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Magneto-structural Correlations of the Antiferromagnetic Interaction in Bis(maleonitrile dithiolato) Nickel(III) Ion-radical Salts – R^+ Ni mnt_2^-

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Abstract

We have studied some R^+ Ni mnt_2^- compounds where the Ni mnt_2^- units, which are $S = ½$ systems, stack as dimers in the solid state. The variations of the cations R^+ lead to small changes in the packing in the crystal and, thus, to variations in the antiferromagnetic couplings which are very sensitive to these changes. We have carried out extended Hückel molecular orbital calculations with the structural parameters known from crystal structure data on this series of compounds, and tried to relate the magnetic interactions as measured by susceptibility with the splitting between the pair of highest occupied molecular orbitals. We have come across a wide variety of overlapping patterns in this series and, on the basis of MO results, we expect examples ranging from almost uniform chains to almost isolated dimers. Due to the extensive delocalisation of the unpaired electron density over the ligand framework and the plane-to-plane type overlap within a dimeric unit, many short contact distances between various atoms play important roles as super exchange pathways. Hence, any attempt to arrive at correlations between magnetic data and a few structural parameters, such as interplanar distance, bridging' angle and 'bridging' distance, is doomed to failure.

Introduction

The bis dithiolenes (bdt) complexes (Fig. 1) are a well-studied class of coordination compounds known for their planar geometry, highly delocalised electronic structure, reversible electron transfer behavior and ability to form stacked structures in the solid state, resulting in extended orbital interactions along one direction in the crystal. Hence, they exhibit interesting anisotropic magnetic, electronic and structural characteristics.

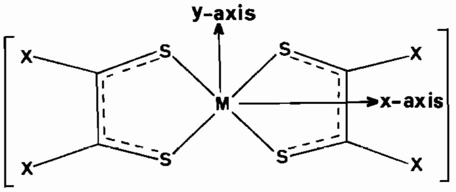

Fig. 1. Molecular structure of the bis(ethylene-1,2-dithiolene) metal complexes, where M can be a variety of elements from the d transition series, X can be various ligand substituents such as H, CH_3, C_6H_5, CF_3, CN etc., R^+ is an organic or inorganic cation and n = 0,1,2.

In this work, we are primarily interested in the correlation of the antiferromagnetic interaction between Ni mnt_2^- units (x = CN, n = 1 and M = Ni in Fig. 1), which are square-planar, formally d^7 Ni(III) systems having one unpaired electron; their structural details are known from crystallographic and electronic structural studies. An earlier study [2] dealt with the solid state magnetic properties of NEt_4^+ Ni mnt_2^- and $Me_3\phi$ P^+ Ni mnt_2^-, wherein a close fit between experimentally determined and theoretical (assuming doublet spins to be coupled into pairs by antiferromagnetic interaction [3]) temperature dependences of magnetic susceptibility was observed. This indicated that the paramagnetic centers are coupled into pairs which are non-interacting, thus giving rise to significant exchange demagnetisation. However, a reinvestigation of a series of R^+ Ni mnt_2^- complexes is warranted for two reasons: (a) The crystal structures of a number of these complexes clearly show that the isolated dimer limit assumed by those investigators [2] is not correct and, rather, a multicenter interaction is indicated. (b) The ground electronic configuration of the monomeric unit was wrongly assumed to be metal d_{xy} in character, whereas it has been conclusively shown both by EPR [4] and later by molecular orbital [5] studies that it is in fact $^2B_{3g}$ (metal d_{xz}), and that the half-filled, out-of-plane π MO is extensively delocalised over the ligand framework.

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TABLE I. Structural and Magnetic Observations on Various R^+ Ni mnt_2^- Complexes

Cation R^+	Shape	Type of stacking, interplanar distance (Å)	Exchange parameter (cm^{-1}) (all antiferromagnetic)
NMe_4^+	Tetrahedral	Alternating chain, 3.5	
NEt_4^+	Tetrahedral	Alternating chain, 3.5	490^a
NBu_4^+	Tetrahedral	Alternating chain, 3.5	205^e
$NMe_3\phi^+$	Pyramidal	Alternating chain, 3.5	
$Me\phi_3P^+$	Pyramidal	Alternating chain, 3.5	620^a
NMP^+	Planar	Alternating chain, 3.5	250^b
Tropylium$^+$	Planar	Uniform chain, 7.0	6^c
$TMPD^+$	Planar	Uniform chain, 7.0	8^d

[a]Ref. 9a. [b]Ref. 9b. [c]Ref. 9c. [d]Ref. 9d. [e]Ref. 9e.

Results and Discussion

The variation in the size and shape of the cation R^+ gives rise to changes in the packing arrangement of the Ni mnt_2^- units in the crystal. Even small changes in the relative orientations result in observable changes in the magnetic properties, as these depend on the extent of the overlap between the molecular orbitals, which is extremely sensitive to relative orientation. A comparative study of all the R^+ Ni mnt_2^- compounds known to date is presented in Table I. The spherical or nearly spherical cations always lead to alternate chain structures of the Ni mnt_2^- units with short interplanar distances, and the planar cations lead to uniform chain segregated stacks (with the exception* of NMP^+) with nearly double the interplanar distance.

