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CONSEQUENCES OF COLUMNAR PACKING IN LOW DIMENSIONAL METAL DITHIOLENES*

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Metal dithiolene complexes are a class of interesting systems known to exhibit low dimensional cooperative magnetic phenomena associated with the columnar crystallographic packing in the solid state. The variety and strength of the exchange interactions can be estimated precisely from magnetic susceptibility and EPR studies. While static susceptibility measurements as a function of temperature give information about the magnitude and sign of the exchange interactions, a careful study of position, width and shape of the EPR resonance as a function of orientation, Zeeman frequency and temperature provides a surprisingly detailed picture of the exchange coupled network, particularly so in the weak exchange regimes. Other consequences of packing such as charge-transfers and conductivity are also presented.

Key Words : Exchange Interaction; Low Dimensional Solids; EPR; Magnetic Susceptibility; X-ray Crystal Structure; Metal Dithiolenes

INTRODUCTION

IN the past few years considerable interest has been focussed on the properties of low-dimensional materials[1–5] since their study is expected to provide a better understanding of the various cooperative phenomena in solids. Also, low-dimensional systems are interesting in their own right since the dimensionality of the system is of great importance for their critical behaviour and also since they display phenomena which are not to be found in higher dimensions.[6] The discovery of a large number of low-dimensional metallic, magnetic and superconducting systems has led to the emergence of a new interdisciplinary area covering organic, inorganic and polymer chemistry along with solid state physics. The encouragement for the detailed investigations of the physics and chemistry of these systems was initially provided by a suggestion from Little[7] that the electron-exciton mechanism may provide the possibility of room temperature superconductivity. Though this prediction has not borne fruit thus far, it is an undeniable fact that it has led to the discovery of a wide variety of interesting phenomena in substances with high anisotropy such as low-dimensional metallic state, metal-insulator transitions, spin-Peierls transitions, highly anisotropic magnetic properties, etc.

Though most examples of magnetic materials are of organic origin, such systems are also provided for by transition metal complexes which have a tendency

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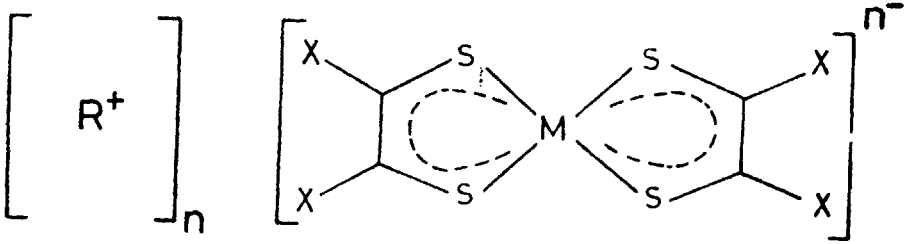
to stack as columnar structures in the solid state.[8] Some familiar examples would be those from partially oxidised metalloporphyrins,[9] metal dithiolene complexes[10] and mixed valent Krogmann's salts.[11] In the author's opinion the interest not only arises from the low-dimensionality based properties but they also provide interesting magnetic studies. In this article, we shall exclusively deal with compounds based on metal dithiolenes with special reference to the nature of stacking given by X-ray crystallography, magnetic properties *via* magnetic susceptibility as well as EPR, charge transfer properties where it is applicable and conduction properties to a smaller extent.

It is true that the metal dithiolenes (Fig. 1) have been studied since the early 1960's by groups of Gray,[12] Schrauzer[13] and Maki.[14] However, further interest has been focussed on the metal dithiolenes because of their overall planar geometry irrespective of the metal or its oxidation state, possibly with a few exceptions. This property allows them to pack effectively to give columnar structures which may provide charge transfer possibilities between the cation and the metal chelate. Other features of metal dithiolenes include the large delocalisation of the highest occupied molecular orbital (HOMO) of the π-system, existence of species with sufficiently high electron affinity to remove an electron from a wide variety of organic donors, good solubility and stability in organic solvents, structural flexibility *via* changes in the central metal atom. *M*, ligand substitution, *X* and the counter ion R^+. The ion R^+ could be a spherical cation like tetraalkylammonium (when we do not need charge transfer effects) or a planar organic moiety like tropylium$^+$, tetramethyl-*p*-phenylenediamine cation radical (TMPD$^+$), tetrathiafulvalenium (TTF$^+$), N-methylphenazinium (NMP$^+$), etc. which can take part effectively in charge transfer interactions.

Recently, we have been interested in the cooperative magnetic phenomena studied through magnetic susceptibility and EPR width measurements and optical properties of metal dithiolenes having columnar packing. A brief introduction to exchange interaction is given in the next section followed by discussion of our



M = *a* variety of transition metal ions such as Fe, Co, Ni, Cu, Au, Pd, Pt, Rh, etc.
X = various ligand substituents such as H, CH_3, C_6H_5, CF_3, CN, etc.
R^+ = inorganic or organic cations.
n = 0, 1 or 2.

FIG 1 Molecular structure of bis(ethylene-1, 2-di thiolato) metal complexes.

results. For convenience, the results are presented and discussed in the following order : crystal structure, magnetic properties, EPR linewidth analysis, charge transfer effects and conductivity.

The Concept of Exchange Coupling

In many materials, the magnetic part of the Hamiltonian can be quite accurately represented as a bilinear interaction in a set of spins S_i and the Hamiltonian is successfully employed in the interpretation of magnetic properties of several compounds in the solid state[15]

$$\mathcal{H}_{ij} = -2J_{ij}\hat{S}_i \cdot \hat{S}_j + \mathbf{D}_{ij} \cdot [\hat{S}_i \times \hat{S}_j] + \hat{S}_i \cdot \tilde{\tilde{\Gamma}}_{ij} \cdot \hat{S}_j. \quad \ldots(1)$$

The first and the last term in the above equation are respectively the isotropic and anisotropic exchanges while the middle term is called the antisymmetric (or asymmetric) exchange. The general exchange Hamiltonian, known as Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian

$$\mathcal{H}_{ex} = -2 \sum_{ij} J_{ij}\hat{S}_i \cdot \hat{S}_j \quad \ldots(2)$$

can be written terms of spin components as

$$\mathcal{H}_{ex} = -2 \sum_{ij} J_{ij}(\alpha S_i^x S_j^x + \beta S_i^y S_j^y + \gamma S_j^z S_j^z). \quad \ldots(3)$$

The values of α, β and γ in equation (3) define the nature of exchange coupling. When $\alpha = \beta = \gamma = 1$, the exchange coupling is said to be Heisenberg in nature. One obtains the Ising case for $\gamma \neq 0$ while $\alpha = \beta = 0$. On the other hand, if $\alpha = \beta \neq 0$ and $\gamma = 0$ we have the XY (2-dimensional) type of exchange. The totally anisotropic situation arises when $\alpha \neq \beta \neq \gamma$. For linear chain interactions, j can be taken to be $i + 1$. A positive value of J_{ij} corresponds to ferromagnetic coupling while a negative value for J_{ij} corresponds to antiferromagnetic coupling. Anisotropic exchange is frequently taken into account by utilising the term $\hat{S}_i \cdot \tilde{\tilde{\Gamma}}_{ij} \cdot \hat{S}_j$ in the Hamiltonian, where Γ_{ij} is the symmetric anisotropic tensor as given by equation (1). For interaction between orbitally nondegenerate states, the magnitude of Γ_{ij} is approximately given as

$$\Gamma_{ij} \simeq \left(\frac{\Delta g}{g}\right)^2 J, \quad \ldots(4)$$

where $\Delta g = |g - 2|$ is the contribution of the orbital moment to the g-factor. The anisotropic exchange coupling is, thus, basically a spin-orbit coupling effect and this corresponds to an effective dipolar coupling, with the principal axis determined by the g-tensor of the complex and hence sometimes referred to as pseudo-dipolar coupling.

