

Magnetic properties of some exchange coupled $[\text{Ni}(\text{mnt})_2]^-$ dimers

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Abstract. The metal dithiolenes exhibit interesting solid state properties owing to the presence of columnar crystallographic packing. Particularly, the *bis*(maleonitriledithiolo)-nickel(III) systems with a variety of organic and inorganic counter ions seem to possess low-dimensional magnetic interactions and charge-transfer properties. The metal chelates show strong alternation in their packing and result in reduced magnetic moments as a consequence of antiferromagnetic exchange coupling between the pairs. We have studied a few interesting dimers through x-ray structure and magnetic susceptibility measurements and the results are used to arrive at a correlation between the observed magnetic behaviour and the structure of the dimeric units.

Keywords. Exchange interaction; magnetic susceptibility; dimers.

1. Introduction

Metal dithiolene complexes show unique low-dimensional magnetic, electrical and optical properties (McCleverty 1968; Miller and Epstein 1976; Jacobs *et al* 1976; Issett *et al* 1980; Miller 1982; Cooper *et al* 1983). This behaviour is due to the fact that these metal chelates possess an overall planar geometry allowing them to stack-up along a particular direction, which is an important requirement for a system to exhibit low-dimensional properties. In addition, they exhibit a number of characteristics which make them particularly attractive candidates as π -acceptor units in the formation of donor-acceptor compounds; they undergo reversible electron-transfer reactions to yield stable species; they possess species with sufficiently high electron affinity to remove an electron from a wide variety of organic donors and structural flexibility available via the changes in the central metal atom, ligand substituent and the counter ion, which can be varied in a systematic way to study the effect of molecular features on the solid state structure and properties.

A variety of Cu(II) and Ni(III) dithiolene complexes were made in order to understand the low-dimensional cooperative phenomena in their solid state and the effect of dimensionality of the exchange coupled network on the solid state properties like magnetic, electrical and optical (Manoharan *et al* 1981; Ramakrishna and Manoharan 1983; Ramakrishna *et al* 1983; Kuppusamy *et al* 1984a, b; Kuppusamy and Manoharan 1985a, b; Kuppusamy *et al* 1985a, b). Our primary emphasis was to deduce the nature and size of the various exchange interactions present in the system. We have shown in a number of cases that EPR in conjunction with magnetic susceptibility measurements can be very useful in extracting these parameters. Though EPR is a more sensitive tool for weakly

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exchange coupled systems ($|J| < 1 \text{ cm}^{-1}$) the magnetic susceptibility measurements can be used for strongly exchange coupled systems. In this paper we present and discuss some of our magnetic susceptibility results on a few strongly exchange coupled $\text{Ni}(\text{mnt})_2^-$ dimers.

2. Experimental

2.1 Preparation of compounds

Tetra-*n*-butylammonium *bis*(maleonitriledithiolato) nickelate(III), $[\text{NBu}_4]^- [\text{Ni}(\text{mnt})_2]^-$ was prepared according to the reported (Davison and Holm 1971) procedure. N-methyl-phenazinium methosulphate, $\text{NMP}^+ \text{CH}_3\text{SO}_4^-$ (Aldrich Chemical Co.), was dissolved in acetonitrile and treated with $[\text{NBu}_4]^+ [\text{Ni}(\text{mnt})_2]^-$ in the same solvent. The resulting dark solution was filtered and cooled in the refrigerator for 24 hours. The black needles were collected on a filter, washed with ice-cold acetonitrile and dried in air. The yield was 60%.

Analysis: Found (%): C 46.98; H 2.3; N 15.70; Calc. (%): C 47.23; H 2.08; N 15.74.

2.2 Magnetic susceptibility measurements

Magnetic susceptibility measurements were carried out on the powder samples at a field of 18.94 kG using PAR Vibrating Sample Magnetometer in the temperature range 4.2–340 K. The error in temperature was ± 0.5 K while that in susceptibility was within 2%. The measured susceptibility values were corrected for underlying diamagnetism using Pascal's constants.

3. Magnetic susceptibility of exchange coupled dimers

Considerable progress has been made towards the understanding of the nature of magnetic interactions in low-dimensional systems (de Jongh and Miedema 1974). The spin Hamiltonian in the case of a low-dimensional system is given by

$$\mathcal{H} = \sum_{i=1}^{N/2} (J_1 S_{2i} S_{2i-1} + J_2 S_{2i} S_{2i+1}), \quad (1)$$

where J_1 and J_2 are the exchange coupling constants of a spin at $2i$, to its neighbouring spins at $(2i-1)$ and $(2i+1)$, respectively. The ratio J_2/J_1 , say α , is termed as the alternation parameter and it defines the dimensionality of the exchange coupled net work. For $\alpha = 1$ we have uniform coupling on both sides and hence the system is said to be 'uniform' or 'linear' chain with dimensionality unity. A zero value to alternation parameter indicates that the reference spin is coupled to only one of its neighbours and this is analogous to the dimerization of the 'pin system leading to exchange coupled dimers. The dimensionality in such a case would be zero. For values of α between 0 and 1, one has the 'alternating' chains with differing J_1 and J_2 .

The case of uniform exchange between spins along the chain has been studied mainly by Bonner and Fisher (1964), and Bulaevskii (1962), while the case of non-uniform or alternating exchange along the chain has been considered by Bulaevskii (1969) and Duffy and Baar (1968). The dimeric model also has been studied and reviewed extensively (Hatfield 1979). Using the Van Vleck (1932) expression for susceptibility the temperature dependence of the molar susceptibility for a system of doublet spins coupled into pairs is given by

$$\chi_M = \frac{Ng^2\beta^2}{3kT} [1 + \frac{1}{3} \exp(-2J/kT)]^{-1} + N\alpha + \chi_M^{\text{dia}}, \quad (2)$$

where $2J$ is the singlet-triplet separation, g is the effective average splitting factor, $N\alpha$ is the temperature independent paramagnetism (TIP) and χ_M^{dia} is the molar diamagnetic susceptibility. This expression, often referred to as the Bleaney-Bowers formula takes into account only the intradimeric interaction ($\alpha = 0$). For systems having significant interdimeric exchange contribution, a molecular field correction term is usually included to the Bleaney-Bowers formula as given by

$$\chi_M^{\text{corr.}} = \chi_M^{BB}/(1 - 2z J' \chi_M^{BB}/Ng^2\beta^2), \quad (3)$$

where χ_M^{BB} is the molar susceptibility of an isolated dimer of $S = \frac{1}{2}$ spins, J' is the interdimer exchange coupling constant and z is the number of nearest neighbours excluding the one to which the reference spin is strongly exchange coupled.