We have used the Hoffmann's approach [7] to orbital actions in dimeric metal complexes to evaluate the first six compounds of Table I, all of which possess alternating chain structures. In Fig. 2 is shown a schematic interaction diagram for two weakly interacting molecular systems. In this limit the molecular orbitals of the dimer will closely resemble the ligand field levels of the monomeric unit, but the pairs of monomeric MOs will be split slightly due to the perturbation from the other unit. In the case of two $S = ½$ systems (assuming that we need to focus on the two HOMOs only), the singlet-triplet gap is given by

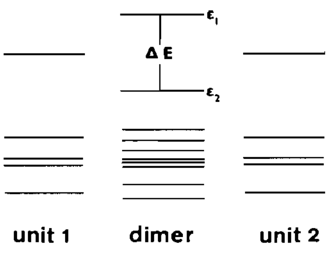

Fig. 2. Schematic interaction diagram for two weakly interacting molecular systems. The focus is on the two HOMOs.

$$2J = E_{\text{triplet}} - E_{\text{singlet}}$$

$$= -2K_{ab} + \frac{2(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \qquad (1)$$

where J_{aa} and J_{ab} are the one-center and two-center coulomb repulsion integrals defined as

$$J_{ij} = \int \phi_i^*(1)\phi_j^*(2) \frac{1}{r_{12}} \phi_i(1)\phi_j(2)d\tau$$

and K_{ab} is the two-center exchange integral defined as

$$K_{ij} = \int \phi_i^*(1)\phi_j^*(2) \frac{1}{r_{12}} \phi_j(1)\phi_i(2)d\tau$$

Equation (1) can be used to understand the qualitative changes in the singlet–triplet splittings (as determined by magnetic measurements) as a function of structural parameters by focussing on the quantity $(\epsilon_1 - \epsilon_2)$; the other terms are assumed to vary only slightly in closely related structures of dimers. This approach has been successfully applied to understand the magneto-structural correlations in a series of di-μ-hydroxo bridged copper(II) compounds experimentally characterised by Hatfield and coworkers [8].

We have evaluated the quantity $(\epsilon_1 - \epsilon_2)$ in the extended Hückel framework, by first performing a self-consistent charge calculation on the monomer and then carrying over the metal ionization potentials thus obtained for the case of the dimer. In Table II are presented some 'important' structural parameters along with the $\Delta E = \epsilon_1 - \epsilon_2$ calculated as above, for a series of R^+ Ni mnt_2^- complexes which were known to stack with an alternating chain struc-

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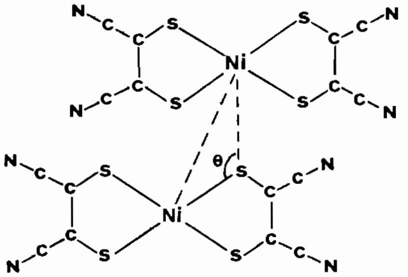
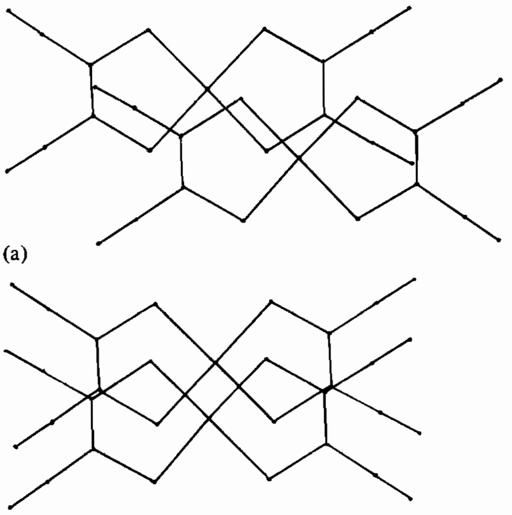
*It has been found that in the case of NMP^+ Ni mnt_2^- a second type of complex, which is presumably a uniform chain structure, results, and that this shows a strong EPR signal [6].

TABLE II. Some Important Structural Parameters and ΔE (= $\epsilon_1 - \epsilon_2$) of R^+ Ni mnt_2^- Compounds



Compound	R_{Ni-Ni} (Å)[a]	R_{Ni-S} (Å)	θ_{bridge}	$R_{interplanar}$ (Å)	ΔE (eV)
$NEt_4^+Ni\ mnt_2^-$	$4.14^{(a)}$	3.52	90.54	3.51	0.135
	$4.34^{(b)}$	3.74	91.35	3.55	0.523
$PMe\phi_3^+Ni\ mnt_2^-$	$4.40^{(a)}$	3.59	96.8	3.41	0.414
	$4.45^{(b)}$	3.71	95.0	3.56	0.501
$NMe_3\phi^+Ni\ mnt_2^-$	$4.41^{(a)}$	3.53	99.0	3.32	0.512
	$3.82^{(b)}$	3.78	75.0	3.54	0.503
		3.80	65.0		
$NMP^+Ni\ mnt_2^-$	$4.12^{(a)}$	3.91	83.5	3.65	0.300
		4.10	75.4		
	$4.21^{(b)}$	3.94	77.2	3.62	0.450
		4.04	81.9		
$NBu_4^+Ni\ mnt_2^-$	$4.43^{(a)}$	3.65	94.0	3.52	0.105
	$4.03^{(b)}$	3.64	94.2	3.59	0.059
		3.62	93.7		

[a] (a) and (b) are the two types of dimer overlaps, see Fig. 3.