The antisymmetric exchange ($D_{ij} = -D_{ji}$) is also known as Dzialoshinski-Moriya exchange coupling constant and its magnitude is given by

$$|D_{ij}| \simeq \left(\frac{\Delta g}{g}\right) J_{ij} \qquad \ldots(5)$$

For D_{ij} to be non-zero, (*i*) the *g*-values of the interacting centres must be different and (*ii*) there must not be a centre of inversion at the midpoint of the line joining the two centres. For these two reasons, the occurrence of this type of exchange is limited to only a few systems.

The isotropic exchange, J_{ij} tends to align the spins parallel or antiparallel depending on the sign of J_{ij} and dominates the static properties such as susceptibility and specific heat. The anisotropic exchange tensor also tends to align the spins parallel or antiparallel but defines a direction along which the coaligned spins have maximum energy—much like the classical dipole-dipole interaction. The antisymmetric vector tends to align the spins perpendicular to each other, thus opposing J_{ij}.

Since the exchange interactions depends strongly on the particular orbitals occupied by the individual electrons, it is the orbital dependence that gives rise to anisotropic and antisymmetric exchanges. In the case of orbital singlet ground states, orbital effects enter only as a perturbation and the anisotropic and antisymmetric terms are much smaller than the dominant isotropic exchange. However, when the ground states are orbitally degenerate, or nearly so, there are no limits on their magnitudes relative to isotropic exchange and very great simplifications are necessary in the Hamiltonian for measurements to provide significant information about exchange coupling.[16]

The isotropic exchange interaction has basically two effects—static and dynamic. Exchange coupling has the effect of lifting all the degeneracy between states of different total spin as well as some degeneracy between the states of the same total spin. The magnitude of the splitting is determined by the strength of the coupling which can be estimated by measuring some property which varies with temperature, assuming Boltzmann distribution. Magnetic susceptibility and specific heat are the most commonly studied such properties. For a discussion of the dynamic effects, it is convenient to regard J_{ij} as a spin-flipping frequency. One can in principle measure J_{ij} (hereafter referred to as J) from dynamic properties such as line width, provided the theory is good enough to relate these two quantities.

The nature of exchange coupling network in a low dimensional system is schematically represented in Fig. 2. The study of dimensionality of such interaction requires a precise estimation of the parameters α, J' and J. Although J is most often determined by static susceptibility measurements, EPR is a more sensitive tool particularly for a very small J or for small interchain interactions J' and interdimer interactions αJ which are masked in the gross susceptibility.

Consequences of Exchange Coupling

In general, EPR in systems with strong exchange leads to an exchange narrowed line whose shape, angular dependence, field dependence, etc., yield information

J or J_0 : intrastack exchange
J' : interstack exchange
α : alternation parameter
$\alpha = 1$: uniform chain
$\alpha < 1$: alternating chain
$\alpha = 0$: exchange coupled dimers
J'/J and α give the dimensionality
$J'/J = 0$ and $\alpha = 0 \rightarrow$ *zero*-dimensional
$J'/J = 0$ and $\alpha = 1 \rightarrow$ *one*-dimensional

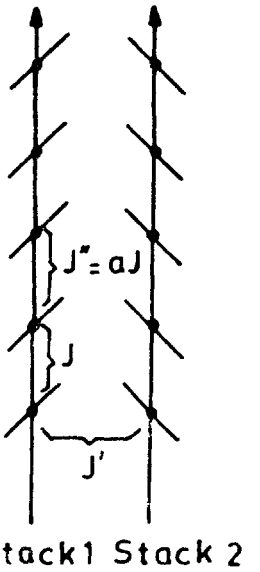


FIG 2 Exchange coupled network in a low-dimensional system.

about the dimensionality of the exchange coupled network and about the local magnetic interactions. Experimental and theoretical studies on low-dimensional systems have been extensively discussed by de Jough and Miedema,[17] Hone and Richards[18] and recently Hatfield *et al.*[19] In the case of EPR of low-dimensional systems, the following two qualitative differences are expected : (*i*) the line shape should be non-Lorentzian; and (*ii*) the angular and temperature dependences are quite different from what is predicted for three-dimensional systems.

The change in line shape and the magnitude of line width with magnetic field direction differ sharply from the predictions of standard exchange narrowing theories that have been found to hold for 3-*d* systems. In 3-*d* systems only the short-time behaviour ($t < \hbar/J$) of the spin correlation is important and so the line width can be adequately given by the relation

$$\Delta\omega_{1/2} = \sqrt{3}\,\Delta B_{pp} = \left(\frac{\pi}{2}\right)^{1/2} \frac{\langle \Delta\omega^2 \rangle}{\omega_e}, \qquad \ldots(6)$$

where $\langle \Delta\omega^2 \rangle$ is the mean-square deviation from the Larmor value and ω_e is the exchange frequency. The above relation holds good except for a possible change in the coefficient $(\pi/2)^{1/2}$.

The short-time expansion upon which the exchange narrowing formula (eq. 6) is based is quite insensitive to dimensionality with ω_e depending only on the number of neighbours and their distances but not on their geometrical arrangement. However, the shape of the resonance is crucially dependent on the dimensionality of the motion. The effect of the dimensionality of interaction (*d*) is particularly

strong if the spin-time correlation function $\psi(\tau)$ is characterised by diffusion by high temperature. In such cases we have

$$\psi(\tau) \alpha \langle S_i(\tau)\, S_i(0)\rangle \alpha\tau^{-d/2}. \qquad ...(7)$$

The integral $\int_0^\infty \psi(\tau)\, d\tau$ converges when $d = 3$ since the $\tau^{-3/2}$ decay of $\psi(\tau)$ is sufficiently rapid to make the integral converge and hence the long time diffusive tail does not seriously alter the exchange narrowing formula. On the other hand in the case of 1-d diffusive motion the function decays as $\tau^{-1/2}$ which does not make the integral converge. This leads to a line shape which is the Fourier Transform of exp $[-At^{3/2}]$ and is somewhat in between Gaussian and Lorentzian. This 1-d line shape for a derivative line is shown in Fig. 3 along with Gaussian and Lorentzian shapes. This non-Lorentzian line shape has been verified in $N(CH_3)_4$ $MnCl_3$ (TMMC) by Dietz *et al.* and in α-Cu^{II} (N-methylsalicylaldiminato)$_2$ by Bartowski[20] aad Morosin.[21]

In reality, however, in numerous seemingly 1-d transition metal complexes and organic ion-radical salts, nearly Lorentzian lines characteristic of 3-d are observed.[22]

