Magnetism: Molecules to Materials V

Edited by Joel S. Miller and Marc Drillon

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Preface

The development, characterization, and technological exploitation of new materials, particularly as components in 'smart' systems, are key challenges for chemistry and physics in the next millennium. New substances and composites including nanostructured materials are envisioned for innumerable areas including magnets for the communication and information sector of our economy. Magnets are already an important component of the economy with worldwide sales exceeding $30 billion per annum. Hence, research groups worldwide are targeting the preparation and study of new magnets especially in combination with other technologically important properties, *e. g.*, electrical and optical properties.

In the past few years our understanding of magnetism and magnetic materials, thought to be mature, has enjoyed a renaissance as it is being expanded by contributions from many diverse areas of science and engineering. These include (*i*) the discovery of bulk ferro- and ferrimagnets based on organic/molecular components with critical temperature exceeding room temperature, (*ii*) the discovery that clusters in high, but not necessarily the highest, spin states due to a large magnetic anisotropy or zero field splitting have a significant relaxation barrier that traps magnetic flux enabling a single molecule/ion (cluster) to act as a magnet at low temperature; (*iii*) the discovery of materials exhibiting large, negative magnetization; (*iv*) spin-crossover materials that can show large hysteretic effects above room temperature; (*v*) photomagnetic and (*vi*) electrochemical modulation of the magnetic behavior; (*vii*) the Haldane conjecture and its experimental realization; (*viii*) quantum tunneling of magnetization in high spin organic molecules; (*viii*) giant and (*ix*) colossal magnetoresistance effects observed for 3-D network solids; (*x*) the realization of nanosize materials, such as self organized metal-based clusters, dots and wires; (*xi*) the development of metallic multilayers and the spin electronics for the applications. This important contribution to magnetism and more importantly to science in general will lead us into the next millennium.

Documentation of the status of research, ever since William Gilbert's *de Magnete* in 1600, provides the foundation for future discoveries to thrive. As this millennium begins the time is appropriate to pool our growing knowledge and assess many aspects of magnetism. This series entitled *Magnetism: Molecules to Mate-*

rials provides a forum for comprehensive yet critical reviews on many aspects of magnetism that are on the forefront of science today.

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1 Metallocenium Salts of Radical Anion Bis(Dichalcogenate) Metalates

Vasco Pires Silva da Gama and Maria Teresa Duarté

1.1 Introduction

For the last 30 years metal-bis(1,2-dichalcogenate) anionic complexes have been extensively used as building blocks for the preparation of both conducting and magnetic molecular materials. Several of these materials show remarkable features and have made a significant contribution to the development of molecular materials science.

It is worth mentioning some examples of the molecular materials based on metal-bis(1,2-dichalcogenate) anionic complexes based that have made a significant contribution to the field of molecular material science, in the last decades. A large number of molecular conductors and even superconductors based on metal-bis(1,2-dichalcogenate) anionic acceptors have been obtained [1] and $Me_4N[Ni(dmit)_2]_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) was the first example of a π acceptor superconductor with a closed-shell donor [2]. The spin-Peierls transition was observed for the first time in the linear spin chain system $TTF[Cu(tdt)_2]$ [3] (TTF = tetrathiafulvalene; tdt = 1,2-ditrifluoromethyl-1,2-ethylenedithioate). The co-existence of linear spin chains and conducting electrons, was observed for the first time in the compounds $Per_2[M(mnt)_2]$ (M = Ni, Pd, Pt) [4] (mnt = 1,2-dicyano-1,2-ethylene-dithiolato), presenting competing spin-Peierls and Peierls instabilities of the spin chains and 1D conducting electronic systems. A purely organic system with a spin-ladder configuration was observed for the first time in the compound $DT-TTF_2[Au(mnt)_2]$ [5] (DT-TTF = dithiophentetrathiafulvalene). A spin transition was observed in the compound $[Fe(mnt)_2rad]$ [6], where rad = 2-(*p-N*-methylpyridinium)4,4,5,5-tetramethylimidazoline-1-oxyl. Ferromagnetic ordering was reported for $NH_4[Ni(mnt)_2]H_2O$ [7].

The discovery of the first molecule-based material exhibiting ferromagnetic ordering, the electron-transfer (ET) salt $[Fe(Cp^*)_2]TCNE$ (TCNE = tetracyanoethylene), with $T_C = 4.8$ K, in 1986 [8, 9], was a landmark in molecular magnetism and gave a significant impulse to this field. Since then among the strategies followed to obtain cooperative magnetic properties, considerable attention has been given to the linear-chain electron-transfer salts based on metallocenium donors and on planar acceptors. [10, 11]. Besides $[Fe(Cp^*)_2]TCNE$, bulk ferromagnetism was reported

for other ET salts based on decamethylmetallocenes and on the conjugated polynitriles TCNE [12] and TCNQ [13] (TCNQ = 7,7,8,8-tetracyano-p-quinodimethane). An extensive study of these salts was made, covering a variety of aspects including the structure-magnetic property relationship [10], and the effects of spin variation and of spinless defects [10]. Furthermore they provided a valuable basis to test the various models that were proposed in order to explain the magnetic coupling and magnetic ordering in the molecule-based magnets [14, 15].
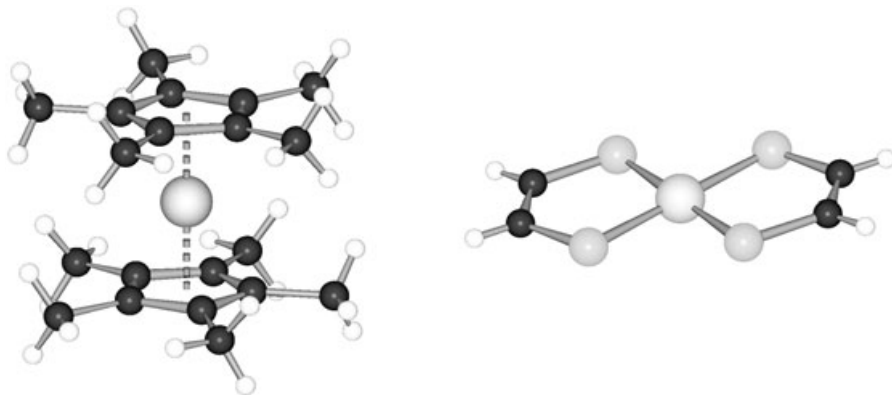
Fig. 1.1. Molecular structure of [Fe(Cp*)$_2$][Ni(edt)$_2$], showing the basic donor and acceptor molecules studied in this review.