The interdimer interactions can also be included by using the following analytical expression developed by Hatfield and coworkers (Hatfield 1981; Hatfield *et al* 1982):

$$\chi_M = \frac{Ng^2\beta^2}{kT} \left[\frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3} \right], \quad (4)$$

where $x = J/kT$. The parameters A to F are defined as follows:

$$A = 0.25,$$

$$B = -0.12587 + 0.22752\alpha,$$

$$C = 0.019111 - 0.13307\alpha + 0.509\alpha^2 - 1.3167\alpha^3 + 1.0081\alpha^4,$$

$$D = 0.10772 + 1.4192\alpha,$$

$$E = -0.0028521 - 0.42346\alpha + 2.1953\alpha^2 - 0.82412\alpha^3,$$

$$F = 0.37754 - 0.067022\alpha + 5.9805\alpha^2 - 2.1678\alpha^3 + 15.838\alpha^4.$$

In the above expressions α is the alternation parameter as defined in (1) and the expressions are valid for $0 < \alpha < 0.4$. By measuring the molar susceptibility as a function of temperature and by fitting the data into (2), (3) or (4) one can get J , g and α with fair precision.

4. Structure of $Ni(mnt)_2^-$ dimers

The $Ni(mnt)_2^-$ systems generally exhibit two types of crystallographic packing. In the first type the metal chelate anions stack among themselves uniformly with

identical Ni–Ni distances along the stack direction giving rise to a linear (1D) chain system (Manoharan *et al* 1981; Ramakrishna and Manoharan 1983). A typical uniform chain packing is shown in figure 1. Such linear chain systems have been shown to have J values in the order of a few cm^{-1} or less. In the second type of structure (Fritchie 1966; Kobayashi and Sasaki 1977; Mahadevan *et al* 1983; Kuppusamy *et al* 1985a) there is an alternation of the interplanar spacing and hence alternating Ni–Ni distances along the stack direction, with varying degree of alternation. This alternation invariably results in dimerisation of the anions along the stack direction and this occurs involving the metal ions bridging to one of the sulphur atoms of the other anion of the same dimer. An example is shown in figure 2. The Ni . . . S (bridging, out-of-plane) distances range from 3.45 Å to 4 Å compared to the Ni–S (in-plane) distance ~ 2.15 Å.

The system $[\text{NMP}]^+ [\text{Ni}(\text{mnt})_2]^-$ has an alternating type of stack (Kuppusamy *et al* 1985a). A projection of the packing arrangement onto the *ab* plane of the triclinic unit cell is shown in figure 3. The Ni atom has an approximate square-planar configuration with all the four Ni–S distances equal within experimental error. The average Ni–S distance within a chelate is 2.138 Å while that of Ni . . . S (out-of-plane) is 4.0 Å. The Ni–Ni contact within the dimer is 4.16 Å and that between two dimers is 7.87 Å. Hence the packing can be best described as dimeric with the dimers stacked along the *a*-axis of the unit cell.

Figure 4 shows the perpendicular projection of one anion onto the plane of the other anion of the same dimer. The interplanar distance between the two chelate planes is 3.58 Å. The compounds $[\text{NEt}_4]^+ [\text{Ni}(\text{mnt})_2]^-$ (Kobayashi and Sasaki 1977) and $[\text{N}(\text{Ph})_3\text{Me}]^+ [\text{Ni}(\text{mnt})_2]^-$ (Fritchie 1966) also have been reported to have a similar packing, though the Ni–Ni alternations along the stack axis are not quite different. $[\text{NBu}_4]^+ [\text{Ni}(\text{mnt})_2]^-$ is structurally isomorphous to $[\text{NBu}_4]^+ [\text{Cu}(\text{mnt})_2]^-$, whose structure is known (Forrester *et al* 1964). A projection of the structure onto

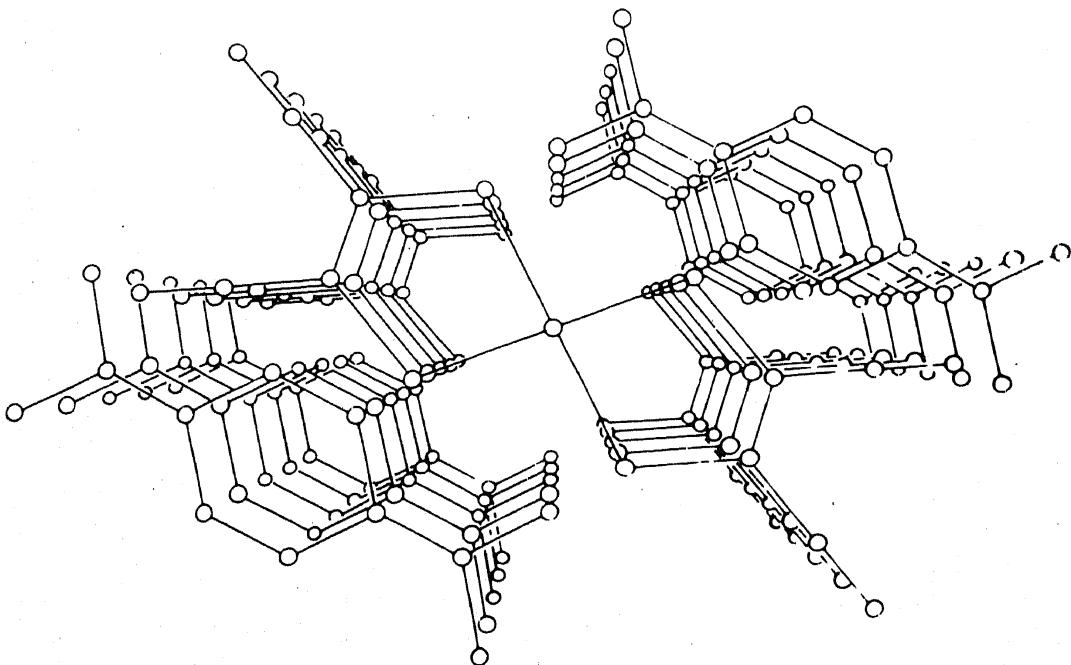


Figure 1. An example of uniform stack: $\text{TMPD}^+ \text{Ni}(\text{mnt})_2^-$.