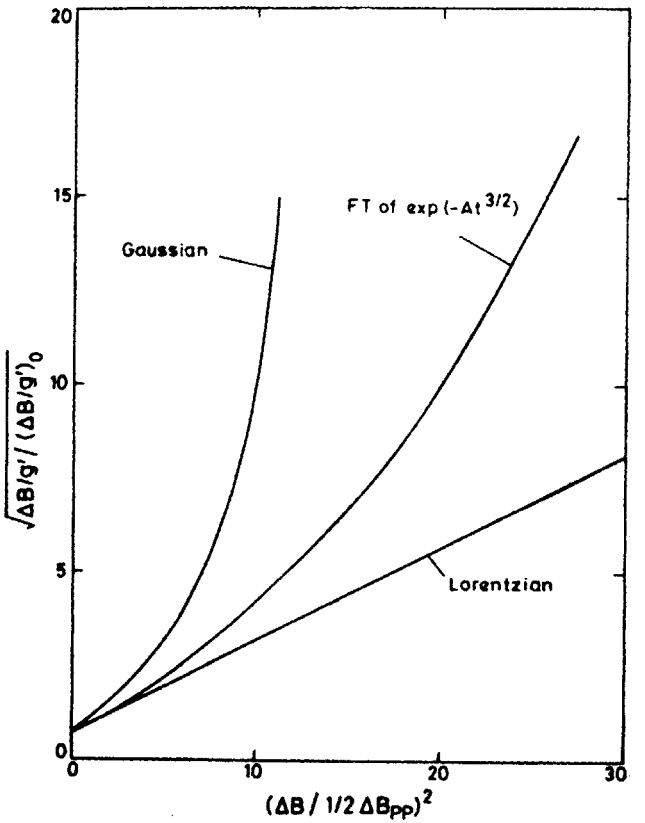


FIG 3 Analysis of Gaussian, Lorentzian and 1-d line shapes.

The reason is that it apparently takes only a small J' (interchain exchange) to change the observed line shape from the exp $[-t^{3/2}]$ to Lorentzian. Weak interchain contributions effectively cut off the slow diffusive decay $t^{-1/2}$ of 1-d systems and hence, the integral $\int_0^\infty \psi(\tau)\, d\tau$ is made to converge. It has been predicted that J'/J greater than 10^{-3} is required to suppress the diffusive behaviour of spins along the chain and to get nearly Lorentzian shapes.

Spin Correlation Functions

In the study of spin dynamics a spin time correlation function such as $\langle S_i^z(t)\, S_i^z(0)\rangle$ is usually defined. The time evolution of $S_i^z(t)$ is given by $\mathcal{H}_e$ as

$$S_i^z(t) = \exp\left((i\mathcal{H}_e \frac{t}{\hbar}\right) S_i^z(0) \exp\left(-\mathcal{H}_e \frac{t}{\hbar}\right). \qquad ...(8)$$

The hyperfine interactions involve two-spin correlations and the normalised correlation function is given by

$$C_{ij}(t) = \left[\frac{3}{S(S+1)}\right] \langle S_i^z(t)\, S_j^z(0)\rangle. \qquad ...(9)$$

The two-spin autocorrelation function $C_{ii}(t)$ for $i = j$ has been computed by Windsor[23] for classical spins, by Blume and Hubbard[24] at high temperature and by Carboni and Richards[25] for finite linear chains. A Gaussian form of $C(t)$ was suggested by Anderson and Weiss[26] for exchange coupled spins.

The contribution of hyperfine interactions to the line width is given by

$$\Gamma_h = \int_0^\infty (a^{(0)} + a^{(1)} \cos \omega_0 t)\, C(t)\, dt, \qquad ...(10)$$

where $a^{(0)}$ and $a^{(1)}$ are the secular ($\Delta m = 0$) and non-secular ($\Delta m = \pm 1$) hyperfine second moments while ω_0 is the Zeeman frequency. The time evolution due to $\mathcal{H}_Z$ is contained in the cos $\omega_0 t$ coefficient of the non-secular term. In the high temperature limit Γ_h is given by

$$\Gamma_h = a^{(0)}\, g^{(0)} + a^{(1)}\, g(\omega_0), \qquad ...(11)$$

where $g(\omega)$ are the Fourier components of the autocorrelation function $C(t)$.

$$2g(\omega) = \int_{-\infty}^{+\infty} C(t) \exp(i\omega t)\, dt. \qquad ...(12)$$

The dipolar interactions involve four spin correlations of the form

$$C_{ijkl}(t) = \left[\frac{2}{2S(S+1)}\right]^2 \langle S_i^+(t)\, S_j^+(t)\, S_k^-(0)\, S_l^-(0)\rangle, \qquad ...(13)$$

where i, j, k and l refer to various sites in the crystal with $i \neq j$ and $k \neq l$. Even after restricting to only diagonal correlation, a further approximation of strong decoupling is used to get

$$C_{ijkl}(t) \simeq \langle S_i^+(t)\, S_i^-(0)\rangle^2 \propto C^2(t). \qquad \ldots(14)$$

With the above approximation, the dipolar contribution to the observed linewidth is given by

$$\Gamma_d = M_2^{(0)} f(0) + M_2^{(1)} f(\omega_0) + M_2^{(2)} f(2\omega_0), \qquad \ldots(15)$$

where $M_2^{(0)}$, $M_2^{(1)}$ and $M_2^{(2)}$ are respectively the secular ($\Delta m = 0$) and nonsecular ($\Delta m = \pm 1, \pm 2$) dipolar second moments while $f(\omega)$ is the Fourier component of $C^2(t)$, given as

$$2f(\omega) = \int_{-\infty}^{+\infty} C^2(t) \exp(i\omega t)\, dt. \qquad \ldots(16)$$

Now the total contribution to the observed line width is

$$\Gamma_{\text{total}} = \frac{\sqrt{3}}{2} \Delta B_{pp} = \Gamma_h + \Gamma_d. \qquad \ldots(17)$$

Since the spin correlations arising from $\mathcal{H}_e$ are isotropic, the angular and frequency-dependent line width provides enough equations to obtain the individual Fourier components. The Fourier components thus obtained can be fitted to a one parameter form of $C(t)$—either Gaussian form of Anderson-Weiss[26] or Blume-Hubbard[24] model, to get an exchange parameter for the system.

In highly 1-d systems the secular contributions to second moment are likely to be enhanced as

$$M_2^{\text{low-d}} = M_2^{\text{total}} + \eta M_2^{(0)} \qquad \ldots(18)$$

The enhancement parameter η ranges from 0 to ∞ with $\eta = 0$ corresponding to the usual 3-d cases where $\omega_e \gg \omega_0$ when secular and nonsecular terms contribute equally. The limit $\eta \to \infty$ leads formally to an angular dependence dominated by $M_2^{(0)}$. In practice, η values of order unity are consistent with Lorentzian lines and slightly enhanced secular components. For simplicity it is generally assumed that the same enhancement holds for both hyperfine and dipolar contributions.

EPR IN VARIOUS J REGIMES

The magnitude of dipolar local field depends on the inverse-cube-distance $\left(1/r_{ij}^3\right)$ between the spins and is generally dominated by the nearest neighbour interactions. On the other hand the exchange interaction is a function of the separation of the spins as well as the overlap of the orbitals containing the unpaired spins.

Another important interaction that has to be considered is the hyperfine interaction which arises due to the interaction between electron and nuclear magnetic moments. The dipolar interaction dominates over the hyperfine term in the usual case of 3 to 5Å separations between the spins. For separations greater than ~5Å, the dipolar contribution is reduced and now depending on the relative magnitude of the exchange term with respect to the hyperfine term one gets either a single exchange narrowed line or hyperfine multiplets or a combination of both resulting in incompletely averaged broadened EPR line. Further, the two broadening mechanisms depend on the Zeeman magnetic field direction. Hence, a careful analysis of the relative magnitudes of all these terms will provide a good guess about the nature and relative magnitudes of various interactions. The analysis of the spectrum further requires a knowledge of the J-regime with respect to the temperature of observation (kT).

