Enhancement of the Magnetic Susceptibility of an Organic Complex

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The magnetic properties of [1,2-di(4-pyridinio)ethylene]$_x^{2x+}$[1,2-di(4-pyridyl)ethylene]$_{1-x}$(7,7,8,8-tetracyano-*p*-quinodimethane)$_3^{2x-}$, $(H_2DPE)_x^{2x-}(DPE)_{1-x}(TCNQ)_3^{2x-}$, are dependent upon the stoicheiometry: for $x > ½$ the susceptibility decreases with increasing values of x whereas for $x \approx ½$ it is enhanced above the Curie law value.

The quest for molecular *ferri*magnets by Kahn[1] and *ferro*magnets by Miller and Epstein[2] has provided some interesting organometallic examples. Several exotic organic radicals have also been studied but, to date, only two organic ferromagnets have been reported.[3,4] Torrance *et al.*[3] have observed ferromagnetic behaviour in some batches of poly-*s*-triaminobenzene whereas Korshak *et al.*[4] have obtained a low yield of ferromagnetic particles from the polymerisation of 1,4-bis(2,2,6,6-tetramethyl-4-hydroxy-4-piperidyl-1-oxyl)butadiyne. Nevertheless, there is a burgeoning interest in magnetic materials and in this work we show that antiferromagnetic interactions in $(H_2DPE)_x^{2x+}(DPE)_{1-x}(TCNQ)_3^{2x-}$ may be suppressed by spin dilution [DPE = 1,2-di(4-pyridyl)ethylene; TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane].

Black microcrystalline samples were obtained by the reaction of H_2DPE dichloride, Li^+TCNQ^-, and neutral TCNQ (1 : 2 : 1 mole ratio) in acetonitrile and by crystallising the product from a solution of DPE and TCNQ (1 : 3 mole ratio). Recrystallisation gave homogeneous samples of $(H_2DPE)_x^{2x+}(DPE)_{1-x}(TCNQ)_3^{2x-}$ with $0.2 < x < 0.9$. The overall stoicheiometry of 1 : 3 was determined initially by elemental analysis and confirmed by *X*-ray crystallography.[5] The ratio of $TCNQ^-$ to $TCNQ^0$ (and, thus, H_2DPE^{2+} to DPE^0) was determined spectrophotometrically from the ratio of the molar absorption coefficients at 395 and 842 nm.

The magnetic susceptibility was determined by the Faraday method and corrected for core diamagnetism using Pascal's constants. The properties are dependent upon the charge density on the TCNQ lattice which for $(H_2DPE)_x^{2x+}$-$(DPE)_{1-x}(TCNQ)_3^{2x-}$ can be readily varied. Several batches were investigated and the stoicheiometric variation of the susceptibility is shown in Figure 1a. For $x > 1/2$, the ratio χ (300 K)/χ (Curie law) is less than unity and decreases with increasing values of x, whereas for $x \approx 1/2$ the susceptibility is enhanced above the spin-1/2 Curie law value, there being a spread of values but with nearly all showing enhanced magnetic behaviour. The highest value observed was χ (300 K) = 0.01 emu mol^{-1} [χ (300 K) = 8 χ (Curie law)]. Analysis by atomic absorption spectroscopy has confirmed that the samples were free of inorganic ferromagnetic contaminants and, thus, that the observed enhancement is genuine.