(a)

(b)

Fig. 3. Overlapping of the monomeric units in $NMe_3\phi^+$ Ni mnt_2^- showing a projection perpendicular to the mean molecular plane. (a) and (b) are the two types of dimers a given unit forms with the neighbour on either side. The structural parameters are given in Table II.

ture. It is clearly seen in all the above cases that both the neighbours on either side of each Ni mnt_2^- unit interact, although to different extents, as is evident from the two different ΔEs obtained from the calculation. This suggests a reinterpretation of all the earlier magnetic data (presented in Table I, where the J values were obtained on the assumption that the isolated dimer approximation is valid) on the basis of interacting dimers.

For example on the basis of ΔE^2 it is seen that $NMe_3\phi^+$ Ni mnt_2^- is magnetically an almost uniform chain with a strongly alternating structure (see Fig. 3 for the two types of structural dimers) with the ratio $\Delta E_1^2/\Delta E_2^2$ being equal to 1.04. On the other hand, NEt_4^+ Ni mnt_2^- is a strongly alternating chain; magnetically it approaches the isolated dimer limit (see Fig. 4 for the two types of structural dimers), with the ratio of $\Delta E_1^2/\Delta E_2^2$ being equal to 15.01.

Conclusions

We have seen the extreme sensitivity of the packing arrangement and also ΔE to the cation R^+. Even for a given R^+, many of the compounds show two different types of overlap and different ΔEs, confirming that these are alternate stacks in the magnetic sense. As the ratio of $\Delta E_1^2/\Delta E_2^2$ varies between 1.04 to 15.01, we expect that the susceptibility behavior of this series of complexes will fit using the alternating chain spin Hamiltonian with varying

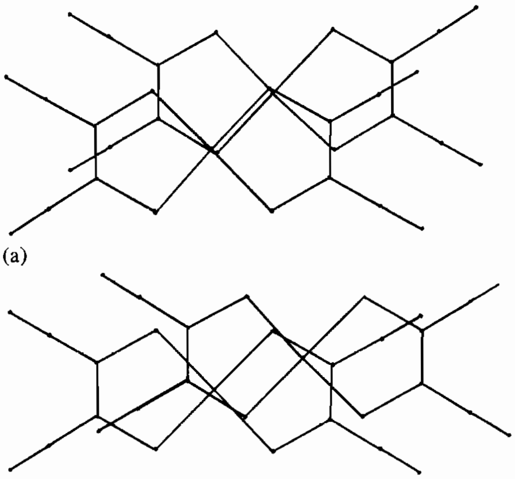


Fig. 4. Overlapping of the monomeric units in NEt$_4^+$ Ni mnt$_2^-$ showing a projection perpendicular to the mean molecular plane. (a) and (b) are the two types of dimers a given unit forms with the neighbour on either side. The structural parameters are given in Table II.

α, the alternation parameter. There also seems to be an interesting possibility of alternating antiferromagnetic and ferromagnetic interactions within a chain if accidental degeneracy ($\Delta E = 0$) is achieved for the neighbour on one side and a large ΔE with the neighbour on the other. The case of NBu$_4^+$ Ni mnt$_2^-$ could be near such a situation, and we are undertaking EPR and magnetic susceptibility studies to investigate this more thoroughly.

Due to extensive delocalisation of the electron density in the Ni mnt$_2^-$ unit (*ca.* 75% of the spin density has been shown to be on the ligand), several short contact distances, such as Ni–Ni, Ni–S, S–S, S–N, S–C and C–N, play significant roles in the superexchange pathway. Hence, no simple correlation of J is possible with few structural parameters. In fact, in NEt$_4^+$ Ni mnt$_2^-$ and PMeϕ_3^+ Ni mnt$_2^-$, larger Ni–Ni distance, larger Ni–S$_{\text{bridge}}$ distance and larger interplanar distances lead to larger ΔE values! Hence, it is quite clear that other structural parameters must be important in making the correlation between structure and ΔE. There seems to be at least some correlation between J values and ΔE; compounds having a smaller ΔE have a smaller J. In this comparison, however, one must concentrate on the larger of the two ΔE values obtained for a single compound. However, a general mechanism of spin correlation is proposed as (a) delocalisation to an in-plane-bonded sulfur by metal 3d$_{xz}$-sulfur 3p$_z$ orbital overlap; (b) overlap of sulfur 3p$_z$ with 4s and 4p$_z$ of the bridged nickel atom; (c) spin polarization of the unpaired electron in the 3d$_{xz}$ of the bridged nickel atom.

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