Following the report of ferromagnetism for [Fe(Cp*)$_2$]TCNE, metal bis-dichalcogenate planar acceptors were also considered as suitable candidates for use in the preparation of ET salts with the radical metallocenium donors, and in the search for new molecular magnets the first metal bis-dichalcogenate based compounds were reported in 1989 [16, 17]. In particular the monoanionic forms of the metal bis-dichalcogenate (Ni, Pd, Pt) complexes seem particularly promising for ''the synthesis of mixed-stack molecular charge-transfer salts that display cooperative magnetic phenomena due to (1) their planar structures, (2) delocalized electronic states, $S = 1/2$ spin state for the monomeric species, and (3) the possibility of extended magnetic interactions mediated by the chalcogen atoms'' [17].

The work with ET salts based on metallocenium donors and on planar metal bis-dichalcogenate radical anions is summarized in this chapter. Most of the materials studied to date are decamethylmetallocenium based ET salts, other compounds based on different metallocenium derivatives have also been reported and will be

[M(edt)$_2$]

[M(tdt)$_2$] (X = S)
[M(tds)$_2$] (X = Se)

[M(mnt)$_2$]

[M(bdt)$_2$] (X = S)
[M(bds)$_2$] (X = Se)

[M(dmit)$_2$] (X = S)
[M(dmio)$_2$] (X = O)

[M(α-tpdt)$_2$]
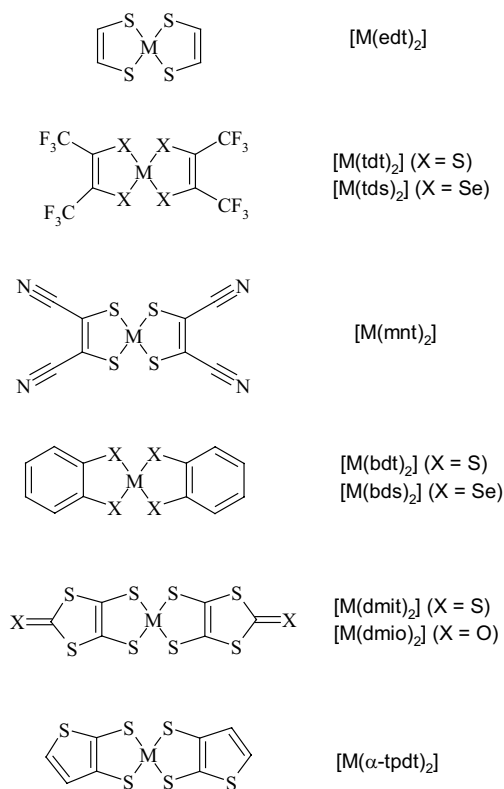
Scheme 1.1 Schematic representation of the metal bis-dichalcogenate acceptors studied in this chapter.

referred to. The metal bis-dichalcogenate complexes mentioned in this chapter are represented in Scheme 1.1.

As magnetic ordering is a bulk property, particular attention will be given to the supramolecular arrangements which determine the magnetic behavior. The crystal structure of the compounds will be correlated with the magnetic behavior of these ET salts. The magnetic coupling in the ET salts based on decamethylmetallocenium donors has been analyzed mainly through McConnell I [18] or McConnell II [19] mechanisms, and this issue is still a subject of controversy [15, 20]. Of these models, McConnell I has been most often used in the interpretation of the magnetic behavior of these salts, as, in spite of its simplicity, it has shown good agreement with the experimental observations. In this chapter the interpretation of the magnetic coupling will be analyzed in the perspective of this model. However, it should be mentioned that the validity of the McConnell I mechanism has been questioned both theoretically [21] and experimentally [22].

1.2   Basic Structural Motifs

1.2.1   ET Salts Based on Decamethylmetallocenium Donors

In most of the ET salts based on decamethylmetallocenium donors, due to the planar configurations of both the C_5Me_5 ligands and of the metal bis-dichalcogenate acceptors the crystal structures are, with a few exceptions, based on linear chain arrangements of alternating donor and acceptor molecules. In these salts four distinct types of linear chain arrangements have been observed and are represented schematically in Figure 1.2. The type I chain arrangement corresponds to the most simple case of an alternated linear chain motif $\cdot\cdot A^-D^+A^-D^+A^-D^+\cdot\cdot$, similar to that observed in several salts based on metallocenium donors and on acceptors such as TCNE and TCNQ [10]. In the case of the type II chain, the donors alternate with face-to-face pairs of acceptors, $\cdot\cdot A^-A^-D^+A^-A^-D^+\cdot\cdot$, as in this arrangement there is a net charge $(-)$ per repeat unit, $A^-A^-D^+$, charge compensation is required. For the type III arrangement the linear chains consist of alternated face-to-face pairs of acceptors with side-by-side pairs of donors, $\cdot\cdot A^-A^-D^+D^+A^-A^-D^+D^+\cdot\cdot$. Finally in the type IV arrangement, the acceptors alternate with side-by-side pairs of donors, $\cdot\cdot A^-D^+D^+A^-D^+D^+\cdot\cdot$, in this case there is a net charge $(+)$ per repeat unit, $D^+D^+A^-$, which must be compensated. For most of the ET salts based on types I and III arrangements (neutral chains), only one type of chain arrangement was observed. However, in the case of compounds based on types II and IV arrangements (charged chains), more complex crystal structures could be observed, resulting from the required charge neutralization. Table 1.1 summarizes the unit cell parameters, space group symmetry, and the type of observed linear chain ar-

I   II   III   IV

Fig. 1.2. Representation of the basic types of mixed chain sequences observed in the ET salts based on metallocene donors and on metal bis-dichalcogenate acceptors.

Table 1.1. Unit cell parameters and chain type for the mixed chain salts.