The properties may be partially understood by considering

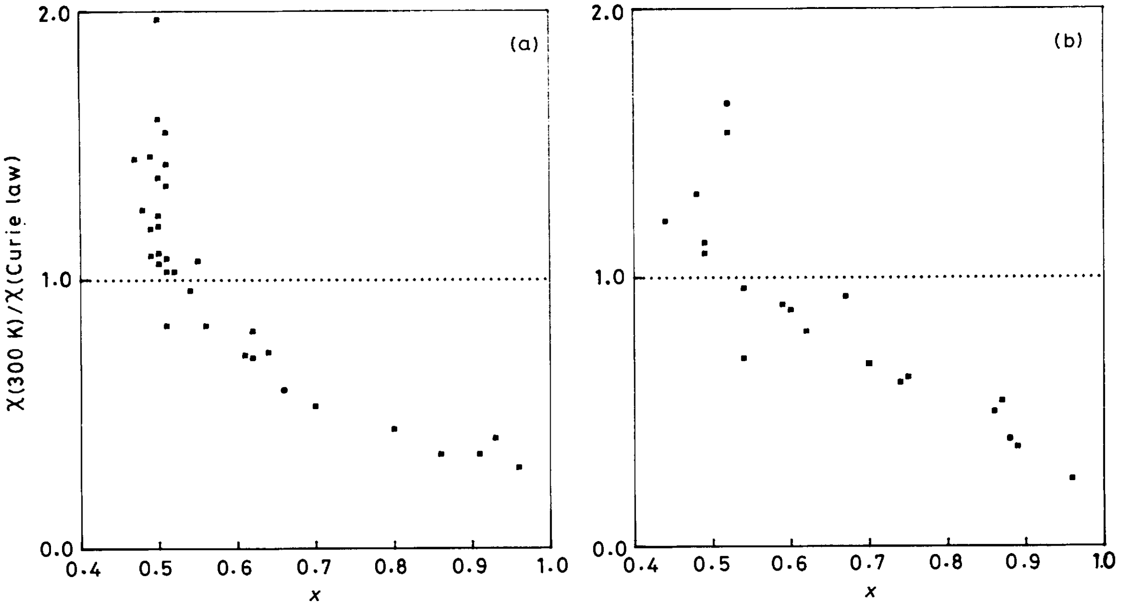

Figure 1. Stoicheiometric dependence of the reduced susceptibilities of (a) $(H_2DPE)_x{}^{2x+}(DPE)_{1-x}(TCNQ)_3{}^{2x-}$ and (b) $(H_2DPA)_x{}^{2x+}(DPA)_{1-x}(TCNQ)_3{}^{2x-}$. For clarity two samples with χ (300 K)/χ (Curie law) = 8 have been omitted from (a). The Curie law value is given by $2N\mu_B{}^2g^2S(S+1)/3kT$, where $S = 1/2$.

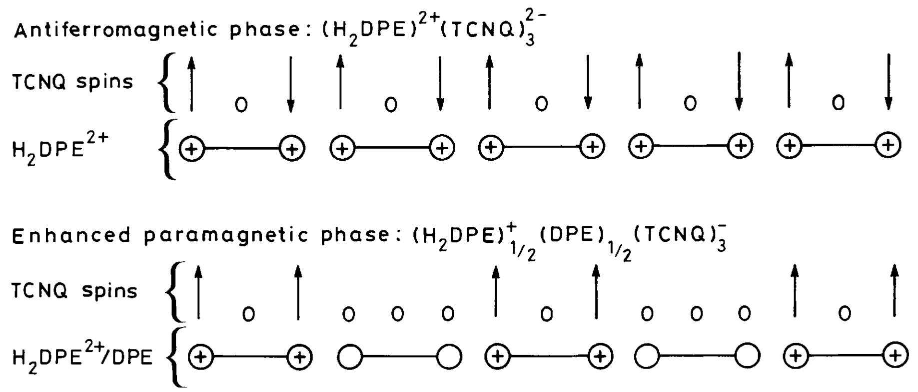

Figure 2. Schematic representation of the charge distribution in the 1 : 3 salt. Radical spins and neutral molecules are indicated by arrows and open circles respectively. In $(H_2DPE)_{1/2}{}^+(DPE)_{1/2}(TCNQ)_3{}^-$ ferromagnetic exchange occurs *via* the extended π-system of the TCNQ stacks.