The possible relative orders of various Hamiltonians are as follows :

(i) $\mathcal{H}_Z \gg \mathcal{H}_{ex} \sim \mathcal{H}_b$;

(ii) $\mathcal{H}_Z \gg \mathcal{H}_{ex} > \mathcal{H}_b$;

(iii) $\mathcal{H}_Z^Q > \mathcal{H}_{ex} > \mathcal{H}_Z^X \gg \mathcal{H}_b$;

and (iv) $\mathcal{H}_{ex} \gg \mathcal{H}_Z^{X,Q} \gg \mathcal{H}_b$,

where $\mathcal{H}_b = \mathcal{H}_{dip} + \mathcal{H}_{hyp}$ and $\mathcal{H}_Z^Q$ and $\mathcal{H}_Z^X$ are respectively the Zeeman Hamiltonian at Q- and X-band frequencies. Also we have, depending on the magnitude of J, the low temperature ($J \gg kT$), the high temperature ($J \ll kT$) and the intermediate temperature ($J \sim kT$) regimes.

Case (i)

When the exchange frequency is of the same order of magnitude as the broadening interaction, the latter is incompletely averaged and one observes a broadened EPR line. In this reqime, for 1-d systems the exchange coupling does not average out the dipolar or hyperfine splittings and a multiline spectrum is observed in contrast to 3-d systems where each spin would have more than two nearest neighbours. In this unique 1-d case, the magnitude of J may be obtained directly from the observed splittings through an application of degenerate perturbation theory,[27] thus avoiding the indirect calculation of J through X line width analysis.

Anderson[28] has considered the effect of weak exchange on a $S = \frac{1}{2}$ spectrum split into a doublet, separated by $2A$ due to hyperfine interaction with a $I = \frac{1}{2}$ nucleus. For $\omega_e < A$ one has two lines at positions $\omega_0 \pm \left(A^2 - \omega_e^2 \right)$ and with width equal to ω_0. The line spacing goes on decreasing as ω_0 increases and when $\omega_e = A$, the doublet collapses to a single line centered at ω_0. In the $\omega_e > A$ limit,

there are two superimposed lines one of which rapidly broadens beyond detection and the other is a narrow line with a width of $A^2/2\omega_e$. This is equivalent of the exchange narrowing formula discussed earlier.

Case (ii)

This situation gives rise to a single exchange-narrowed line, whose width is given by eq. (6). Since Zeeman frequency is greater than exchange frequency, the secular (truncated) second moments will be effective in their contribution to the observed linewidth. Hence, in this regime, the observed linewidths are independent of Zeeman frequency.

Case (iii)

The observed single exchange-narrowed line will show field-dependent linewidth, since the X-band Larmor frequency is smaller than ω_e the non-secular moments corresponding to $\Delta m = \pm 1$ and ± 2 transitions can no longer be neglected but at the same time their contribution at Q-band frequency will be only partial. Hence, the Q-band linewidths will be smaller when compared to X-band widths. (This is true only when the observed resonance is from a set of magnetically equivalent spins). This variation of linewidth Larmor frequency is popularly known as '10/3 effect.'

Case (iv)

Here the truncation is not valid and the full moment must be used in the line width analysis.

The general theories of magnetic resonance depend heavily on the high temperature limit, $kT \gg J$. When kT far exceeds exchange energy or any magnetic term in the spin Hamiltonian, the detailed energy spectrum for interacting spins is not required and the partition functions reduce to the number of available spin states.[29] This avoids the far more difficult problem of finding energy levels and their degeneracies. One dimensional systems remain paramagnetic for $T > 0\,°K$, although in practice weak interchain contributions result in ordered (3-d) states at sufficiently low temperatures.

In the case of very strong exchange ($J \gg kT$) there is breakdown of the high temperature approximation. The extension of exchange narrowing theory and other EPR results to $J \gg kT$ cases has been principally demonstrated in dimerised organic free-radical[30] and Cu(II)[31] systems.

Estimation of Interstack Exchange, J'

Sometimes an estimate of J'/J can be made by using the frequency dependence of the EPR line width. In single crystals, sometimes, except along symmetry directions, the two chains containing magnetically inequivalent species have different g-factors and therefore two separate EPR resonances would be observed in the absence of J'. The coupling J' merges the lines when $J' > \frac{1}{2}\Delta g\beta B$. However, the width of

such an exchange averaged line will be frequency-dependent and will be proportional to the square of the microwave frequency. It can be shown[32,33] that the width of the exchange-averaged line depends on the square of the splitting, ΔB_Q^2 or ΔB_X^2 respectively at Q-and X-band frequencies. This leads to

$$\Delta B_{pp}(Q) - \Delta B_{pp}(X) = \frac{\Delta B_Q^2 - \Delta B_X^2}{B_e} . \qquad ...(19)$$

In the above expression ΔB_{pp} is the peak-to-peak width of the derivative line. The effective interstack exchange field, B_e is given by

$$(g\beta/\hbar)B_e = 4t_c^{-1}\ (\sqrt{3}/2), \qquad ...(20)$$

where t_c is the correlation time for interchain spin diffusion and is given by

$$t_c = 0.16\hbar\ \frac{|J|^{1/3}}{|J|^{4/3}}. \qquad ...(21)$$

The angular variation of X- and Q-band line widths can thus be used to get the interchain exchange parameters.

Structural Systematics in Metal Dithiolenes

By virtue of their highly planar geometry the metal dithiolenes stack as columnar structures in the solid state. The stronger interactions among units within a chain than between chains lead to anisotropic properties. It is also possible to have differential stronger interactions between two neighbouring units within a chain leading to possible dimerisation. In the donor-acceptor system, however, the donors (D) and acceptors (A) may be present within the same stack or could be present as separate stack also. Based on the nature of the units that make up the stack and as well as how these units are stacked we may get either a mixed stack or a segregated stack with uniform or alternate spacings. Charge transfer, hence, may occur by a direct lateral overlap in the case of a mixed stack ($D^+A^-D^+A^-...$) or by edge wise contacts between separate donor and acceptor chains in the case of segregated stacks. A simple classification is shown in Fig. 4. Furthermore, the alternation of interplanar spacings in segregated stacks of metal dithiolenes, particularly $M(mnt)_2^{n-}$ (mnt : maleonitriledithiolato : n = 1 or 2) systems results in dimerisation of the anions. Consequently, the dimerisation of the cations is also possible if they happen to be grossly planar organic cations like $TMPD^+$ (TMPD : tetramethyl-p-phenylendiammine), NMP^+(NMP : N-methyl-phenazinium) and tropylium ions. Just as it is possible to have interchain interactions in the uniformly stacked mixed or segregated systems it is inherently possible to have interdimer interactions in the alternating stack. Of course the extreme case of an isolated dimer stack can also be envisaged crystallographically. Nevertheless, crystallographic work helps one to guess the dimensionality of the interactions, since magnetic interactions are nothing but manifestations of crystallographic packing.

