Triplet Excitons in Fremy's Salt

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Summary Evidence for a thermally accessible triplet state in Fremy's salt is described, including measurements of the zero-field splitting, the temperature dependence of the magnetic susceptibility, and the singlet–triplet energy gap.

Several authors have inferred the diamagnetic nature of the yellow-orange salt $K_4[(SO_3)_2NO]_2$ (Fremy's salt),[1–4] and attributed this to dimerization of monomeric nitrosodisulphonate ions in the salt. The most recent of these reports provides evidence for the existence of two distinct crystalline forms of Fremy's salt at room temperature.[4] Our observations are restricted to the yellow-orange modification of Fremy's salt (**1**) described therein.

We have noted that the colour of (1) changes from yellow-orange (20°) to brown-orange (100°). We find that the colour change is reversible, and presumably arises from a change in the electronic configuration of (**1**). An excited state has been detected by e.s.r. and static magnetic susceptibility measurements.

At low temperature, powdered samples of (**1**) show a weak, complex spectrum near $g = 2$, which is attributed to monomeric nitrosodisulphonate ions with $S = 1/2$. With increasing temperature, this spectrum decreases in intensity, but additional absorptions extending over thousands of Gauss appear and grow in intensity. These changes are reversible.

The e.s.r. spectrum of a powdered sample of (**1**) at 363 K is shown in Figure 1. The three pairs of absorptions (X, Y, and Z) centred about $g = ca.$ 2 are ascribed to dimeric nitrosodisulphonate ions with $S = 1$, orientated with the three distinct principal axes of the zero-field splitting tensor lying, respectively, along the external magnetic field.[5] Assuming an isotropic g tensor with $g = 2{\cdot}0023$, the zero-field splitting parameters D and E are $\pm 0{\cdot}0746$ ($\pm$ 0·0005) and $\mp 0{\cdot}0044$ ($\pm 0{\cdot}0002$) cm^{-1}, respectively, and are temperature independent (290—390 K) within the experimental error. The zero-field splitting parameter $(D^2 + 3E^2)^{1/2}$ is $\pm$ 0·0776 cm^{-1} as calculated[5,6] from the position of H_{min} (Figure 1), $\nu = 9{\cdot}315$ GHz. The residual monomer obscures the observation of any double quantum transition in the $g = 2$ region.

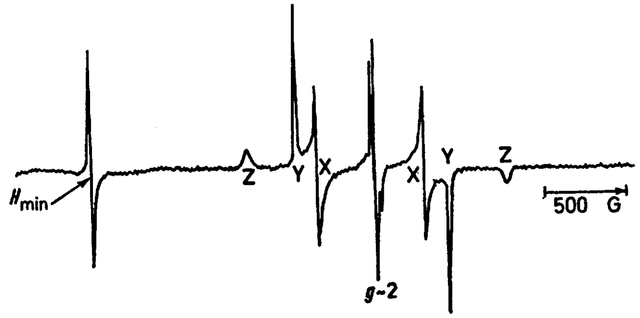

FIGURE 1. *X-band first derivative e.s.r. spectrum of a powdered sample of* (**1**) *at* 363 K.

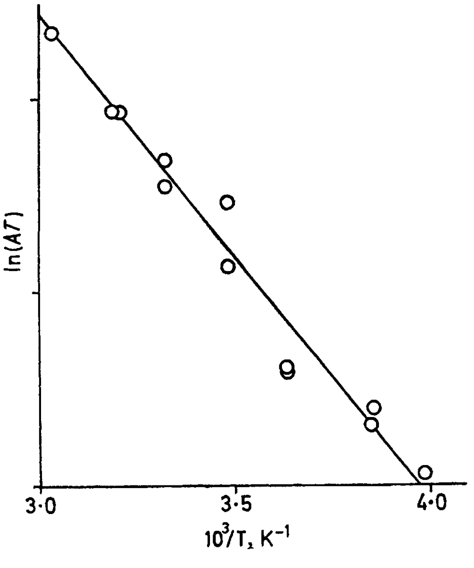

FIGURE 2. *Temperature dependence of the absorption area A (in arbitrary units) of the half-field transition of a powdered sample of* (**1**).

We have measured the temperature dependence of the absorption area A of the half-field transition, and find that it increases exponentially with temperature. Here A is proportional to the static magnetic susceptibility, and is taken to be of the form[6,7] $CT^{-1}[3 + \exp(E_j/kT)]^{-1}$. The relation assumes that the singlet-triplet energy gap E_j is independent of temperature and that interaction between neighbours is negligible. With the approximation $[3 + \exp(E_j/kT)] \simeq \exp(E_j/kT)$, the data plotted in Figure 2 gave a value of $0{\cdot}27 \pm 0{\cdot}01$ eV for E_j.

Moreover, the exponential population growth of the paramagnetic excited state with temperature was observed by static magnetic susceptibility measurements (Faraday method) for two independently prepared powdered samples of (1), as shown in Figure 3. For the above approximated relation, E_a is $0{\cdot}27 \pm 0{\cdot}01$ and $0{\cdot}23 \pm 0{\cdot}01$ eV for these data. The observed molar diamagnetic correction of (**1**) is $-194 \pm 4 \times 10^{-6}$ c.g.s. units.

To our knowledge there are no previous examples of inorganic salts with a thermally accessible triplet state.

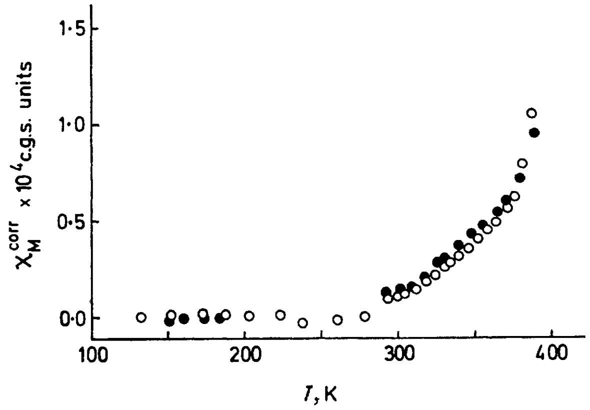

FIGURE 3. *Temperature dependence of the corrected molar susceptibility for two independently prepared powdered samples of* (**1**).

We thank Drs. J. A. Weil and R. C. G. Claridge for their helpful criticisms and suggestions in the preparation of this manuscript, and the National Research Council of Canada for a Scholarship (to B.D.P.) and for financial support.

(*Received, November 2nd,* 1971; *Com.* 1906.)

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[1] A. Hantzsch and W. Semple, *Ber.*, 1895, **28**, 2744.

[2] R. W. Asmussen, *Z. anorg. Chem.*, 1933, **212**, 317.

[3] D. L. Fillmore and B. J. Wilson, *Inorg. Chem.*, 1968, **7**, 1592.

[4] W. Moser and R. A. Howie, *J. Chem. Soc.* (*A*), 1968, 3039.

[5] M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, 1963, **6**, 545.

[6] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, 1961, **35**, 1002.

[7] D. Bijl, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.*, 1959, **30**, 765.