the charge distribution on the TCNQ lattice. $(H_2DPE)_x{}^{2x+}$-$(DPE)_{1-x}(TCNQ)_3{}^{2x-}$ is one of an isostructural series of twelve known salts[6] in which the TCNQ units stack in columns, with uniform interplanar spacing, in a direction parallel to the length of the dication. As the positive charges are at opposite ends of the H_2DPE^{2+} cation, with little or no delocalisation onto the ethylene bridge, we assume that the negative charges are predominantly localised on the peripheral TCNQ molecules of the ionic formula unit (Figure 2). Spins on adjacent TCNQ sites couple antiferromagnetically and, thus, the susceptibility of $(H_2DPE)^{2+}(TCNQ)_3{}^{2-}$ is low, whereas in $(H_2DPE)_{1/2}{}^+(DPE)_{1/2}(TCNQ)_3{}^-$, neutral TCNQ units separate the spins and the susceptibility increases with decreasing x. For the optimum stoicheiometry, $x \approx 1/2$, the data imply that the neutral and ionic units alternate, in regions at least, causing the antiferromagnetic coupling to be suppressed and the susceptibility is enhanced above the expected Curie law value of 1.25×10^{-3} emu mol^{-1} at 300 K for a well developed spin-1/2 system (see Figure 1). The enhancement can be explained if we assume that medium-range interactions along the extended π-lattice correlate the radical spins parallel to each other, within and also between next-nearest-neighbouring formula units. The variation of the susceptibility probably arises from differences in the homogeneity of the samples, those showing greatest enhancement being closest to the regular alternating structure.

Few molecular ferromagnets are known and $(H_2DPE)_{1/2}{}^+(DPE)_{1/2}(TCNQ)_3{}^-$ is the first completely organic salt to show a reproducible, albeit variable, enhancement of the room temperature susceptibility. A preliminary investigation of the 1,2-di(4-pyridyl)ethane congener, $(H_2DPA)_x{}^{2x+}(DPA)_{1-x}(TCNQ)_3{}^{2x-}$, has revealed that its susceptibility is also dependent upon spin density (Figure 1b) and is enhanced above the Curie law value when $x \approx 1/2$. This suggests that the technique employed may be applicable to other systems.

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References

1 O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834; Y. Pei, O. Kahn, and J. Sletten, *J. Am. Chem. Soc.*, 1986, **108**, 3143; Y. Pei, M. Verdaguer, O. Kahn, J. Sletten, and J.-P. Renard, *ibid.*, 1986, **108**, 7428; O. Kahn, in 'Organic and Inorganic Low-dimensional Crystalline Materials, NATO ASI Series B,' eds. P. Delhaes and M. Drillon, Plenum Press, New York, 1987, p. 93; O. Kahn, Y. Pei, M. Verdaguer, J.-P. Renard, and J. Sletten, *J. Am. Chem. Soc.*, 1988, **110**, 782; O. Kahn, *J. Chim. Phys.*, 1988, **85**, 1113.

2 J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769; J. S. Miller and A. J. Epstein, *ibid.*, 1987, **109**, 3850; S. R. Chittipeddi, A. J. Epstein, J. H. Zhang, W. M. Reiff, I. Hamberg, D. B. Tanner, D. C. Johnson, and J. S. Miller, *Synth. Metals*, 1987, **19**, 731; J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201; *Science*, 1988, **240**, 40; *Acc. Chem. Res.*, 1988, **21**, 114; A. J. Epstein, S. Chittipeddi, A. Chakroborty, and J. S. Miller, *J. Appl. Phys.*, 1988, **63**, 2952; W. M. Reiff, *ibid.*, 1988, **63**, 2957; J. H. Zhang, W. M. Reiff, and J. S. Miller, *Hyperfine Interactions*, 1988, **42**, 1099.

3 J. B. Torrance, S. Oostra, and A. Nazzal, *Synth. Metals*, 1987, **19**, 709.

4 Yu. V. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, and V. N. Spector, *Nature*, 1987, **326**, 370.

5 G. J. Ashwell, A. T. Fraser, and P. J. Martin, 'Proceedings of the Materials Research Society Symposium on Electrical, Optical and Magnetic Properties of Organic Solid State Materials,' Boston, 1989.

6 G. J. Ashwell, S. C. Wallwork, and P. Rizkallah, *Mol. Cryst. Liq. Cryst.*, 1983, **91**, 359; G. J. Ashwell, 'Prace Nauk Instytutu Chemii Organicznej Fizycznej Politechniki Wroclawskiej, Seria Monografie, No. 31,' 1986.