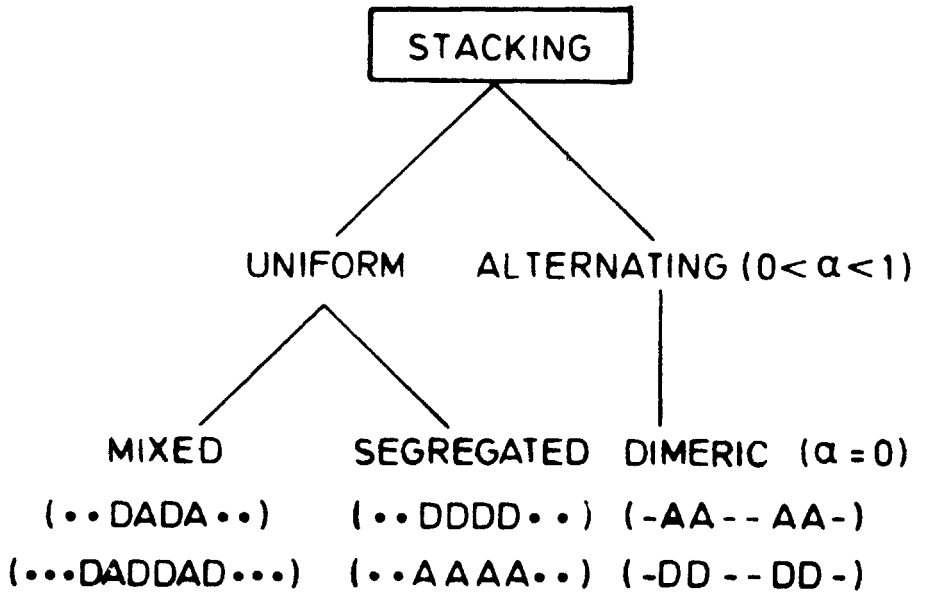


FIG 4 A schematic classification of stacking in crystals of metal dithiolenes.

TABLE I

Packing in some metal dithiolene complexes

Compound	Nature of stack	*M–M* distance (s) along the stack (Å)	Reference
(NEt_4) Ni(*mnt*)$_2$	alternating	4.14, 4.31	34
(PPh_3Me) Ni(*mnt*)$_2$	alternating	4.40, 4.45	35
(Trop) Ni(*mnt*)$_4$	segregated, uniform	7.458	36
(TMPD) Ni(*mnt*)$_2$	segregated, uniform	7.334	37
$(NPhMe_3)$ Ni(*mnt*)$_2$	alternating	3.83, 4.41	38
(NMP) Ni(*mnt*)$_2$	segregated, alternating	4.16, 7.87	39
(Cudmp$_2$) Ni(*mnt*)$_2^a$	uniform	13.25	40
(NMP) Au(*mnt*)$_2$	mixed	7.739	41
(NMP)$_2$ Cu(*mnt*)$_2$	mixed	11.417	42
(MB)$_2$ Cu(*mnt*)$_2$	segregated, alternating	7.115, 10.743	43
$(NMe_4)_2$ Cu(*mnt*)$_2$	alternating	7.811, 7.841	44
(NMP) Ni(*bdt*)$_2^b$	mixed	10.148	45
(NEt_4) Ni(*bdt*)$_2^b$	uniform	7.576	46
(NBu_4) Ni(*sdt*)$_2^c$	uniform	8.874	47
(NBu_4) Au(*tdt*)$_2^d$	uniform	9.336	48

The nature of packing arrangements found in a variety of dithiolenes studied by us, with also some examples[34–38] from other works, are found in Table I.

On the one hand we have highly uniform stacks in $Trop^{+}Ni(mnt)_2^{-}$, $TMOD^{+}Ni(mnt)_2^{-}$, etc. with grossly planar anions while the $Cu(mnt)_2^{2-}$ systems show a quite varied behaviour. The $Cu(mnt)_2^{2-}$ geometry varies from total planarity to non-planarity involving upto a maximum of 40° dihedral angle between the two chelate planes.[43,44,49] Even among the simpler copper dithiolene complexes variations seem to occur not only in the dihedral angle between the chelate planes but also in the Cu-Cu distances which vary from completely isolated anions to totally dimerised spins as is manifested in their magnetic properties. The donor-acceptor complexes $Trop^{+}Ni(mnt)_1^{-}$ and $TMPD^{+}Ni(mnt)_2^{-}$ have segregated uniform stacks while $NMP^{+}Ni(mnt)_2^{-}$ has highly alternating segregated stacks. $NMP^{+}Au(mnt)_2^{-}$ is a very good example of a mixed stack leading to charge transfer interactions between the two units. Some of the interesting structures are shown in Figs. 5, 6 and 7. Just as packing manifests itself in magnetic interactions as is shown by magnetic susceptibility and EPR data strong structural evidences such as changes in bond length, etc, manifest themselves in charge transfer (*vide supra*).

Magnetism in Low Dimensional Compounds

In the last two decades considerable progress has been made towards the understanding of the nature of magnetic interactions in low dimensional systems.[17] Of particular importance is the magnetic susceptibilty and low-lying excited states of antiferromagnetic (AF) 1-*d* Heisenberg chains. Both uniform[50,51] and non-uniform or alternating[52,53] exchanges between spins along the chain have been considered. The Hamiltonian for these cases is

$$\mathcal{H} = \sum_{i=1}^{N/2} (J\,\hat{S}_{2i}\cdot\hat{S}_{2i-1} + \alpha\, J\,\hat{S}_{2i}\cdot\hat{S}_{2i+1}). \qquad \ldots(22)$$

The parameter α is defined as the alternation factor such that $\alpha = 1$ is the uniform chain and $\alpha < 1$ is the alternating chain, reaching the limiting case of an isolated AF dimer at $\alpha = 0$. The susceptibility of the uniform infinite chain is non-vanishing at 0 °K and its magnitude at 0 °K has been estimated to be $\chi_0 = 0.0591\, g^2\beta^2 N/|J|$. The two non-uniform chains at either extreme of α are essentially similar at low temperatures with χ vanishing exponentially.

The Linear Chain Model

Bonner and Fischer[50] carried out calculations on systems of rings from 4 to 12 spins and extrapolated the results to infinite-length chain. The susceptibility has been shown to display a rounded maximum with the value

$$|J|\,\chi_{max}/(Ng^2\beta^2) \simeq 0.07346 \qquad \ldots(23)$$

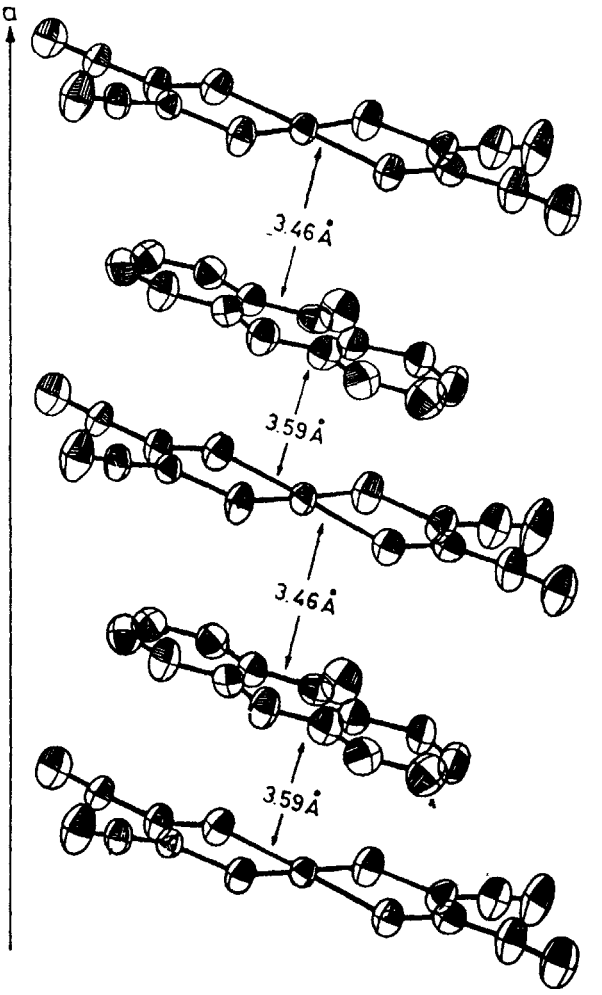


FIG 5 A side view of the packing in NMP Au(*mnt*)$_2$: an example of a mixed stack.

at the temperature

$$kT_{max}/|J| \simeq 1.282 \qquad \ldots(24)$$

Hall[54] has recently developed an analytical expression for the susceptibility as a function of temperature using the tabulated results of Bonner.

