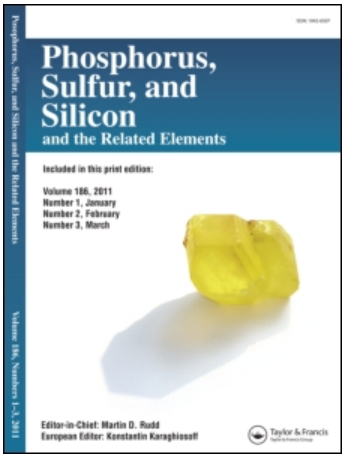

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Recent Studies on the Magnetic Behaviour of Thiazyl Radicals: Methyl-Benzodithiazolyl

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The title radical (MBDTA) is characterised by X-ray diffraction and solid state magnetic measurements. It exhibits very strong antiferromagnetic exchange interactions which are modelled using an expression for a two-dimensional Heisenberg square-lattice.

Keywords: thiazyl radical; dithiazolyl; organic magnet; bistability

INTRODUCTION

For some time we have been interested in developing thiazyl radicals as organic ('metal free') magnets.[1] We have focused on a particular family of thermally stable π radicals isoelectronic with the $S_3N_2^{+\bullet}$ ring (Scheme 1).[1] Initial results on the dithiadiazolyl radicals (DTDA) indicated that high magnetic ordering temperatures may be achieved[2] but the large majority tend to associate as closed shell, diamagnetic, dimers in the solid state.[3] In order to inhibit dimerisation we have begun to investigate the

related dithiazolyl radicals (DTA) in which the dimerisation energy has been estimated[4] at *ca.* 0 kJmol^{-1} (*cf* DTDA at *ca.* 35kJmol^{-1})[3].

DTDA DTA

SCHEME 1 The isoelectronic radicals DTDA, $S_3N_2^{+\bullet}$ and DTA

RESULTS

We instigated research in the area of DTA radicals by a re-examination of methyl-benzodithiazolyl (MBDTA), first reported by Wolmershauser in 1984. The radical was reported[5] to be paramagnetic, but no structural data was presented.

Synthesis and structure

MBDTA was prepared according to the literature method[5] and crystals were isolated by vacuum sublimation. The structure[6] of MBDTA and a packing diagram in the *bc* plane are shown in Figure 1.

EPR Studies

Room temperature EPR studies on MBDTA in CH_2Cl_2 solution exhibit a well-defined 1:1:1 triplet due to coupling to the unique N

atom (Fig. 2). No additional hyperfine coupling to the aromatic H atoms was resolved, indicating considerable spin density on the heterocyclic ring.

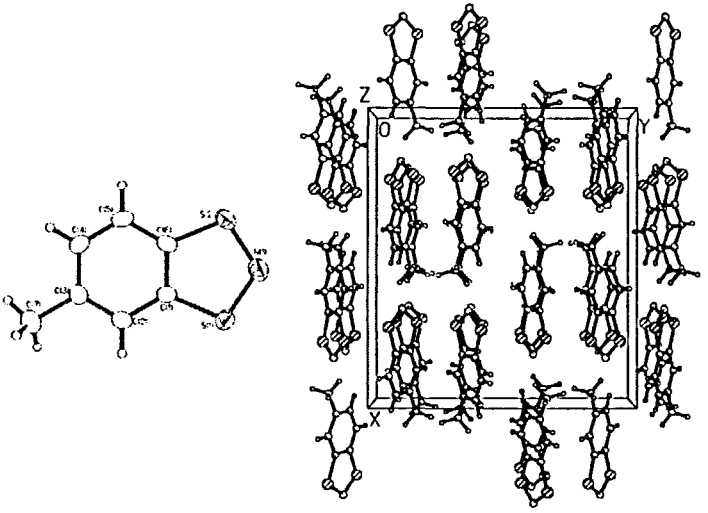

FIGURE 1 Molecular and crystal structure of MBDTA[6]

