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Review

New trends of molecular magnetism

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Contents

Abstract

The history of molecular magnetism began in 1951 with the study of a dinuclear complex, copper(II) acetate [B. Bleaney, K.D. Bowers, Proc. R. Soc. A 214 (1952) 451], however it was not until the 1990s that it received a strong impetus with the discovery of the first molecular-based solids that exhibited spontaneous magnetization [R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141; D. Gatteschi, A. Caneschi, L. Pardi, R. Sessoli, Science 165 (1994) 1054]. Many important discoveries have been made since then by European teams in particular [ESF Scientific Programme Molecular Magnets (MM), October 2, 1999]: the synthesis of the first bimetallic molecular magnets and organic magnets with the highest Curie temperature known so far; the synthesis of room-temperature molecular-based magnets; the discovery of spin cross-overs that occur with large hysteresis at room temperature; new photomagnetic processes, including light-induced excited spin state trapping; the synthesis of the first molecular-based magnetic superconductor; the first characterization of the magnetic tunneling effect.

Keywords: Molecular materials; New ferromagnets; Ferrimagnets; Antiferromagnets

1. Introduction

Molecular materials are systems that may be considered as built of discrete molecules, the so-called "building blocks". This structural feature creates great opportunities for the modeling of electrical, magnetic and optical properties of materials through the selection of appropriate constituent molecules. At the same time, it is also a challenge for developing new synthetic methods that would make it possible to control the directional arrangement of molecules in the space crystal lattice. In reality macro properties of materials

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are always determined by the joint mutual interactions of molecules in the crystalline structure.

The faculty of Chemistry of University of Wrocław is not only the main polish center on coordination chemistry but also the place where investigation of molecular magnetism in Poland has started. It took place in the 1960s and in 1970s in the magnetic laboratory, equipped with a few modern susceptometers and magnetometers which were already functioning.

It is crucial that there is intense research cooperation with national and international scientific teams in many magnetic research areas.

We are approaching a period where we can expect a breakthrough in electronics as well as a transition from microelectronics to molecular electronics. We are heading towards the next stage of miniaturization of microelectronic elements and devices. This undoubtedly is one of the biggest challenges, which chemistry above all must rise to, by synthesizing new molecular materials with pre-programmed properties, with special attention to their molecular magnetic properties.

2. Molecular magnetism and new materials group (University of Wrocław, Wrocław)

2.1. Magnetism of dimeric copper(II) carboxylates

Copper(II) carboxylates have been extensively studied from different points of view because the carboxylato anions exhibit different bonding modes influencing their properties. Most of them are biologically active substances, metal-ion-drugs [5].

We have studied the magnetic properties of copper(II) in many compounds and the results were published in approximately 80 papers co-authored with Melnik and co-workers [6–8]. Examples include magnetic data for two dimeric complexes of general formulae: $[Cu\{L\}_2(X)]_2$ (**1**) (where L = 2-methylthionicotinate (2-MeSnic), and X = H_2O, CH_3OH, DMF, DMSO) and $[Cu\{2\text{-MeSnic}\}_2(py)_2]_2$ (**2**) (where py is pyridine) [6–8]. The magneto-structural characterization of these copper(II) complexes is important because of their biological activity.

The tetrakis(μ-carboxylato)-bridged Cu^{II} system (I) displays intramolecular antiferro-magnetic exchange coupling between two paramagnetic metal ions [9,10]. The strength of this coupling is measured by the coupling constant J within the usual isotropic Heisenberg–Dirac–van Vleck model: $H = -2JS_1S_2$; $S_1 = S_2 = 1/2$ ($2J$ represents the singlet–triplet energy gap). Very strong intramolecular antiferro-magnetic coupling has been observed in tetrakis μ-carboxylato-bridged Cu^{II} complexes ($2J \sim -300\,\text{cm}^{-1}$) depending on the nature of the carboxylic acid and the apical ligands [7,9,10, and references therein]. A dimeric Cu^{II} structure, in which very asymmetrically coupled Cu^{II} ions essentially do not interact, is rarely observed, complex (**2**) is in fact only the second example in the literature.

Fig. 2 (complex **1**) presents the χ_M versus T relationship, where χ_M is corrected molar magnetic susceptibility, and which shows a maximum at about room temperature, a feature characteristic of antiferromagnetically coupled copper(II) pairs. At low temperatures a contribution from a Cu^{II} mononuclear impurity can be observed.