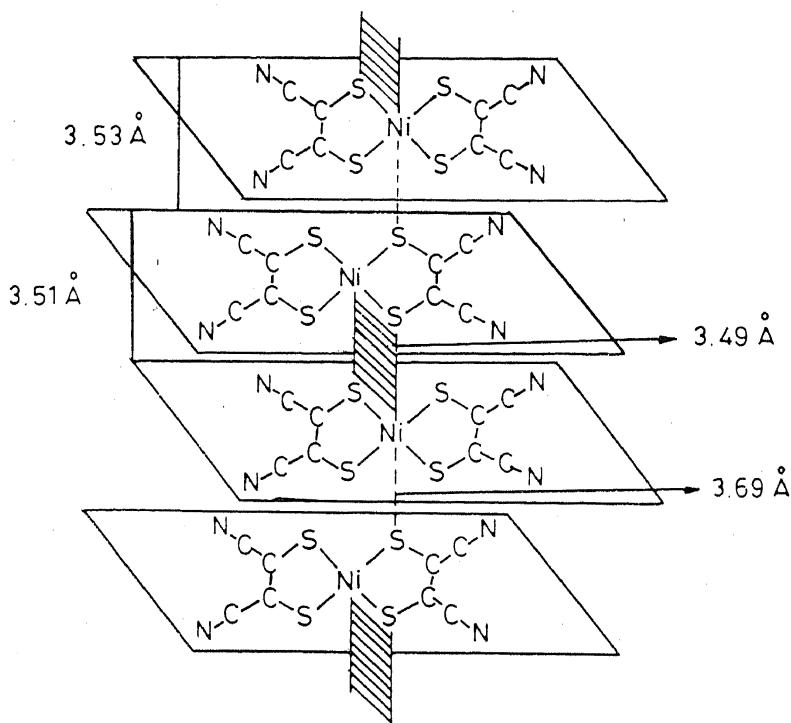


Figure 2. The anion stack of $\text{NEt}_4\text{Ni}(\text{mnt})_2$ showing the alternation in the Ni-S overlaps.

the *ab* plane in figure 5a shows the presence of $[\text{Cu}(\text{mnt})_2]^-$ dimers along the *a*-axis of the monoclinic lattice. Also shown in figure 5b is a projection of the pair as viewed down the stack axis. The Cu atoms in this structure have nearest Cu neighbours at 4.026 Å and 4.431 Å corresponding to respectively within the dimer and between the dimers.

5. Results and discussion

5.1 Magnetic susceptibility of $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$

All the alternating type $\text{Ni}(\text{mnt})_2^-$ systems show reduced magnetic moments (1.1 to 1.4 BM) at room temperature indicating the presence of antiferromagnetic coupling leading to a singlet ground state with a corresponding low-lying, thermally accessible triplet excited state. The temperature dependence of the paramagnetic susceptibility of $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ is shown in figure 6. A broad maximum characteristic of low-dimensional antiferromagnetic coupling is seen around 210 K. A least squares minimization procedure with an error function F of the form,

$$F(J, g, N\alpha) = \sum_i (\chi_i^{\text{cal}} - \chi_i^{\text{obs}})^2 / (\chi_i^{\text{cal}})^2, \quad (4)$$

was used with J , g and $N\alpha$ as variable parameters. The best fit was obtained for the data in the temperature range 90–340 K by using expressions (2) and (4) for

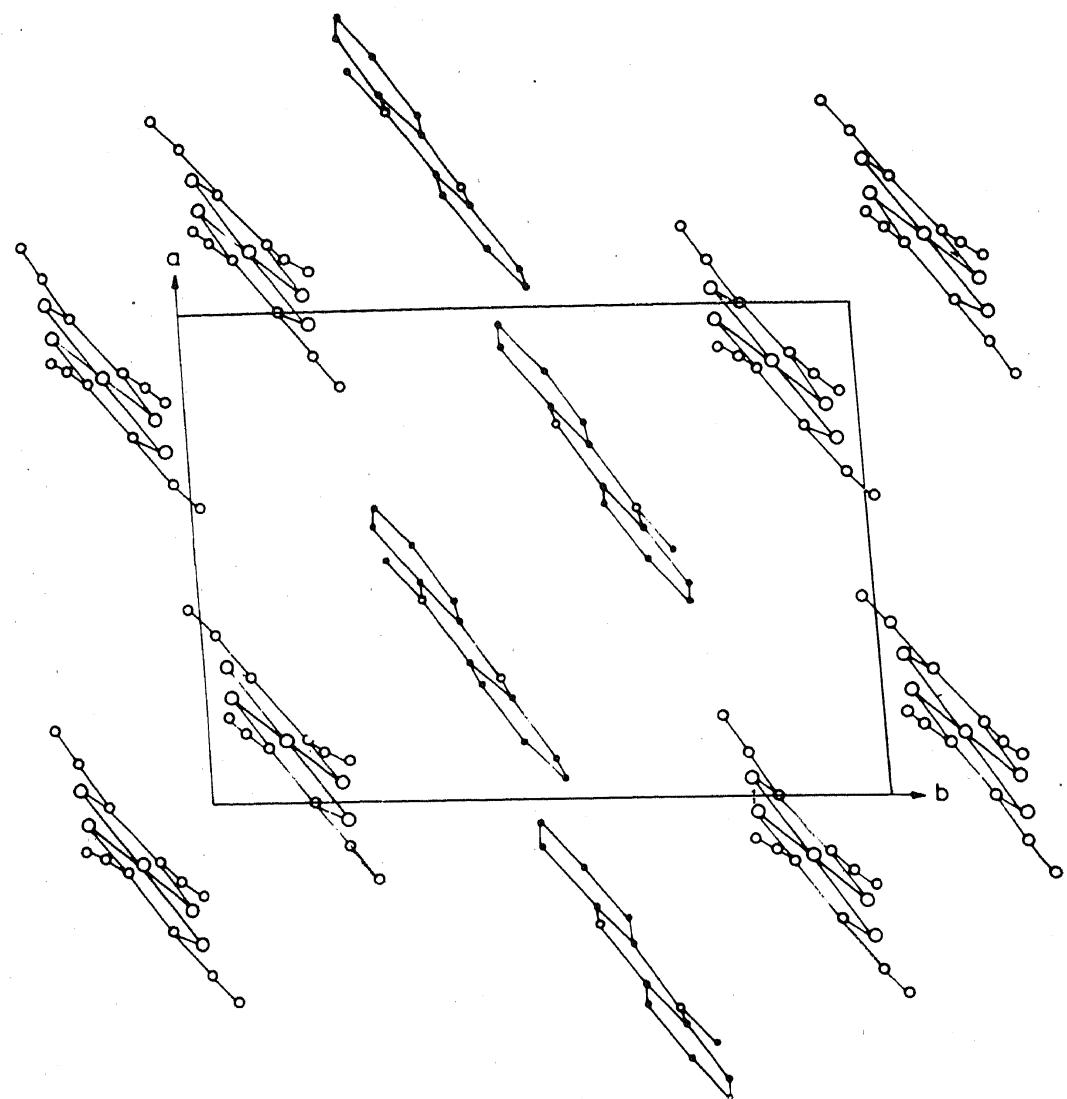


Figure 3. Projection of the packing arrangement in $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$ onto the ab plane.