The Alternating Chain Model

This model has been studied in detail by Duffy and Baar[53] as well as by Bonner and Friedberg[55] and Diederix *et al.*[56] In the range $0 < \alpha < 1$, Hatfield and coworkers[57,58] have developed expressions for the normalised susceptibility χ_r ($\chi_r = |J|/(Ng^2\beta^2)$) as a function of reduced temperature T_r($T_r = kT/|J|$ with α as a variable parameter.

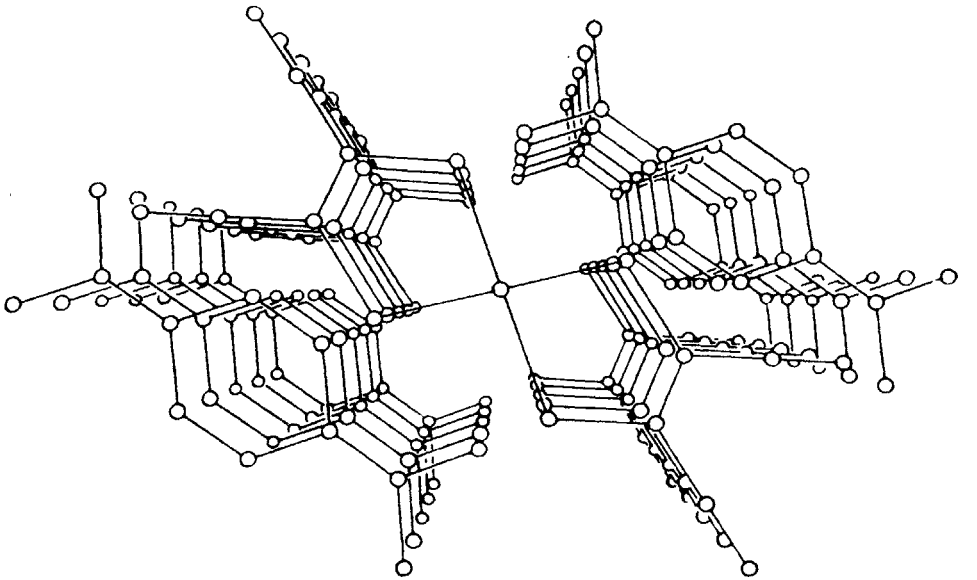


FIG 6 The packing in TMPD Ni(mnt)$_2$ as viewed along the stack direction : an example of a segregated uniform stack.

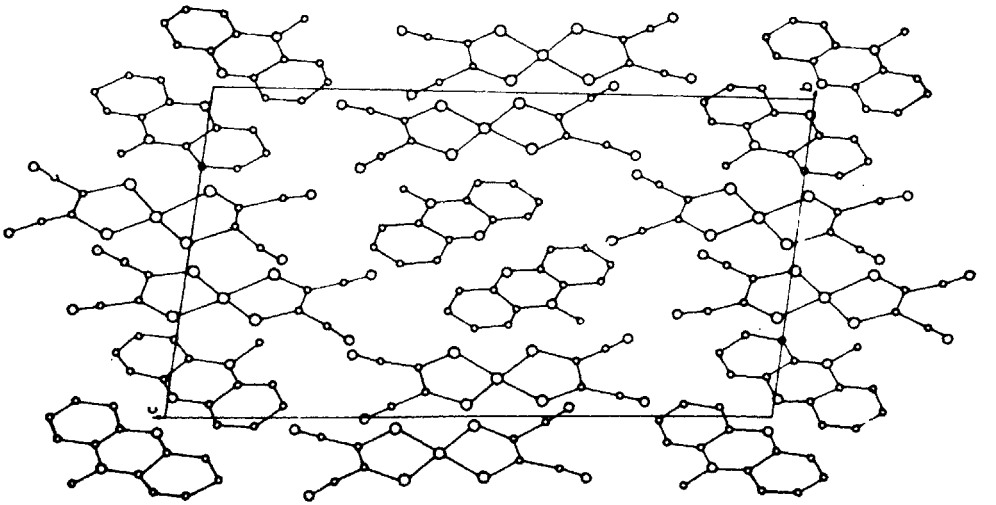


FIG 7 Projection of the structure of NMP Ni(mnt)$_2$ onto the bc plane : an example of an alternating stack.

The Dimer Model

This model is obtained when the alternation parameter α is set equal to zero. Using the Van Vleck expression[59] for susceptibility, the molar susceptibility for an exchange coupled pair of $S = \frac{1}{2}$ spins is given as

$$\chi_M = \frac{Ng^2\beta^2}{3kT}[1 + 1/3 \exp(-2J/kT)]^{-1}. \quad ...(25)$$

This expression is often referred to as Bleaney-Bowers formula.

In all the above models corrections such as for interchain exchange interaction (J') are applied by inclusion of a molecular field correction term given by

$$\chi^{corr} = \chi_H/(1 - 2zJ'\chi_H/Ng^2\beta^2), \quad ...(26)$$

where χ_H is the magnetic susceptibility of an isolated Heisenberg chain of $S = \frac{1}{2}$ spins and z is the number of the nearest neighbours in adjacent chains.

The magnetic susceptibility results on a few Ni(III) and Cu(II) dithiolene systems are summarised in Table II. In the case of Ni(III) complexes the packing generally results in antiferromagnetic coupling the magnitude of this coupling is highly dependent on the Ni–Ni distance. When Ni–Ni distances are > 7.5Å there is weak intrachain exchange estimated to be less than $1cm^{-1}$ by EPR. In the other extreme when the metal-metal distances are of less than 5Å the nickel dithiolenes, particularly Ni(*mnt*)$_2^-$ tend to dimerise with large values for $-2J$ of the order of $100cm^{-1}$ or more. However, in the intermediate cases, the magnitude of AF coupling is highly sensitive to *M-M* distance (cf. TMPD Ni(*mnt*)$_2$ and Trop Ni(*mnt*)$_2$) and probably dependent on the nature of superexchange pathway which may involve the cationic species.

TABLE II

Magnetic susceptibility results of some Ni(III) and Cu(II) dithiolenes

System	$2J(cm^{-1})$	Ref.
($PMePh_3$) Ni(*mnt*)$_2$	−620	60
(NEt_4) Ni(*mnt*)$_2$	−490	60
(NMP) Ni(*mnt*)$_2$	−241	61
(NBu_4) Ni(*mnt*)$_2$	−226	61
(Trop) Ni(*mnt*)$_2$	−8.8	36
(NMP)$_2$ Cu(*mnt*)$_2$	−0.13	42
(NEt_4)$_2$ Cu(*mnt*)$_2$	< 1	63

While gross planarity is a rule in donor-acceptor systems containing Ni(*mnt*)$_2^-$ ions large deviations from planarity and hence, its consequent effects on magnetism have been noted in the copper dithiolenes. It is interesting to note that all the salts containing planar copper dithiolenes have very little exchange possibly because of the unavailability of the orbitals like d_{xy}, d_{yz} and d_{z^2} for the unpaired electron. However, the nonplanarity seems to provide a mixed ground state wave function resulting in an enhanced overlap leading to a higher magnitude for exchange interactions.