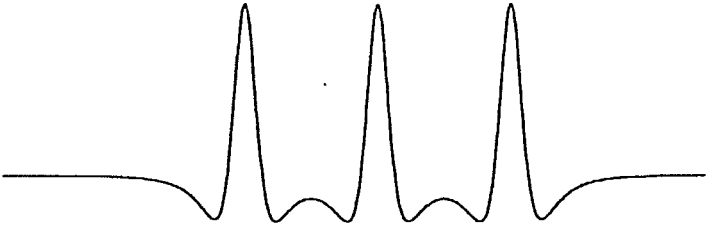

FIGURE 2 Second derivative solution X-band EPR spectrum of MBDTA in CH_2Cl_2 at 298 K ($g = 2.003$, $a_N = 11.4G$)

Magnetic Properties

The room temperature effective magnetic moment of MBDTA is *ca.* 1.3 B.M., a little lower than that anticipated for an S = ½ paramagnet. The molar susceptibility, χ, of MBDTA passes through a broad maximum at 140 K (Fig. 3), indicative of the onset of short range antiferromagnetic order. There is no evidence[6] to indicate long range magnetic order down to 1.8K.

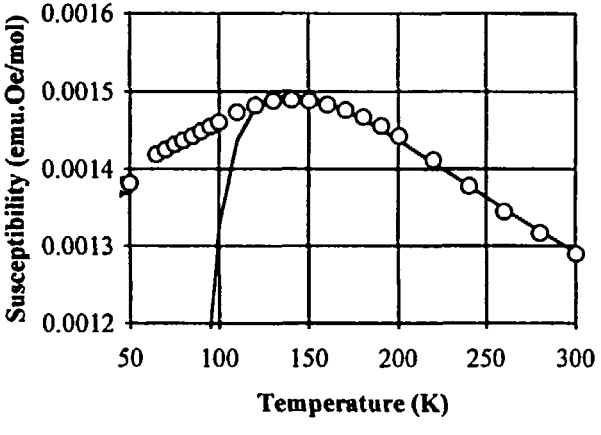

FIGURE 3 Variation of χ as a function of temperature for MBDTA. The solid line represents the fit to a two-dimensional Heisenberg square lattice of S = ½ spins.

DISCUSSION

A likely mechanism for magnetic exchange between MBDTA radicals in the solid state is the McConnell I mechanism;[7] Direct

exchange between regions of positive unpaired spin density leads to antiferromagnetic coupling between neighbouring molecules. [Interactions between areas of positive and negative spin density, caused by spin polarisation, gives rise to ferromagnetic exchange].

EPR studies, coupled with theoretical calculations, indicate that the unpaired spin density resides in a π^* orbital predominantly localised on the heterocyclic ring. As a consequence, the magnetic exchange pathway is dominated by exchange interactions through the close intermolecular S...S heterocyclic contacts in the *bc* plane [3.7-3.8Å].[6] Since S atoms exhibit regions of positive spin density then this interaction is antiferromagnetic. However, the large separation of these antiferromagnetically coupled layers along the *a* axis precludes the observation of long range order. Indeed a fit of the high temperature data to a high temperature series expansion for a square lattice of Heisenberg S=½ spins[8] predicts both the position and height of the maximum in the susceptibility extremely well. The best fit yielded an exchange constant of -72 K.

CONCLUSION

Whilst MBDTA does not exhibit long range order, the magnetic interaction observed is exceptionally strong. Exchange interactions of this magnitude can be anticipated to give rise to ordering temperatures of the order of 10^2 K, close to or above room temperature. However, in order to achieve this goal a three-dimensional network of interactions needs to exist which will

facilitate long range order. This will require considerable control of solid state structure and/or more delocalisation of the spin density onto the heterocyclic ring so that exchange interactions can be propagated in all three dimensions. We are currently investigating these possibilities.

ACKNOWLEDGEMENTS

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