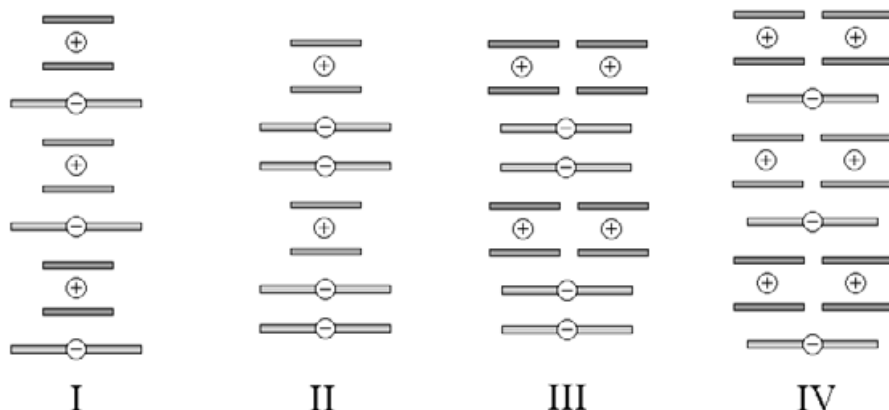| Compound	Chain Type	Space Group	a, Å	b, Å	c, Å	α, °	β, °	γ, °	Vol., Å^3	Z	T, °C	Ref.
[Fe(Cp*)$_2$][Ni(edt)$_2$]	I	C2/m	13.319	13.699	8.719	90.00	125.06	90.00	1302	2	20	23
[Cr(Cp*)$_2$][Ni(edt)$_2$]	I	C2/m	13.44	13.66	8.96	90.0	124.2	90.0	1320	2	20	23
[Fe(Cp*)$_2$][Ni(tdt)$_2$]	I	C2/c	14.417	12.659	18.454	90.00	95.17	90.00	3354	4	-70	16
[Mn(Cp*)$_2$][Ni(tdt)$_2$]	I	C2/c	14.302	12.697	18.415	90.00	94.63	90.00	3333	4	(a)	24
[Fe(Cp*)$_2$][Pt(tdt)$_2$]	I	$P\overline{1}$	8.490	10.278	10.936	106.79	103.95	101.98	846	1	-70	25
[Fe(Cp*)$_2$][Ni(tds)$_2$]	I	$P\overline{1}$	8.581	10.464	11.132	107.96	103.65	101.82	881	1	20	26
[Mn(Cp*)$_2$][Ni(tds)$_2$]	I	$P\overline{1}$	8.582	10.472	11.158	108.41	103.57	101.79	882	1	20	27
[Cr(Cp*)$_2$][Ni(tds)$_2$]	I	$P\overline{1}$	8.580	10.547	11.138	109.49	103.20	101.76	881	1	20	28
[Fe(Cp*)$_2$][Pt(tds)$_2$]	I	$P\overline{1}$	8.606	10.521	11.138	108.81	102.89	101.30	891	1	20	26
[Mn(Cp*)$_2$][Pt(tds)$_2$]	I	$P\overline{1}$	8.618	10.560	11.239	109.49	102.78	101.30	899	1	20	28
[Cr(Cp*)$_2$][Pt(tds)$_2$]	I	C2/c	11.352	21.848	14.969	90.00	103.73	90.00	3607	4	20	28
α-[Fe(Cp*)$_2$][Pt(mnt)$_2$]	II	C2/m	16.802	21.095	12.942	90.00	94.52	90.00	4473	6	20	16
β-[Fe(Cp*)$_2$][Pt(mnt)$_2$]	I	$P\overline{1}$	12.106	14.152	14.394	108.94	96.37	90.51	2312	3	23	16
[Fe(Cp*)$_2$]$_2$[Cu(mnt)$_2$]	IV	$P\overline{1}$	9.713	11.407	11.958	100.90	113.20	92.66	1185	1	25	29
[Fe(Cp*)$_2$][Ni(dmit)$_2$]	III	$P\overline{1}$	11.347	14.958	10.020	97.68	94.36	109.52	1575	2	-120	17
[Mn(Cp*)$_2$][Ni(dmit)$_2$]	III	$P\overline{1}$	11.415	14.940	10.020	97.40	94.58	109.63	1582	2	(a)	30
α-[Fe(Cp*)$_2$][Pd(dmit)$_2$]	III	$P\overline{1}$	9.907	12.104	14.464	82.44	85.80	82.73	1703	2	20	31
[Fe(Cp*)$_2$][Pt(dmit)$_2$]	III	$P\overline{1}$	9.996	11.554	15.108	109.72	97.62	93.78	1616	2	20	31
[Fe(Cp*)$_2$][Ni(dmio)$_2$]MeCN	IV	C2/m	16.374	10.84	19.530	90.00	88.02	90.00	3431	4	(a)	32
[Fe(Cp*)$_2$][Pd(dmio)$_2$]	III	$P\overline{1}$	14.133	14.620	16.055	88.43	80.25	86.38	3260	4	20	31
[Fe(Cp*)$_2$][Pt(dmio)$_2$]	III	$P\overline{1}$	14.133	14.620	16.055	88.43	80.25	86.38	3260	4	20	31
[Fe(Cp*)$_2$][Ni(dsit)$_2$]	III	$P\overline{1}$	9.650	11.439	16.643	71.14	73.24	89.72	1657	2	20	31
[Fe(Cp*)$_2$][Ni(bdt)$_2$]	IV	$P\overline{1}$	9.731	19.044	35.677	105.22	94.91	97.99	6266	8	20	33
[Mn(Cp*)$_2$][Ni(bdt)$_2$]	IV	$P\overline{1}$	9.760	19.101	35.606	105.02	94.72	98.15	6293	8	20	33
[Cr(Cp*)$_2$][Ni(bdt)$_2$]	IV	$P\overline{1}$	9.782	17.885	19.163	74.84	81.58	82.91	3189	4	20	33
[Mn(Cp*)$_2$][Co(bdt)$_2$]	IV	$P\overline{1}$	9.738	19.119	35.698	105.27	94.36	98.34	6298	8	20	33
[Cr(Cp*)$_2$][Co(bdt)$_2$]	IV	$P\overline{1}$	9.772	17.896	19.198	75.12	81.45	82.09	3191	4	20	33
[Fe(Cp*)$_2$][Pt(bdt)$_2$]	IV	$P\overline{1}$	7.763	19.126	35.564	104.50	95.26	97.87	6314	8	20	33
[Cr(Cp*)$_2$][Pt(bdt)$_2$]	IV	$P\overline{1}$	9.787	19.241	35.587	103.98	94.69	98.31	6387	8	20	33
[Fe(Cp*)$_2$][Ni(bds)$_2$]MeCN	IV	$P\overline{1}$	11.720	16.282	9.606	100.66	106.03	81.75	1723	2	-120	17
[Fe(Cp*)$_2$][Ni(α-tpdt)$_2$]	I	P2$_1$/c	20.360	10.237	15.443	90.00	107.54	90.00	3069	4	20	34
[Cr(Cp*)$_2$][Ni(α-tpdt)$_2$]	I	P2$_1$/c	10.053	10.281	15.577	90.00	104.89	90.00	1556	2	20	35
[Fe(C$_5$Me$_4$SCMe$_3$)$_2$][Ni(mnt)$_2$]	I	$P\overline{1}$	9.619	9.622	11.253	79.72	78.66	76.62	984	1	22	36
[Fe(C$_5$Me$_4$SCMe$_3$)$_2$][Pt(mnt)$_2$]	I	$P\overline{1}$	9.591	9.681	11.252	78.17	78.47	77.38	984	1	22	36