The magnetic susceptibility data were best fitted to the modified Bleaney–Bowers equation [1]:

$$\chi_M^{corr} = \left\{ \frac{Ng_{\text{dim}}^2\beta^2}{3kT}\left[1 + \frac{1}{3}\,e^{-2J/kT}\right]^{-1} \right\}(1-x) + \left(\frac{Ng_{\text{mom}}^2\beta^2}{4kT}\right)x$$

where x is the percent of monomeric impurity and other symbols have their usual meaning. Minimization of the deviation $R = \sum(\chi_i^{calcd} - \chi_i^{expt})^2/(\chi_i^{calcd})^2$ was the criterion used to determine the best fit. Singlet–triplet energy gaps ($2J$) of all the complexes were found and compared.

The value of $|2J|$ for the copper(II) 2-methylthionicotinate dimers tends to increase according to the series of terminal ligands: DMSO < DMF < CH_3OH < H_2O.

Some workers have proposed that larger $2J$ values are attributed to a weaker σ-donation by the axial ligand, with suggestion that there is a corresponding increase in the ligand field of the four carboxylato oxygen atoms around the metal ion [9–11]. Our results maintain that the magnitude of magnetic coupling is rather sensitive to the Cu–O–C–O–Cu geometry, which depends more on steric effects of the terminal ligand than on its σ-donation (nucleophilicity) [7].

Another type of Cu^{II} dimer was obtained with 2-methylthionicotinic acid and pyridine ligands, (**2**) Fig. 1. The temperature dependence of the magnetic susceptibility and moment for $[Cu(2\text{-MeSnic})_2(py)_2]_2$ (**2**) is outlined in Fig. 2. The value of μ_{eff} 1.91 BM at 300 K decreases to 1.71 BM at 5 K and to 1.54 BM at 1.9 K. This behavior is consistent with very weak antiferromagnetic interaction between the copper(II) magnetic centers. The data were fit to the Bleaney–Bowers equation [1]. The best-fit parameters are: $2J = -1.30\,\text{cm}^{-1}$, $g = 2.12$, $R = 1.82 \times 10^{-3}$. The observed singlet–triplet energy gap of $-1.30\,\text{cm}^{-1}$ suggests that the magnetic orbitals are unfavourably oriented in this case to provide good overlap for a magnetic interaction [9]. The Cu···Cu separation 4.453 Å.

Psomas et al. [12] have described a novel dinuclear Cu^{II} complex of tetrakis[(2,4-dichlorophenoxy)acetato] bis(2,2′-bipyridylamine)dicopper(II) where two bridging carboxylate ligands are bound to two Cu^{II} metal ions in an asymmetric fashion with a Cu···Cu separation above 4.0 Å. The magnetic data show a very weak antiferromagnetic interaction between the two metal ions with $2J = -1.6\,\text{cm}^{-1}$. The complex $[Cu(2\text{-MeSnic})_2(py)_2]_2$ is only the second example of the abovementioned dinuclear structural type, in which the observed antiferromagnetic interaction is very weak [9].