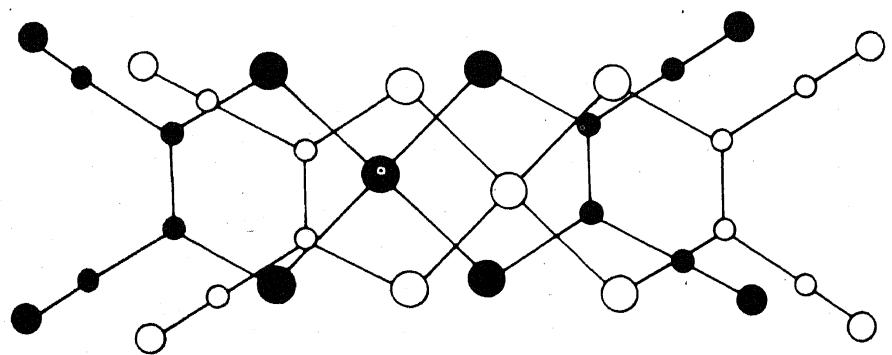


Figure 4. A perpendicular projection of one anion onto the plane of the other anion of $[\text{NMP}] [\text{Ni}(\text{mnt})_2]$.

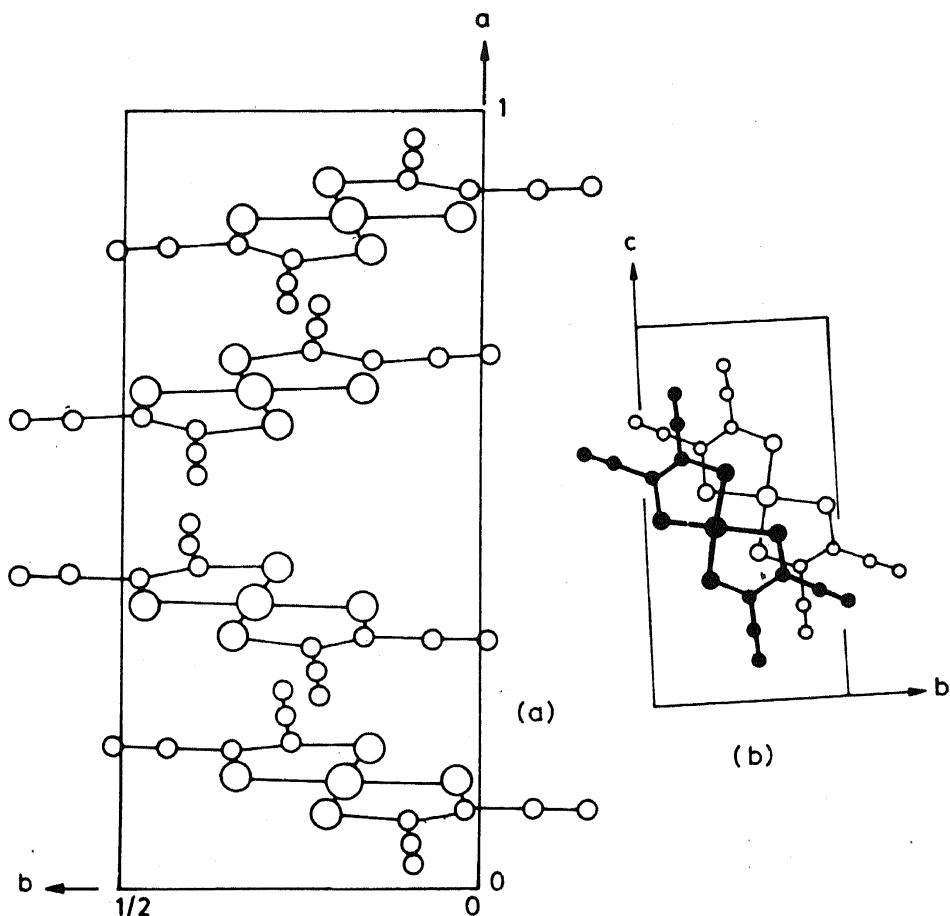


Figure 5. (a) A projection down the c -axis showing the $[Cu(mnt)_2]^-$ anions from the side (b) A projection down the a -axis showing the $[Cu(mnt)_2]^-$ dimer as viewed down the stack axis.

$2J = -241 \pm 2 \text{ cm}^{-1}$, $g = 2.061 \pm 0.002$ and $N\alpha = 206 \pm 5 \times 10^{-6} \text{ emu/mole}$. The singlet-triplet separation ($2J$, -241 cm^{-1}) is in the range expected for similar antiferromagnetically coupled $Ni(mnt)_2^-$ dimers (Weiher *et al* 1964).

Below 90 K an increase in susceptibility is noted (figure 6) contrary to the expectation that it must drop to a constant value ($N\alpha$) at lower temperatures in the case of antiferromagnetic coupling. Sometimes such an increase is attributed to the presence of Curie type (monomeric) impurities and due allowance is then given for their contributions at higher temperatures before interpreting the data. However, in the present case, the plot of $(\log \chi)$ vs $(\log T)$ as seen in figure 7 shows a power-law behaviour of χ on T as

$$\chi = A T^{-\alpha}$$

or

$$\log (\chi) = \log (A) - \alpha \log (T), \quad (5)$$

with $\alpha = 0.85$. This clearly rules out the presence of monomeric impurities, for which α must have been unity.