(a) Not given.

rangements for mixed chain ET salts based on metallocenium donors and metal bis-dichalcogenate acceptors.

While in the case of the cyano radical based salts, most of the observed structures present a type I structural arrangement, in the case of the ET salts based on metal bis-dichalcogenate acceptors a much larger variety of arrangements was observed, as described above. The structural motifs in the [M(Cp*)$_2$][M'(L)$_2$] ET salts are primarily determined by factors such as the dimensions of the anionic metal bis-dichalcogenate complexes, the tendency of the acceptors to associate as dimers, the extent of the π system in the acceptor molecule, and the charge density distribution on the ligands.

In the case of the [M(edt)$_2$]$^-$ based salts, with the smaller acceptor, the size of the acceptor is similar to the size of the C$_5$Me$_5$ ligand of the donor and only type I structural motifs (DADA chains) were observed. For the intermediate size

anionic complexes, $[M(tdx)_2]^-$, $[M(mnt)_2]$ and $[Ni(\alpha\text{-tpdt})_2]^-$, the most common structural motif obtained in ET salts based on those acceptors is also of type I. For the larger anionic complexes, $[M(bdx)_2]^-$ and $[M(dmix)_2]^-$, types III and IV chain arrangements were observed, in both cases acceptor molecules (type IV) or face-to-face pairs of acceptors (type III) alternate with side-by-side pairs of donors. The complexes $[M(mnt)_2]^-$ and $[M(dmix)_2]^-$, (M = Ni, Pd and Pt), frequently undergo dimerization in the solid state [37], and they are the only acceptors where the chain arrangements have face-to-face pairs of acceptors (structural motifs II and III). The variety of structural arrangements observed in the $[M(mnt)_2]^-$ based compounds can be related to both the large extent of the π system and the high charge density on the terminal nitrile groups [38], as well as to the tendency of these complexes to form dimers.

1.2.2   ET Salts Based on Other Metallocenium Donors

Besides the decamethylmetallocenium based salts, in the compounds based on other metallocenium derivatives, mixed linear chain arrangements were only observed in the case of the salts $[Fe(C_5Me_4SCMe_3)_2][M(mnt)_2]$, M = Ni and Pt, which present type I structural motifs.

Some ET salts based on other metallocenium derivatives and on the acceptors $[M(mnt)_2]^-$ and $[M(dmit)_2]^-$ (M = Ni and Pt) have also been reported. In the case of these compounds, the crystal structure consists of segregated stacks of donors, $\cdot\cdot D^+D^+D^+D^+\cdot\cdot$, and acceptors, $\cdot\cdot A^-A^-A^-A^-\cdot\cdot$, which is a common situation in molecular materials, in particular in the case of molecular conductors. In spite of the fact that for most salts the dominant magnetic interactions between the metal bis-dichalcogenate units are antiferromagnetic, there are cases where the interactions are known to be ferromagnetic, as in the case of the compounds n-Bu$_4$N[Ni(α-tpdt)$_2$] [34] and NH$_4$[Ni(mnt)$_2$](H$_2$O, which was the first metal bis-dichalcogenate based material to present ferromagnetic ordering, with T_C = 4.5 K [7]. The unit cell parameters of the ferrocenium derivative salts with crystal structures based on segregated acceptor stacks are shown in Table 1.2.

Table 1.2. Unit cell parameters for the segregated stack salts.

Compound	Space Group	a, Å	b, Å	c, Å	α, °	β, °	γ, °	Vol., Å^3	Z	T, °C	Ref.
[Fe(Cp)$_2$]$_2$[Ni(mnt)$_2$]$_2$[Fe(Cp)$_2$]	$P\bar{1}$	12.030	13.652	15.462	87.91	77.62	72.56	2365	2	(a)	39
[Fe(C$_5$Me$_4$SMe)$_2$][Ni(mnt)$_2$]	$P\bar{1}$	8.649	14.080	15.358	65.27	77.77	80.78	1654	2	22	36
[Fe(C$_5$H$_4$R)$_2$][Ni(mnt)$_2$] (b)	P2$_1$/n	7.572	28.647	16.374	90.00	93.10	90.00	3547	4	22	40
[Fe(Cp)(C$_5$H$_4$CH$_2$NMe$_3$)][Ni(mnt)$_2$]	P2$_1$/n	12.116	30.094	7.139	90.00	103.97	90.00	2531	4	20	41
[Fe(Cp)(C$_5$H$_4$CH$_2$NMe$_3$)][Pt(mnt)$_2$]	P2$_1$/n	12.119	30.112	7.244	90.00	103.97	90.00	2565	4	20	41
[Co(Cp)$_2$][Ni(dmit)$_2$]	$P\bar{1}$	19.347	25.289	9.698	100.60	96.02	76.01	4517	8	20	42
[Co(Cp)$_2$][Ni(dmit)$_2$]$_3$2MeCN	$P\bar{1}$	8.913	21.370	7.413	99.19	91.06	101.40	1363	1	(a)	43

(a) Not given. (b) $[Fe(C_5R)_2]^+$ = 1,1'-bis[2-(4-(methylthio)-(E)-ethenyl]ferrocenium.