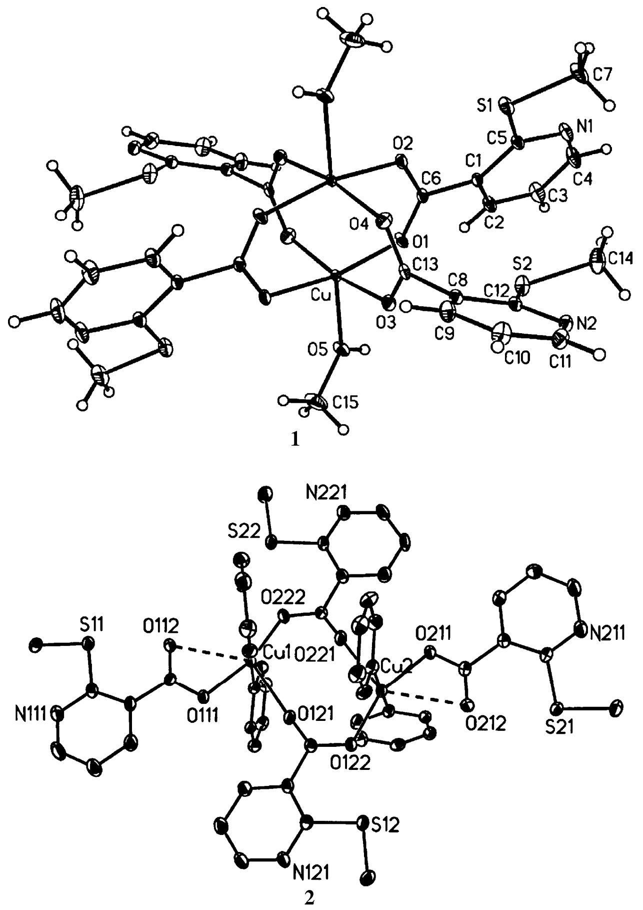


Fig. 1. ORTEP view of the complex $[Cu(2\text{-}MeSnic)_2(CH_3OH)_2]_2$ (**1**) which represents dimeric complexes type (**1**) and the ORTEP plot of $[Cu(2\text{-}MeSnic)_2(py)_2]_2$ (**2**), Ref. [7].

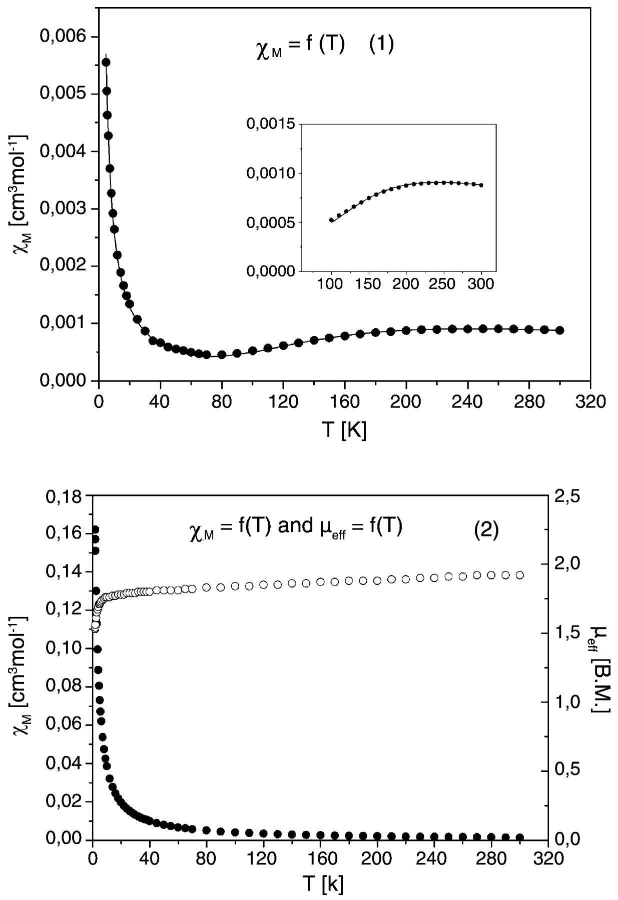


Fig. 2. Temperature dependence of the magnetic susceptibility (complexes type (**1**)) and the magnetic susceptibility and the magnetic moment of complex (**2**), Ref. [8].

2.2. Exchange interaction in polymeric copper(II) ferromagnets

Structural and magnetic studies of binuclear and polynuclear complexes containing multidentate bridging ligands, in which such metal-metal interactions as magnetic coupling, energy or electron transfer, and intervalence transfer [13–15] may occur, are of a considerable interest from the standpoint of inorganic, bio-inorganic and coordination chemistry [14,16–18].

The design and molecular magnetism of polynuclear complexes are of considerable interest for designing new magnetic materials and for investigating the structure and the role of the polymetallic active sites in biological systems.

One of the most interesting features in molecular magnetism is the ability of some polyatomic ligands to provide pathways for exchange coupling between atoms that are not directly bonded. The study of intramolecular exchange interactions has been extended to a large number of dinuclear and polynuclear compounds with a great variety of bridging ligands such as carboxylato, hydroxo, oxalato, pseudohalides of the type XCN (X = O, S, Se).

Among these systems, the copper(II) carboxylates have been the subject of numerous magneto-structurally investigations, especially with nitrogen donor ligands [19,20]. Different coordination modes of carboxylato groups led to the formation of mononuclear and polynuclear structures.

We have recently synthesized [21] and characterized the magnetic properties [22] of a two-dimensional polymer of formula [Cu(pyridine-2-carboxylate)Cl] in which ferromagnetic exchange occur between the copper(II) ions via dichloro and *syn-anti*-carboxylate bridges.