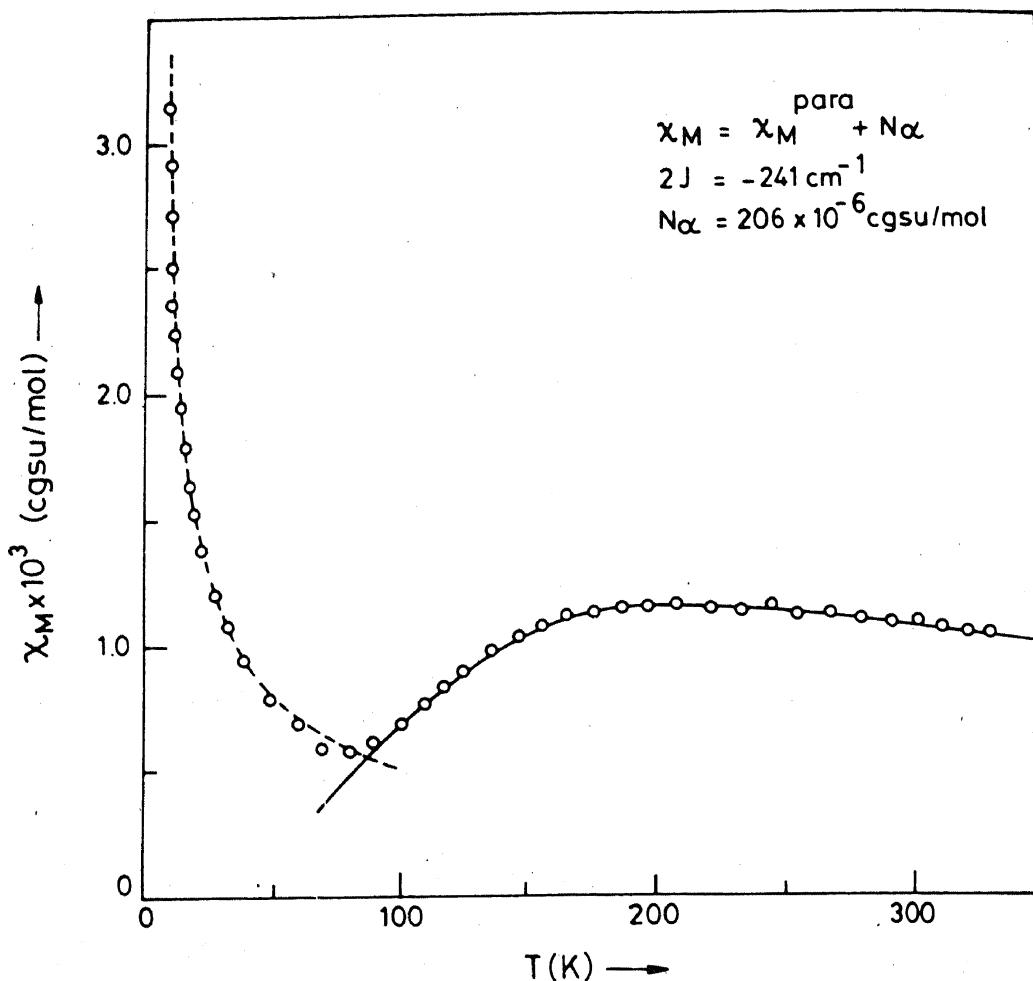


Figure 6. Temperature variation of χ_M^{para} of [NMP] $[\text{Ni}(\text{mnt})_2]$. The solid line above 90 K represents the theoretical susceptibility calculated from (2) while that below 70 K represents the susceptibility calculated by using the ECP model (7).

The power-law divergence has already been recognised in the case of uniform as well as alternating chains (Bulaevskii 1962; Bondeson and Soos 1980) as a characteristic property of the system. The occurrence of chemical or packing defects is quite general in low-dimensional systems and can have drastic consequences on the magnetic and transport properties. Finite chain effects produce divergent susceptibilities associated with odd length segments and the susceptibility deviates from Curie law as shown by (5), with α ranging between 0.72 and 0.89. Bulaevskii (1962) and Bondeson and Soos (1980) have studied this in detail based on the 'Random exchange in Heisenberg antiferromagnetic chains (REHAC)' model.

Tippie and Clark (1981) have proposed the 'exchange coupled pair (ECP)' model for random exchanges in alternating chains. In their model the system is supposed to be having a set of independent exchange-coupled pairs with the value of J distributed randomly with a probability function $P(J)$ given by