1.3 Solid-state Structures and Magnetic Behavior

After listing the general characteristics of the crystal structures of ET salts based on metallocenium donors and metal bis-dichalcogenate acceptors, we will discuss them based on the systematization proposed in Section 1.2 and correlate the supramolecular crystal motifs with the magnetic properties.

1.3.1 Type I Mixed Chain Salts

The magnetic behavior of the salts based on type I chains shows a considerable similarity, namely, in most cases, the dominant magnetic interactions are FM and several of these salts exhibit metamagnetic behavior. Table 1.3 summarizes the key magnetic properties of type I compounds.

1.3.1.1 [M(Cp*)$_2$][Ni(edt)$_2$]

The compounds [M(Cp*)$_2$][Ni(edt)$_2$], with M = Fe and Cr, are isostructural and the crystal structure [23] consists of a parallel arrangement of 1D alternated type I chains, $\cdots A^- D^+ A^- D^+ A^- D^+ \cdots$. In Figure 1.3(a) a view along the chain direction ([101]) is presented for [Fe(Cp*)$_2$][Ni(edt)$_2$]. The chains are regular and the Ni atoms sit above the Cp fragments from the donors, intrachain DA contacts, d (d = interatomic separation), shorter than the sum of the van der Waals radii (d_W), $Q_W = d/d_W < 1$, were observed. These contacts involve a Ni atom from the acceptor and one of the C atoms from the C$_5$ ring, with a Ni–C distance of 3.678 Å ($Q_W = 0.99$). For this compound the shortest interchain interionic separation was found in the in-registry pair II–IV, with AA C–C contacts of 3.507 Å ($Q_W = 1.11$), as shown in Figure 1.3(b). The out-of-registry pairs I–II, II–III and I–IV present a similar interchain arrangement, with DA C–S contacts (C from Me from the donor and an S from the acceptor) of 3.812 Å ($Q_W = 1.11$), the II–III pairwise arrangement is shown in Figure 1.3(c).

At high temperatures, in the case of the [M(Cp*)$_2$][Ni(edt)$_2$] compounds, AFM interactions apparently dominate the magnetic behavior of the compounds, as seen by the negative θ value obtained from the Curie–Weiss fits, −5 and −6.7 for M = Fe and Cr respectively. A considerable field dependence of the obtained θ value for polycrystalline samples (free powder) was observed in the case of [Fe(Cp*)$_2$][Ni(edt)$_2$], suggesting the existence of a strong anisotropy in the magnetic coupling for this compound [23]. This was confirmed by the metamagnetic behavior observed at low temperatures, with $T_N = 4.2$ K and $H_C = 14$ kG at 2 K.

A typical metamagnetic behavior was observed in single crystal magnetization measurements at 2 K [23], shown in Figure 1.4. With the applied magnetic field parallel to the chains a field induced transition from an AFM state to a high field FM

Table 1.3. Magnetic characterization of type I ET salts.

Compound	S_D; S_A	θ, K	Comments	Ref.
[Fe(Cp*)$_2$][Ni(edt)$_2$]	1/2; 1/2	−5	MM (a); T_N = 4.2 K; H_C = 14 kG (2 K)	23
[Cr(Cp*)$_2$][Ni(edt)$_2$]	3/2; 1/2	−6.7	(b)	23
[Fe(Cp*)$_2$][Ni(tdt)$_2$]	1/2; 1/2	15	(b)	16
[Mn(Cp*)$_2$][Ni(tdt)$_2$]	1; 1/2	2.6	MM (a); T_N = 2.4 K	24
[Mn(Cp*)$_2$][Pd(tdt)$_2$]	1; 1/2	3.7	MM (a); T_N = 2.8 K; H_C = 0.8 kG (1.85 K)	24
[Fe(Cp*)$_2$][Pt(tdt)$_2$]	1/2; 1/2	27	(b)	10
[Mn(Cp*)$_2$][Pt(tdt)$_2$]	1; 1/2	1.9	MM (a) T_N = 2.3 K;	24
[Fe(Cp*)$_2$][Ni(tds)$_2$]	1/2; 1/2	8.9	(b)	26, 44
[Mn(Cp*)$_2$][Ni(tds)$_2$]	1; 1/2	12.8	MM (a); T_N = 2.1 K; H_C = 0.28 kG (1.6 K)	28, 44
[Cr(Cp*)$_2$][Ni(tds)$_2$]	3/2; 1/2	4.0	(b)	28
[Fe(Cp*)$_2$][Pt(tds)$_2$]	1/2; 1/2	9.3	MM (a); T_N = 3.3 K; H_C = 3.95 kG (1.7 K)	26
[Mn(Cp*)$_2$][Pt(tds)$_2$]	1; 1/2	16.6	MM (a); T_N = 5.7 K; H_C = 4.05 kG (1.7 K)	28
[Cr(Cp*)$_2$][Pt(tds)$_2$]	3/2; 1/2	9.8	MM (c); T_N = 5.2 K; H_{C1} = 5 kG, H_{C2} = 16 kG, (1.7 K)	28
[Fe(Cp*)$_2$][Ni(α-tpdt)$_2$]	1/2; 1/2	−5.1 (d)	$T_m \approx$ 130 K (e); MM (a); T_N = 2.6 K; H_C = 0.6 kG (1.6 K)	34
[Mn(Cp*)$_2$][Ni(α-tpdt)$_2$] (f)	1; 1/2	7.3	FM (g); T_C = 2.2 K	35
[Cr(Cp*)$_2$][Ni(α-tpdt)$_2$]	3/2; 1/2	6.1	(b)	35
[Fe(C$_5$Me$_4$SCMe$_3$)$_2$][Ni(mnt)$_2$]	1/2; 1/2	3	(b)	36
[Fe(C$_5$Me$_4$SCMe$_3$)$_2$][Pt(mnt)$_2$]	1/2; 1/2	3	(b)	36
β-[Fe(Cp*)$_2$][Pt(mnt)$_2$]	1/2; 1/2	9.8	(b)	16

(a) Metamagnetic transition. (b) No magnetic ordering observed down to 1.8 K. (c) Two field induced transitions were observed at low temperatures. (d) Non-Curie-Weiss behavior the given θ value relates to the high temperature region ($T > T_m$). (e) Minimum in χT vs. T. (f) Crystal structure not yet determined. (g) Ferromagnetic transition.

state occurs at a critical field of 14 kG. While for measurements with the applied field perpendicular to the chains, no transition was observed and a linear field dependence was observed for the magnetization, as expected for an AFM.