This compound is a product of a novel oxidative *P*-dealkylation reaction of diethyl 2-pyridyl methylphosphonate ligand with the participation of the copper atom catalyzing oxidation by atmospheric oxygen: $R\text{–}CH_2\text{–}P(O)(OEt)_2 \rightarrow R\text{–}COOH$ [21]. This reaction is a continuation of the further study on the coordination properties of transition metal complexes of phosphonic derivatives of pyridine and quinoline [23–26].The molecular structure of [Cu(pyridine-2-carboxylate)Cl] (Fig. 3) reveals a very distorted five-coordinate stereochemistry ($CuNO_2Cl_2$ chromophore) intermediate between D_{3h} and C_{4v} supported by the calculation of the degree of distortion of coordination polyhedron, which gives a structural index

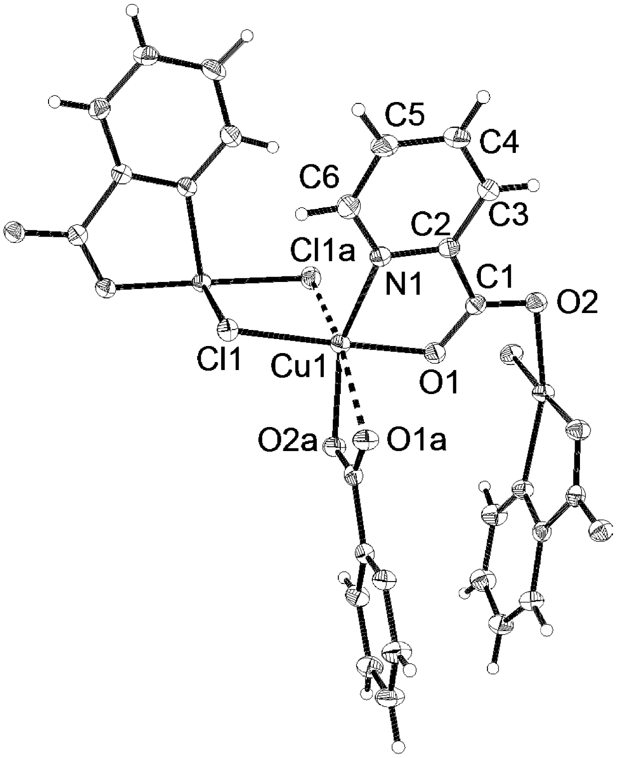


Fig. 3. A perspective view of the polymeric fragment of [Cu(pyridine-2-carboxylate)Cl] with the atom numbering scheme, Ref. [22].

$\tau = 0.39$ (τ distinguishes between square–pyramidal and trigonal–bipyramidal geometries, defined as $\tau = (\beta - \alpha)/60$, where α and β are the largest coordination angles [27].

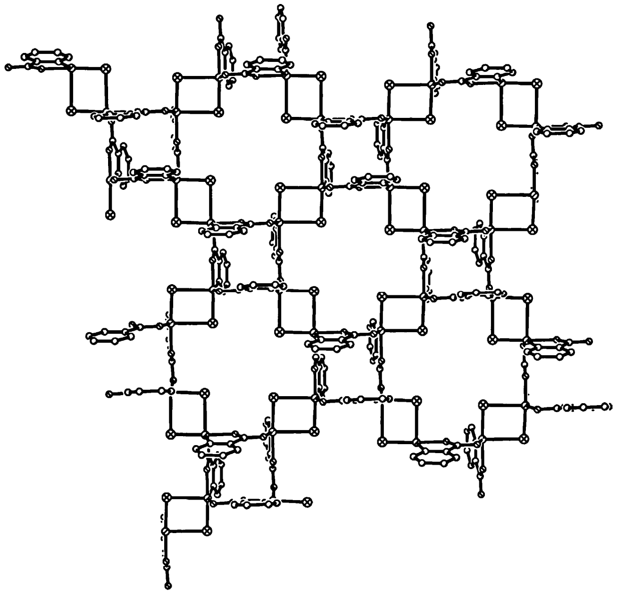


Fig. 4. A projection of the layer along the *z*-axis of [Cu(pyridine-2-carboxylate)Cl], Ref. [22].