$$P(J) = AJ^{-\alpha}, \quad (6)$$

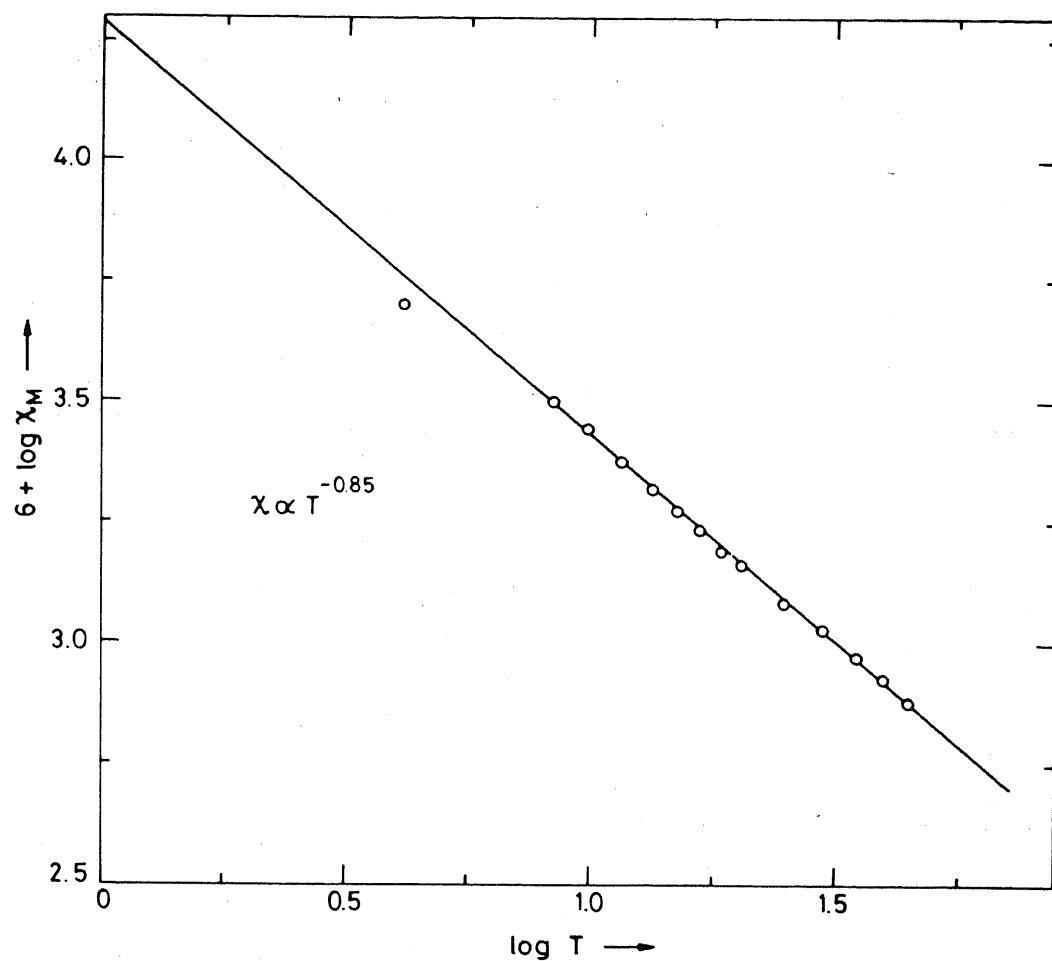


Figure 7. Plot of $\log \chi$ vs $\log T$ showing the power-law divergence with $\alpha = 0.85$.

where A and α are constants, $P(J)$ is normalised by introducing a cut-off at J_0 , the maximum J which occurs between the spin pairs at their minimum separation. For low temperatures ($kT \ll J_0$) and low fields ($g\beta B \ll kT$) the limiting susceptibility is given by

$$\chi = \frac{Ng^2\beta^2}{J_0} \left[\frac{2J_0}{kT} \right] f_1(\alpha), \quad (7)$$

where the function $f_1(\alpha)$ is given by

$$f_1(\alpha) = \int_0^\infty \frac{x^{1-\alpha} e^{-x}}{(1+3e^{-x})^2} dx, \quad (8)$$

with $x = J/kT$. To an accuracy of $\pm 3\%$, f_1 is approximated by

$$f_1(\alpha) = 0.445 \exp(-0.633\alpha). \quad (9)$$

For $[NMP][Ni(mnt)_2]$ the data below 70 K could be fit very satisfactorily into (7) for $\alpha = 0.85$ (figure 6) and for a concentration of random exchanges, $C = 0.05$. Hence it is observed that 5% of the exchanges are distributed randomly with a maximum cut-off at $2J$.

It should be noted from the crystal structure that the dimers are well isolated from each other as is evident from the very different Ni-Ni alternation distances along the a -axis. This would mean that the interdimer interaction (J') is negligible in comparison with J . This was further confirmed as follows: (i) Equation (2) was found to be adequate to interpret the observed data and (ii) the fitting was tried with the expression (4) of Hatfield *et al* (1982) for different values of α , but the best fit was obtained only for $\alpha = 0$.

5.2 Magnetic susceptibility of $[NBu_4][Ni(mnt)_2]$

The magnetic susceptibility was measured on the powder sample of $[NBu_4][Ni(mnt)_2]$ to have an estimate of the exchange coupling constant. The variation of paramagnetic susceptibility with temperature after correcting for temperature independent contributions ($N\alpha + \chi_M^{\text{dia}}$) is shown in figure 8. The susceptibility data could not be fitted satisfactorily into (2) which as such does not take the interdimer interactions into account. Alternatively the data were fitted using (4) by least squares minimization procedures to get $2J = -226 \pm 2 \text{ cm}^{-1}$, $g = 2.061 \pm 0.002$ and $\alpha = 0.045 \pm 0.005$. The agreement is excellent as shown in figure 8. As the $Ni(mnt)_2^-$ chains are well separated by the bulky $[NBu_4]^+$ cations no correction for the interchain interaction was considered significant.

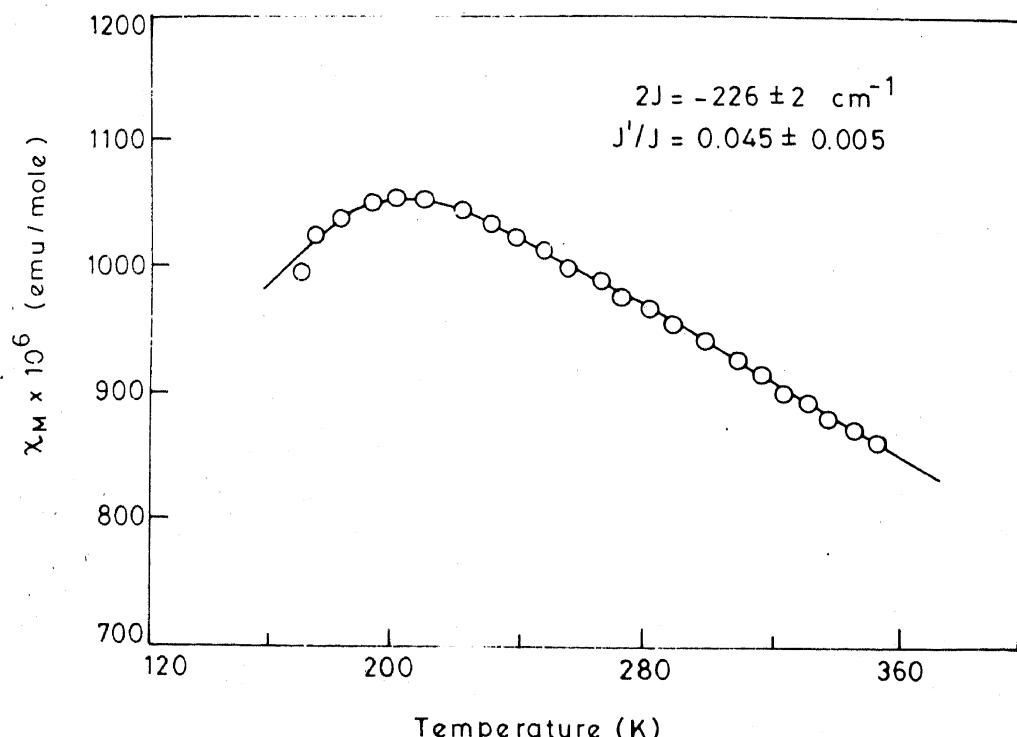


Figure 8. χ vs T for $[NBu_4][Ni(mnt)_2]$. The solid line is the theoretical fit for (4) with $2J = -226 \pm 2 \text{ cm}^{-1}$ and $J'/J = 0.045 \pm 0.005$, while the circles are experimental values.