The magnetic behavior of [Fe(Cp*)$_2$][Ni(edt)$_2$] is consistent with the coexistence of FM intrachain interactions, due to DA intrachain short contacts, with AFM interchain interactions, resulting from the AD and AA interchain contacts. The nature of the intra and interchain magnetic interaction is in good agreement with the predictions of the McConnell I mechanism [26]. In this case the interchain interactions must be particularly large as they seem to be the dominant interactions
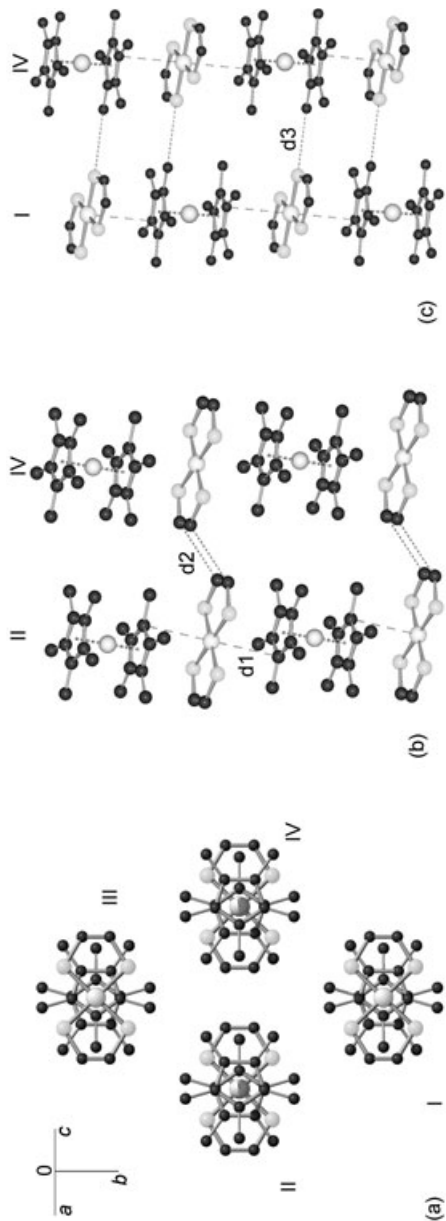
Fig. 1.3. (a) Perspective view of the crystal structure of [Fe(Cp*)$_2$][Ni(edt)$_2$] along the chain direction. (b) Interchain arrangement of the pair II–IV, d1 corresponds to the DA closest intrachain contact (3.678 Å, Q_W = 0.99) and d2 to the closest interchain contact (3.507 Å, Q_W = 1.11). (c) Interchain arrangement of the pair II–III, d3 is the closest interchain contact (3.812 Å, Q_W = 1.11). Hydrogen atoms were omitted for clarity.
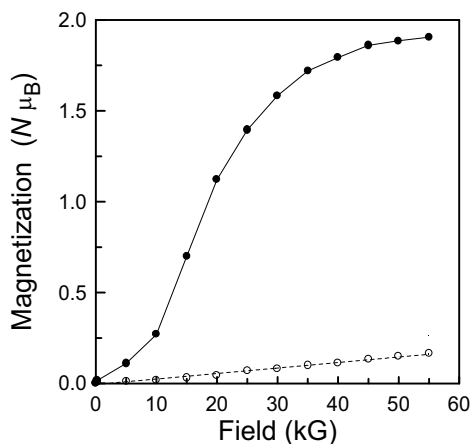
Fig. 1.4. Magnetization field dependence at 2 K, for a single crystal of [Fe(Cp*)$_2$][Ni(edt)$_2$], the closed symbols refer to measurements with applied field parallel to the DADA chains and the open symbols to the measurements with the applied field perpendicular to the chains.

at high temperatures, and they also lead to a quite high value for the critical field in the metamagnetic transition.

1.3.1.2   [M(Cp*)$_2$][M′(tdx)$_2$]

The [Fe(Cp*)$_2$][Ni(tdt)$_2$] and [Mn(Cp*)$_2$][M′(tdt)$_2$] with M′ = Ni, Pd and Pt are isostructural, and, as in the case of the [M(Cp*)$_2$][Ni(edt)$_2$] salts, a crystal structure based on an arrangement of parallel alternating DA linear chains [16] is observed, but with differences in the intra and interchain arrangements. A view normal to the chains of [Fe(Cp*)$_2$][Ni(tdt)$_2$] is shown in Figure 1.5(a). In these compounds the chains have a zigzag arrangement and the Cp sits above one of the NiS$_2$C$_2$ fragments of the acceptor, as shown for [Fe(Cp*)$_2$][Ni(tdt)$_2$] in Figure 1.5(b). In this compound, no intrachain DA short contacts were found and the closest interatomic separation between the acceptor and the Cp ring corresponds to Ni–C contacts of 4.120 Å (Q_W = 1.11). In this salt the most relevant interchain contacts concern the out-of registry pairs I–II and I–IV, these arrangements are similar and the first one is shown in Figure 1.5(b). These pairs show interchain DA C–S contacts, involving C atoms of the Me groups of the donors and S atoms of the acceptors, with a separation of 3.728 Å (Q_W = 1.08).

The magnetic behavior of the compounds [Fe(Cp*)$_2$][Ni(tdt)$_2$] and [Mn(Cp*)$_2$][M′(tdt)$_2$], with M′ = Ni, Pd and Pt, is dominated by the intrachain DA FM interactions, as seen by the positive θ values obtained from the Curie-Weiss fits (Table 1.3). At low temperatures the [Mn(Cp*)$_2$][M′(tdt)$_2$] salts exhibit metamagnetic transitions, with T_N = 2.4, 2.8 and 2.3 K for M′ = Ni, Pd and Pt respectively, H_C = 600 G for M′ = Pd [24]. This behavior is attributed to the coexistence of FM intrachain interactions with interchain AFM interactions.