It is also fascinating to report the presence of ferromagnetic exchange in the nonplanar (NBu_4)$_2$ Cu(*dcm*)$_2$ (*dcm*)[49] with a Cu–Cu distance of only ~ 4.5Å.

Electron Paramagnetic Resonance

The static susceptibility results are extended and complemented by EPR studies since the integrated EPR absorption is proportional to the susceptibility. EPR helps to probe the electronic structure of the molecule through principal spin Hamiltonian parameters and relate them structurally to the lattice through the orientation of the axes of g- and A- tensors. Furthermore, the study of spin dynamics in coupled spin systems of low dimensionality is probed by EPR through the behaviour of absorption line width and line shape. Above all, EPR studies could provide very accurate estimate of the magnitude of weak exchanges ($J_0 < 2\text{cm}^{-1}$) and small interchain couplings which are otherwise masked in the gross susceptibility. We have already discussed in our earlier section the manifestation of exchange in the EPR line width and line shape. A brief summary of the EPR results of metal dithiolene systems carried out in our laboratory is given below. The important results obtained by EPR investigation are collected in Table III.

Table III

Some examples and results of metal dithiolenes studied by EPR

System	Parameter(s)	Value (cm^{-1})	Ref.
Trop Ni(*mnt*)$_2$	isotropic exchange	8.8	36
	anisotropic exchange	0.26	
	intersite exchange	0.02	
TMPD Ni(*mnt*)$_2$	isotropic exchange	8 ± 2	37
	anisotropic exchange	0.15	
NMP Ni(*mnt*)$_2$	AF exchange ($2J$)	-241	39
$NBu_4Ni(sdt)_2^a$	isotropic exchange	0.52	64
	anisotropic exchange	0.05	
NMP_2 Cu(*mnt*)$_2$	isotropic exchange	0.06	42
$(NMe_4)_2$ Cu(*mnt*)$_2$	isotropic exchange	0.08	62
	interchain exchange	0.005	
$(NBu_4)_2Cu(dcm)_2^b$	ferromagnetic exchange	0.17	49

[a] *sdt* : stilbene-1, 2-dithiolato
[b] *dcm* : dicyanomethyl dithiocroconate

A reasonably good estimate of the isotropic exchange, J or J_0 is obtained in the case of strong exchange cases using the formula

$$\sqrt{\frac{3}{2}}\ \Delta B_{pp} = M_2^+/J, \qquad \ldots(27)$$

where M_2^t is the total second moment of the broadening mechanisms. We have found from our experience that the above expression is quite successful in fitting the observed line width in the case of Cu(II) systems, which have hyperfine dominated line widths.

The Ni(III) dithiolenes are characterised by the absence of nuclear hyperfine interactions and hence the EPR line broadening effects come purely from dipolar interactions. However, it has been observed in (Trop) Ni(*mnt*)$_2$ [36] and in TMPD Ni(*mnt*)$_2$ [37] that the observed line width could not be interpreted based on purely dipolar interactions. Considerable contribution of anisotropic exchange has been noted in the above systems (*see* Table III). Recently, the same effect has been shown to be responsible for the anamalous, variation of line width with orientation of the magnetic field in the system (NBu_4) Ni(*sdt*)$_2$.[64] Though it is not very uncommon to observe anisotropic exchange in Cu(II) systems,[65] the study of it in Ni(III) systems is quite new.

Another interesting aspect of our investigation is the precise estimate of interstack exchanges (J') from EPR data. For example, in (Trop) Ni(*mnt*)$_2$[36] there are inequivalent stacks but only a single EPR line is observed at all orientations due to exchange-averaging of the two resonances. By simulation techniques the interstack exchange frequency has been shown to be 450 $\pm$ 30 MHz at 300 K. Further the temperature dependency of J' has been established by analysing the spectra at lower temperatures.

On the other hand frequency- and temperature-dependent EPR measurements on (NMe_4)$_2$ Cu(*mnt*)$_2$ show the presence of temperature-independent J' while the isotropic exchange is temperature-dependent.[62] If one wonders why J or J' or none of them should depend on temperature, the possible explanation could be crystal contraction on cooling. At least, in one case (Trop Ni(*mnt*)$_2$)[36] it has been confirmed that there is indeed crystal contraction by measuring the unit cell dimensions at lower temperatures. The question of which parameter will be affected depends on the 'anisotropy' in the crystal contraction. If the contraction is intrachain, the *M-M* distances would decrease resulting in an increase in J on cooling. On the other hand if the different chains are brought closer (inter stack contraction) one would expect an increase in J' at lower temperatures. Hence, depending upon the actual change in the lattice on cooling and the consequent overlap effects we observe different temperature effects.

Charge Transfer in Metal Dithiolenes

The charge transfer interaction has been observed in a number of $M(mnt)_2^{n-}$ systems with $TMPD^+$, NMP^+ and $Trop^+$ as the counter ions. We have come across many interesting CT systems, viz., mixed stacks (e.g., (NMP)$_2$ Cu(*mnt*)$_2$, (NMP)$_2$ Co(*mnt*)$_2$, (NMP)$_2$ Ni(*mnt*)$_2$ and (NMP) Au(*mnt*)$_2$ with lateral overlap between the donor (D) and the acceptor (A) and segregated uniform stack (e.g., Trop Ni(*mnt*)$_2$ and TMPD Ni(*mnt*)$_2$), where charge transfer occurs *via* edge-wise interchain short contacts. In the former cases, the EPR spin Hamiltonian parameters are found to be modified to an extent depending upon the nature of the HOMO of the metal chelate and the mode of D-A overlap in the solid state. For example, in the case of Co(II) diluted in (NMP)$_2$ Ni(*mnt*)$_2$ the observed EPR parameters ($g_y = 2.699$ and $A_y = 39 \times 10^{-4}$ cm^{-1}) are significantly different when compared to the values ($g_y = 2.798$ and

$A_v = 56 \times 10^{-4}$ cm^{-1}) obtained for Co(II) diluted in $(NBu_4)_2$ Ni(mnt)$_2$. A similar effect has been noted in the case of Ni(III) in NMP Au(mnt)$_2$ ($g_v = 2.134$) compared to Ni(III) in the non-CT lattice, NBu_4 Au(mnt)$_2$ ($g_v = 2.156$).

Further in both the cases the direction cosines of the principal values of the g- and A-tensors are expected to be modified due to CT effect. This investigation is under progress.

In TMPD Ni(mnt)$_2$ system the charge transfer interaction has been confirmed by various studies.[37] For example, while the normal C = N distance is in the range 1.125Å (in NEt_4 Ni(mnt)$_2$) a value as large as 1.148Å has been observed in TMPD Ni(mnt)$_2$. This value is rather close to that in Ni(II) system $(TMPD^+)_2$ Ni(mnt)$_2^{2-}$ (1.155Å).[66] Further the TMPD moiety has a very pronounced quinonoid structure (closer to $TMPD^{2+}$). The above two facts suggest that there is a charge transfer from $TMPD^+$ to Ni(mnt)$_2^-$ in the solid state. The optical spectrum of this system shows a more intense CT band at 11,420 cm^{-1} as detected by deconvolution techniques. In the infrared absorption, the C ≡ N stretch is shifted by 20cm^{-1} towards lower energy as compared to the C ≡ N in NEt_4 Ni(mnt)$_2$. Finally, magnetic susceptibility and EPR measurements also show quite clearly the interaction between the two ion-radical moieties. It should also be noted that the two moieties form self-aggregates even in solution as detected by EPR.