5.3 Structure-magnetism of dimers

The available magnetic and structural data on $[\text{Ni}(\text{mnt})_2]^-$ dimers may be used to make a few generalizations regarding the strength of exchange coupling and the structure of the dimer. A schematic view of the structure of a typical dimer is shown in figure 9. In all the known $[\text{Ni}(\text{mnt})_2]^-$ dimers the Ni-Ni distance ranges from 4.0 to 4.4 Å. While direct Ni-Ni bonding at this distance is clearly ruled out, the superexchange mechanism involving empty $3d_{xy}$ and $3d_{z^2}$ orbitals of sulphur as proposed by Weiher *et al* (1964) has to be invoked to account for the observed spin-spin coupling. A schematic sketch of the superexchange pathway is presented in figure 10. In this mechanism a delocalization of the odd electron from a nickel $3d_{xy}$ orbital into the empty $3d_{xy}$ orbital of an in-plane bonded sulphur atom occurs which in turn polarises by spin-exchange the weak bond that is formed by the

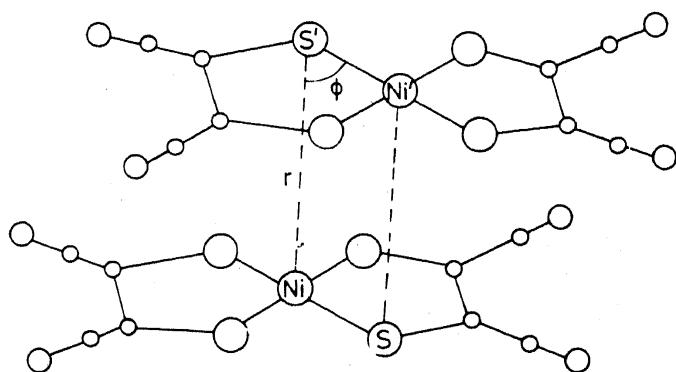


Figure 9. Structure of a typical $[\text{Ni}(\text{mnt})_2]^-$ dimer.

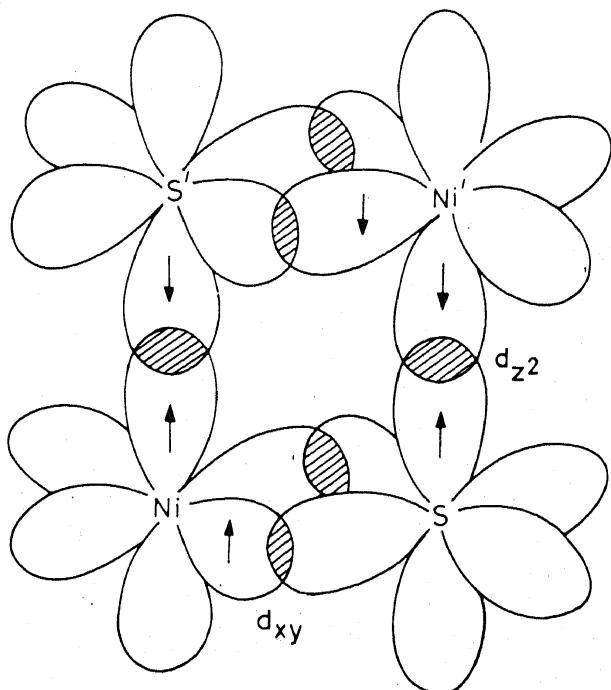


Figure 10. Superechange pathway for the antiferromagnetic exchange coupling $[\text{Ni}(\text{mnt})_2]^-$ dimers (Weiher *et al* 1964).

interaction of doubly occupied d_{z^2} orbital of Ni' with the empty $\text{S}-\text{d}_{z^2}$ orbital. Now the spin correlation between the odd electron in $\text{Ni}'-\text{d}_{xy}$ and the polarised electrons of the $\text{Ni}'-\text{S}$ weak bond results in an antiferromagnetic alignment of the two odd electrons. This coupling is further enhanced by the cooperative interaction of the two correlation pathways. Such a pair wise correlation should depend very critically on the nickel-out-of-plane sulphur distance (r) as well as the $\text{Ni}-\text{S}'-\text{Ni}'$ bridge angle (ϕ). A collection of such parameters along with the known exchange coupling constants is presented in table 1.

The relative disposition of the two $[\text{Ni}(\text{mnt})_2]^-$ units in a dimer as viewed down the normal to the chelate plane is shown in figure 11 for the compounds listed in table 1. A comparison of the overlap in $[\text{NMP}]^-[\text{Ni}(\text{mnt})_2]$ (figure 4) with those in figure 11 shows that in the former case the overlap is different. In $[\text{NMP}]^-[\text{Ni}(\text{mnt})_2]$ there are two out-of-plane sulphur atoms which are almost equidistant from the nickel atom and with different bridging angles. The other three systems, $[\text{NBu}_4]^+$, $[\text{NEt}_4]^+$ and $[\text{P}(\text{Ph})_3\text{Me}]^+$ have almost identical disposition with a distinct $\text{Ni}-\text{S}'-\text{Ni}'$ overlap.

In the case of hydroxo-bridged $\text{Cu}-\text{Cu}$ dimers a linear dependence of J on ϕ has been observed (Crowford *et al* 1976; Hatfield 1974; Hodgson 1975) while in the case of chloro as well as sulphur bridged $\text{Cu}-\text{Cu}$ dimer, J has been shown to depend on ϕ/r (Hatfield *et al* 1980; Hatfield 1983). An inspection of the parameters in table 1 shows that in $[\text{Ni}(\text{mnt})_2]^-$ cases both ϕ and r are important. A plot of $-2J$ versus ϕ/r for the four systems in figure 12 shows a linear variation of J with ϕ/r . The deviation of $[\text{NMP}]^+$ system from the fit is quite reasonable as there are two different superexchange pathways available. However, we need additional data on similar systems to confirm the linear dependence. The exchange coupling constant ($-2J$) or more precisely the singlet-triplet separation is related to ϕ/r as

$$-2J = 106.5 \text{ deg}^{-1} (\phi/r \text{ deg.cm}^{-1}) - 2240 \text{ cm}^{-1}. \quad (10)$$

It must, however, be mentioned that the form and correctness of the above expression is to be tested with data on a few more similar systems and also be justified by theoretical calculations. At present we are carrying out the susceptibility and structural studies on two more dimeric systems namely, $[\text{NPhMe}_3]^-[\text{Ni}(\text{mnt})_2]$ (Mahadevan *et al* 1983) and [crystal violet] $[\text{Ni}(\text{mnt})_2]$ and we hope to come out with more data to substantiate the above predictions. Also we

Table 1. Structure and magnetic data for $[\text{R}]^+[\text{Ni}(\text{mnt})_2]^-$ dimers.