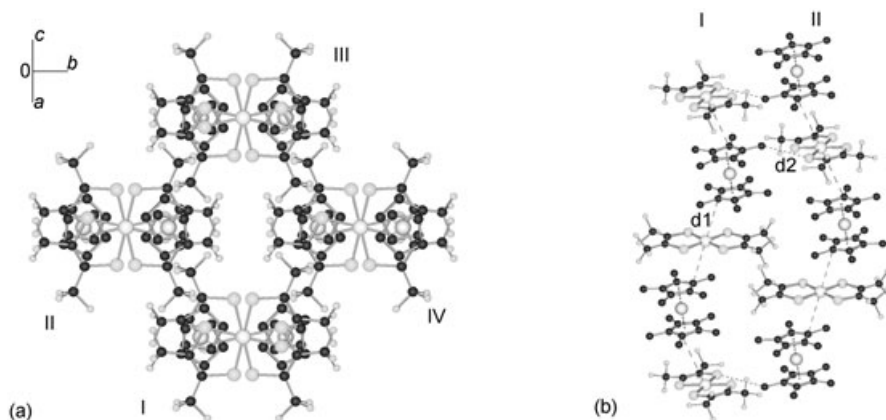**Fig. 1.5.** (a) View of the crystal structure of $[Fe(Cp^*)_2][Ni(tdt)_2]$ along the chain direction (Me groups were omitted for clarity). (b) Interchain arrangement of the pair I–II, d1 corresponds to the DA closest intrachain contact (4.120 Å, $Q_W = 1.11$) and d2 to the closest interchain contact (3.728 Å, $Q_W = 1.08$). Hydrogen atoms were omitted for clarity.

The compounds $[Fe(Cp^*)_2][Pt(tdt)_2]$, $[M(Cp^*)_2][Ni(tds)_2]$, with M = Fe, Mn and Cr, [25–28] and $[M(Cp^*)_2][Pt(tds)_2]$, with M = Fe and Mn, [26, 28] are isostructural and the crystal structure consists of a parallel arrangement of alternated type I chains. The intrachain arrangement is similar to that of $[Fe(Cp^*)_2][Ni(edt)_2]$, with the Cp sitting above the Ni or Pt atoms from the acceptor, but distinct interchain arrangements were observed in these compounds. A view normal to the chains is shown in Figure 1.6(a) for $[Fe(Cp^*)_2][Pt(tds)_2]$. Short intrachain DA contacts were observed in most of these salts, involving M (Ni or Pt) and carbons from the Cp rings from the donors, for the Pt–C contact in $[Fe(Cp^*)_2][Pt(tds)_2]$ the interatomic separation is 3.826 Å ($Q_W = 0.98$). For this series of compounds the shortest interchain interionic separation was found in the in-registry pair I–II, shown in Figure 1.6(b), and it corresponds to an AA Se–Se contact, with a distance of 4.348 Å ($Q_W = 1.09$). In the other interchain arrangements the interchain contacts are considerably larger and the closest separations occur for the I–IV pair (Figure 1.6(c)) involving two C atoms from the donor Me groups, with a separation of 4.263 Å ($Q_W = 1.33$) in the case of $[Fe(Cp^*)_2][Pt(tds)_2]$. However $[Cr(Cp^*)_2][Pt(tds)_2]$ is not isostructural with these compounds, the intra and interchain arrangements are similar to those described above for $[Fe(Cp^*)_2][Pt(tds)_2]$ [28].

The magnetic behavior of the compounds $[Fe(Cp^*)_2][Pt(tdt)_2]$, $[M(Cp^*)_2][Ni(tds)_2]$ and $[M(Cp^*)_2][Pt(tds)_2]$ (M = Fe, Mn and Cr) is clearly dominated by the strong intrachain DA FM coupling, as can be seen by the high positive θ values (Table 1.3). The coexistence of an intrachain AFM interaction is responsible for the metamagnetic transitions, which are observed in several of those compounds, with T_N = 2.1, 3.3, 5.7 K and H_C = 0.28, 3.95, 4.05 kG

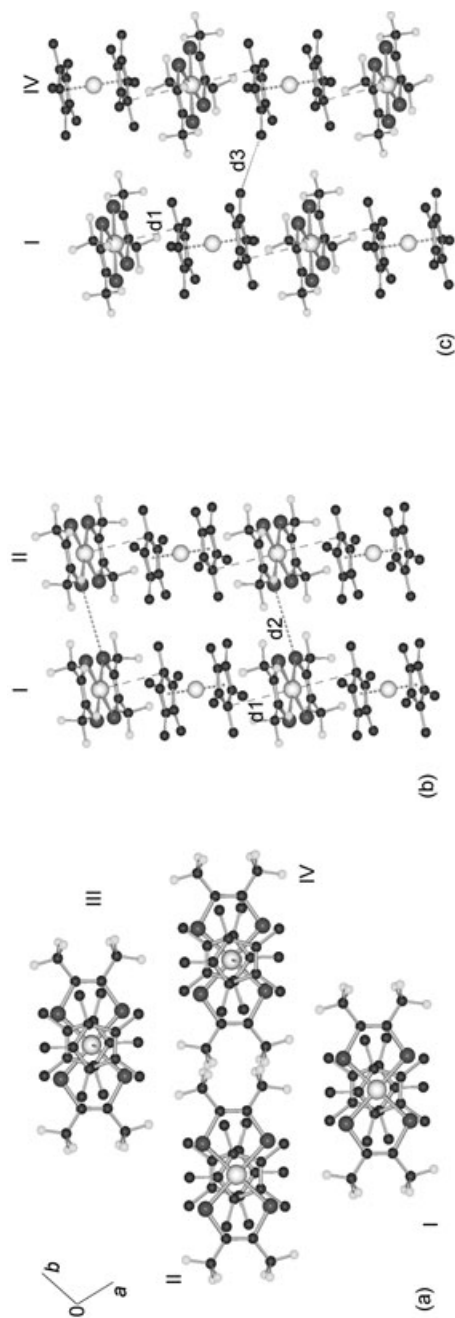**Fig. 1.6.** (a) Perspective view of the crystal structure of [Fe(Cp*)$_2$]|Pt(tds)$_2$] along the chain direction. (b) Interchain arrangement of the pair I–II, d1 corresponds to the DA closest intrachain contact (3.826 Å, Q_W = 0.98) and d2 to the closest interchain contact (4.263 Å, Q_W = 1.33). Hydrogen atoms were omitted for clarity. (c) Interchain arrangement of the pair I–IV, d3 is the closest interchain contact (4.348 Å, Q_W = 1.09).