Conductivity

The electrical conductivities of several metal dithiolenes, particularly the Ni(mnt)$_2^-$ salts, were measured in order to correlate the packing to the conductivity. One can also find out from such studies the influence of the shape and size of the counter ions. The spherical ions seem to allow closer stocking of the Ni(mnt)$_2^-$ units but the stacking is invariably alternating resulting in poor conductivity ($\sigma = 10^{-8}$ to 10^{-10} mho·cm^{-1}). The planar cations, however, form mixed or segregated stacks and in the latter cases, the conductivity is enhanced.

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References

1. H J Keller *Low-dimensional Cooperative Phenomena* Plenum, New York (1975)
2. H J Keller *Chemistry and Physics of Low-dimensional Metals* Plenum New York (1977)
3. L V Interrante *Proc ACS Symp Ser* No 5 (1974)
4. W E Hatfield *Molecular Metals A NATO Conf Ser* Vol I S VI Plenum New York (1979)
5. J S Miller *Extended Linear Chain Compounds* Plenum New York (1982)

6. M Steiner J Villain and C G Windsor *Adv Phys* **25** (1976) 87
7. W A Little *Phys Rev* **134** (1964) 1416
8. J S Miller and E J Epstein *Progr inorg Chem* (*Ed* S J Lippard) John Wiley and Sons, New York Vol 20 (1976) p 1
9. J L Petersen C S Schramm D R Stojakovic B M Hoffman and T J Marks *J Am chem Soc* **99** (1977) 286
10. A E Underhill and M M Ahmad *Chem Comun* (1981) 67
11. K Krogmann and H D Housen *Z anorg Chem* **358** (1968) 67
12. H B Gray R Williams I Bernal and E Billig *J Am chem Soc* **84** (1952) 3596
13. G N Schrauzer and V P Mayweg *J Am chcm Soc* **84** (1962) 3221
14. A Davison N Edelstein R H Holm and A H Maki *J Am chem Soc* **85** (1963) 2029
15. T Moriya *Magnetism* (*Eds* G T Rado and H Suhl) Academic Press New York Vol 1 (1963) Ch III
16. A P Ginsberg *Inorg Chim Acta Rev* (1971) 45
17. L J de Jongh and A R Miedema *Adv Phys* **23** (1974) 1
18. D W Hone and P M Richards *Ann Rev Mater Sci* **4** (1974) 337
19. W E Hatfield W E Estes W E Marsh M W Pickens L W terr Haar and R R Waller *Extended Linear Chain Compounds* (*Ed* J S Miller) Plenum New York Vol 3, Ch 2 p 43
20. R E Dietz F R Merrit R Dingle D Hone B G Silbernagel and P M Richards *Phys Rev Lett* **26** (1971) 1186
21. R R Bartowski and B Morosin *Phys Rev* **136** (1972) 4209
22. Z G Soos *J chem Phys* **44** (1966) 1729
23. C G Windsor *Proc phys Soc* (*London*) **91** (1967) 353
24. M Blume and J Hubbard *Phys Rev* **B1** (1970) 3815
25. F Carboni and P M Richards *Phys Rev* **177** (1969) 189
26. P W Anderson and P R Weiss *Rev mod phys* **25** (1953) 269
27. K W Plumlee B M Hoffman J A Ibers and Z G Soos *J chem phys* **63** (1975) 1926
28. P W Anderson *J phys Soc Japan* **9** (1954) 316
29. K T McGregor and Z G Soos *Inorg Chem* **15** (1976) 2159
30. P L Nordio Z G Soos and H M McConnel *Ann Rev phys Chem* **17** (1966) 237
31. K T McGregor and W E Hatfield *J chem phys* **62** (1975) 2911
32. R C Hughes B Morosin P M Richards and W Duffy Jr *Phys Rev* **B11** (1975) 1795
33. M Yokota and S Koide *J phys Soc Japan* **9** (1954) 953
34. A Kobayashi and Y Sasaki *Bull chem Soc Japan* **50** (1977) 2650
35. C J Fritchie Jr *Acta Cryst* **20** (1966) 107
36. P T Manoharan J H Noordik E de Boer and C P Keijzers *J chem phys* **74** (1981) 1980
37. B L Ramakrishna and P T Manoharan *Inorg Chem* **22** (1983) 2113
38. C Mahadevan M Seshasayee B V R Murthy P Kuppusamy and P T Manoharan *Acta Cryst* **C39** (1983) 1335
39. P Kuppusamy C Mahadevan M Seshasayee and P T Manoharan *J cryst spectrosc Res* **15** (1985) 359
40. N Venkatalakshmi P Kuppusamy and P T Manoharan (*to be published*)
41. P Kuppusamy N Venkatalakshmi and P T Manoharan *J cryst Spectrosc Res* **15** (1985) 633
42. P Kuppusamy B L Ramakrishna and P T Manoharan *Inorg Chem* **23** (1984) 3886
43. D Snaathorst H M Doesburg J A A J Perenboom and C P Keijzers *Inorg Chem* **20** (1981) 2526
44. C Mahadevan and M Seshasayee *J cryst Spectrosc Res* **14** (1984) 213
45. C Mahadevan P Kuppusamy M Seshasayee and P T Manoharan *J cryst spectrosc Res* **15** (1985) 305

46. P Kuppusamy and P T Manoharan *(to be published)*
47. C Mahadevan P Kuppusamy M Seshasayee and P T Manoharan *J cryst spectrosc Res* **14** (1984) 179
48. M A Mazid M T Razi and P J Sadler *Inorg Chem* **20** (1981) 12872
49. N Venkatalakshmi Babu Varghese R F X Williams and P T Manoharan *Inorg Chem (communicated)*
50. J C Bonner and M E Fischer *Phys Rev* **135** (1964) 640
51. L N Bulaevskii *Zh Eksp Teor Fiz* **43** (1962) 908
52. L N Bulaevskii *Zh Eksp Teor Fiz* **44** (1963) 1008
53. W Duffy Jr and K P Baar *Phys Rev* **165** (1968) 647
54. J W Hall *PhD Dissertation* University of North Carolina Chapel Hill N C 27514 (1977)
55. J C Bonner and S A Frieberg *Proc int Conf Phase Transitions and their Applications in Materials Science (Eds* H K Hanish *et al.)* Pergamon Press New York (1973) p 429
56. K M Diederix H W J Blote J P Groen T O Klaasen and N J Poulis *Phys Rev* **B9** (1979) 420
57. W E Hatfield *J appl phys* **52** (1981) 1985
58. M M Olmstead W K Musker L W terr Haar and W E Hatfield *J Am chem Soc* **104** (1982) 6627
59. J H van Vleck *The Theory of Electric and Magnetic Susceptibilities* Oxford University Press London (1932)
60. J F Weiher L R Melby and R E Benson *J Am chem Soc* **86** (1964) 4329
61. P Kuppusamy and P T Manoharan *(Unpublished)*
62. P Kuppusamy and P T Manoharan *Inorg Chem* **24** (1985) 3053
63. K W Plumlee B M Hoffmann M T Ratajack and C R Kannewurf *Solid State Commun* **15** (1974) 1651
64. P Kuppusamy and P T Manoharan *Chem phys Lett* **118** (1985) 159
65. K T McGregor and Z G Soos *J chem phys* **64** (1976) 2506
66. M J Hove B M Hoffman and J A Ibers *J chem Phys* **56** (1972) 3490