$[\text{R}]^+$	$\text{Ni}-\text{S}^a$ (\AA)	$\text{Ni} \dots \text{S}^b$ (r , \AA)	$\text{Ni} \dots \text{Ni}$ (\AA)	d^c \AA	$\text{Ni}' \dots \text{S}-\text{Ni}$ (ϕ , deg)	$-2J$ (cm^{-1})
$[\text{P}(\text{Ph})_3\text{Me}]^+$	2.147	3.591	4.400	3.353	96.7	620 ^d
$[\text{NEt}_4]^+$	2.149	3.515	4.137	3.516	90.5	490 ^d
$[\text{NBu}_4]^{+e}$	2.147	3.640	4.026	3.541	83.6	226
$[\text{NMP}]^+$	2.142	3.900 (4.096)	4.113	3.581	80.1 (75.4)	241

^a Short in-plane $\text{Ni}-\text{S}$ bond distance;

^b Long out-of-plane bond distance;

^c Interplanar distance;

^d Weiher *et al* 1964;

^e Isomorphous to the $\text{Cu}(\text{III})$ analog (Forrester *et al* 1964).

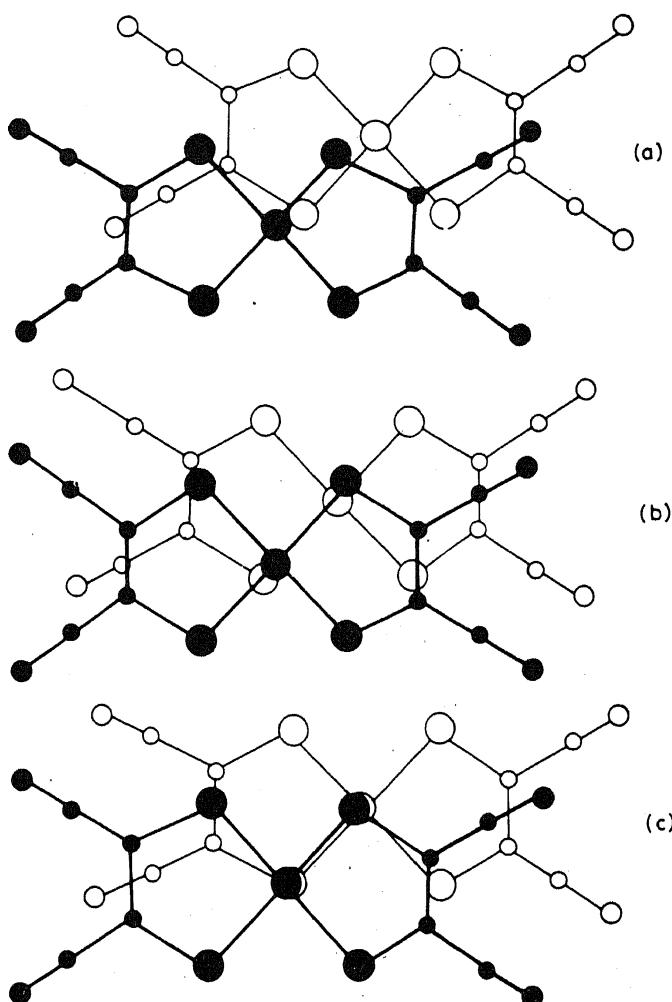


Figure 11. Projection of one of the two $[\text{Ni}(\text{mnt})_2]^-$ ions onto the plane of the other of the dimer (a) $[\text{P}(\text{Ph})_3\text{Me}^+] [\text{Ni}(\text{mnt})_2]$; (b) $[\text{NEt}_4^+] [\text{Ni}(\text{mnt})_2]$; (c) $[\text{NBu}_4^+] [\text{Ni}(\text{mnt})_2]$.

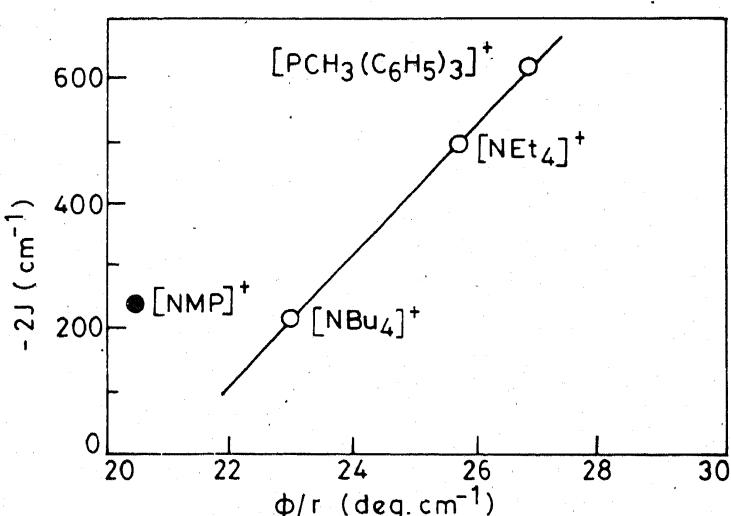


Figure 12. Correspondence between $-2J$ and ϕ/r for $[\text{Ni}(\text{mnt})_2]$ dimers.

are trying to estimate the magnitude of the exchange coupling constant from purely theoretical basis knowing the structure of the dimers.

6. Conclusion

The *bis*(maleonitriledithiolato)nickel(III) complexes show alternation in the metal ion stack and this results in the formation of exchange coupled pairs. The magnetic susceptibility measurements indicate that there is strong demagnetisation due to antiferromagnetic exchange coupling between the ions within the dimer. The exchange coupling constant is very sensitive to the structure of the dimeric unit. The results have been used to obtain a correlation between the structure and magnetism of exchange coupled $[\text{Ni}(\text{mnt})_2]^-$ dimers. A linear dependence of J on ϕ/r has been proposed.

Acknowledgement

This work was supported by a scheme from the Department of Science and Technology, Government of India, New Delhi.

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