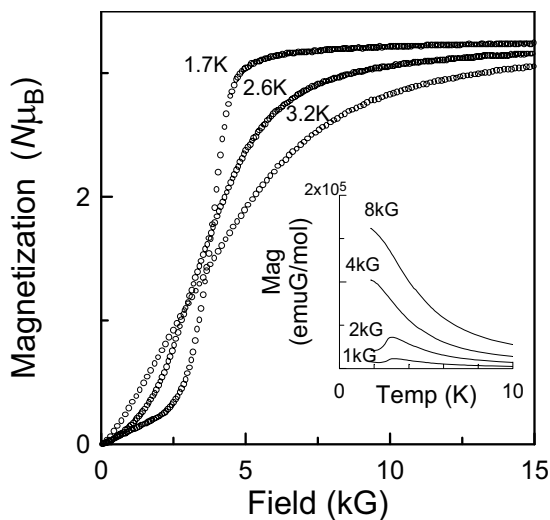**Fig. 1.7.** Magnetization field dependence for [Fe(Cp*)$_2$][Pt(tds)$_2$], at 1.7, 2.6 and 3.2 K. The inset shows the magnetization temperature dependence at 1, 2, 4 and 8 kG.

for [Mn(Cp*)$_2$][Ni(tds)$_2$], [M(Cp*)$_2$][Pt(tds)$_2$] (M = Fe, Pt) respectively. The magnetization field dependence at 1.7, 2.6 and 3.2 K for [Fe(Cp*)$_2$][Pt(tds)$_2$] is shown in Figure 1.7, a sigmoidal behavior typical of metamagnetic behavior is observed for $T < T_N = 3.3$ K [26]. For low applied magnetic fields ($H < H_C$), a maximum in the magnetization temperature dependence can be observed, corresponding to an AFM transition, which is suppressed with fields $H > H_C$, as shown in the inset of Figure 1.7. The critical field temperature dependence obtained from the isothermal (closed symbols) and isofield (open symbols) measurements is shown in Figure 1.8.

In the compounds [Fe(Cp*)$_2$][Pt(tdt)$_2$], [M(Cp*)$_2$][Ni(tds)$_2$] and [M(Cp*)$_2$][Pt(tds)$_2$] (M = Fe, Mn and Cr) the Se–Se (or S–S) contacts, are expected to give rise to strong AFM interchain interactions, as the contacts are relatively short and there is a significant spin density on those atoms. The intrachain DA contacts (along c) and the interchain AA (Se–Se or S–S) contacts (along a) are expected to give rise to quasi-2D magnetic systems (ac plane), as the other interchain contacts are expected to give rise to much weaker magnetic interactions. The situation is quite distinct from that observed in the compounds [M(Cp*)$_2$][Ni(edt)$_2$], [Fe(Cp*)$_2$][Ni(tdt)$_2$] and [Mn(Cp*)$_2$][M′(tdt)$_2$], where the interchain magnetic interactions are expected to be considerably more isotropic, and for these compounds the magnetic systems can be described as quasi-1D. The distinct dimensionality of the magnetic systems is reflected in the fast saturation observed in the isothermals, just above H_C, in the case of the salts with the quasi-2D magnetic systems, unlike the compounds presenting quasi-1D magnetic
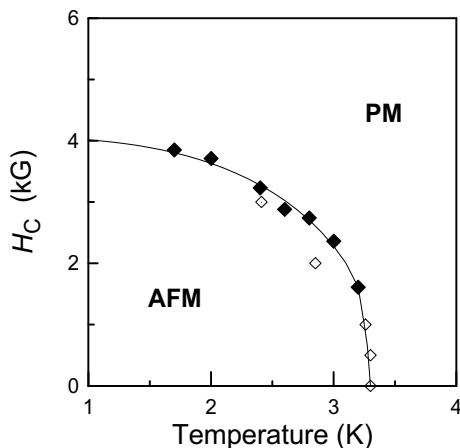
Fig. 1.8. Critical field dependence for $[Fe(Cp^*)_2][Pt(tds)_2]$, where the closed and open symbols correspond to the data obtained with isothermal and isofield measurements respectively.

systems, where saturation occurs only at very high magnetic fields, when the temperature is not much lower than T_N [26].

In the case of $[Cr(Cp^*)_2][Pt(tds)_2]$ metamagnetic behavior was also observed ($T_N = 5.2$ K), but a rather complicated phase diagram was obtained. Below T_N, two field induced transitions were observed to occur, and at 1.7 K the critical fields were 5 and 16 kG, respectively [28]. This is the first example of a metamagnetic transition on a $[Cr(Cp^*)_2]$ based ET salt and the low temperature phase diagram is still under study [28].

The analysis of the crystal structures, the magnetic behavior and atomic spin density calculations of several ET salts based on decamethylferrocenium and on metal-bis(dichalcogenate) acceptors with structures consisting of arrangements of parallel alternating DA linear chains, allowed a systematic study of the intra and interchain magnetic interactions [26]. In the case of these compounds a spin polarization is observed in the metallocenium donors but not in the acceptors described so far. The analysis of the intrachain contacts in the perspective of the McConnell I mechanism suggests the existence of intrachain FM coupling, through the contacts involving the metal or chalcogen atoms (positive spin density) from the acceptors and the C atoms (negative spin density) from the Cp ring of the donors, which shows good agreement with the experimental observations. A variety of interionic interchain contacts were observed in these ET salts, AA (Se–Se, S–S and C–C), DD (Me–Me) and DA (Me–S), and all these contacts were observed to lead to AFM interchain coupling. A strict application of the McConnell I model was not possible in the case of the interchain contacts, as the shortest contacts would involve mediation through H or F atoms, which are expected to present a very small spin density [26]. However the results regarding the nature of the interchain magnetic coupling would be compatible with that model if the contacts involving H or F atoms were neglected, as all the atoms involved in these contacts present a posi-