented in full shortly.

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‡ Molecular weights of this compound determined osmometrically and ebullioscopically in chloroform and dichloromethane give results consistent with a formulation of (I) as $[Fe_2(NO)_2S_4C_4Ph_4]$ suggesting, possibly, that dissociation of (I) occurs in solution.

§ Voltammetry carried out in dichloromethane solution using a rotating platinum electrode, Et_4NClO_4 as supporting electrolyte. Reduction waves occur at −0·21 v and −0·84 v against a saturated calomel electrode 1M in LiCl.

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