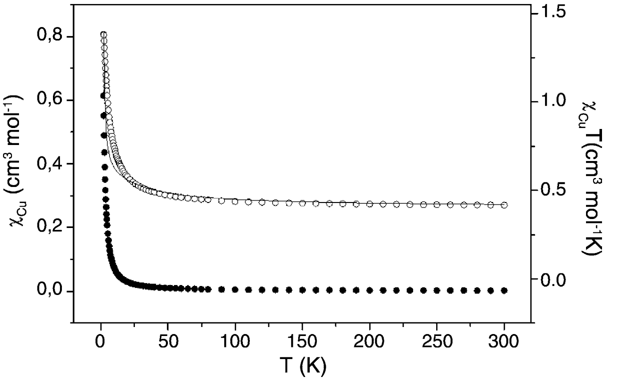
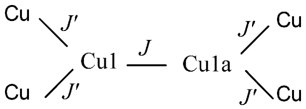


Fig. 5. Plot of χ_{Cu} (●) and $\chi_{Cu}T$ (○) vs. T temperature for [Cu(pyridine-2-carboxylate)Cl]. Calculated temperature dependence of $\chi_{Cu}T$ (—), Ref. [22].

The crystal structure of [Cu(pyridine-2-carboxylate)Cl] (Fig. 4) revealed a unique supramolecular polymeric two-dimensional network. The framework of the structure is a Cu_4 cyclic structure with the Cu(II) centres connected by *syn-anti*-carboxylate bridges, and with a Cu···Cu distance of 4.490(2) Å. The copper ions of an individual tetrameric ring are connected to each other through dichloro bridges. The molecular and crystal structure of $[Cu(pyridine\text{-}2\text{-}carboxylate)Cl]_n$ suggests the scheme presented below for the magnetic exchange interactions,



where J and J' are the exchange coupling via the di-μ-chlorobridge and carboxylate bridges, respectively. The experimental data have been fitted with a dimer equation [1], within a molecular field correction. In the frame of this approximation with the interaction Hamiltonian: $H = -J\hat{S}_1\hat{S}_2$, the best-fit parameters obtained by least-squares fit through Eq. (1) are as follows: $J = 15.0\,\text{cm}^{-1}$, $J' = 0.37\,\text{cm}^{-1}$ ($z = 4$), $g = 2.07$ (Fig. 5). The magnetic properties indicate that the copper ions within a given layer are ferromagnetically coupled but exchange coupling via the dichloro bridge dominates.

This is an example of the strong ferromagnetic coupling observed for coupling occurring through bridging chloride ions in di- and polynuclear copper(II) complexes [28]. The magnetic behavior can range from strongly antiferromagnetic coupled, to moderate or weak and even ferromagnetic coupling as a function of the different coordination modes of the carboxylato group. Weak antiferro- or ferromagnetic interactions are observed in carboxylato bridged copper(II) complexes, in which the carboxylate adopts the *syn-anti*-conformation [22,29–34].

The weak interdimer ferromagnetic coupling observed for [Cu(pyridine-2-carboxylate)Cl] complex is not unexpected in the light of the following electronic and structural features: (i) *syn-anti*-conformation of the carboxylate group, (ii) non-planarity of the bridging network, which is also expected to decrease the overlap of magnetic orbitals in the bridging network hence the exchange pathway could involve both the σ and π orbitals of the carboxylate group, (iii) the low symmetry of the entity allows a weak delocalization of each magnetic orbital on the oxygen atom of the carboxylate bridge from the copper atom.

The carboxylate group exhibits an unusual bridging behavior, since the same carboxylate group acts simultaneously as a monoatomic bridge and a triatomic bridge between the pair of copper ions. The monoatomic bridges can only support a very weak antiferromagnetic interaction. Therefore, the possible contribution to zJ' interdimer exchange coupling may be neglected.

2.3. Di-and polynuclear compounds as new magnetic materials

Our interest in complexes with pseudohalide ligands of the type NCS^- consists of the possibility of the ligand to provide simultaneous coordination to two metal centres, generating structurally and magnetically interesting di- or polynuclear complexes. The magnetic behavior of octahedrally coordinated dimers of nickel(II) with two end-to-end pseudohalide bridging ligands has been studied and correlated with the structural parameters by different authors and some magneto-structural trends have been summarized [35–39]. We investigated the conditions of formation of the thiocyanate bridged Ni^{II}, Co^{II}, Fe^{III} and Cr^{III} [40] and thiocyanatecobalt(II) complexes [41] with imidazole derivatives and the influence of their steric properties both on the stoichiometry as well as on the stereochemistry of the complexes. The results show that bridging by an NCS^- group is possible if the steric conditions of the neutral ligand permit it, as is in the case of the polymeric isomorphous complexes of the formula $[Ni(NCS)_2(HIm)_2]$ (**3**) and $[Co(NCS)_2(HIm)_2]$ (**4**) (HIm = imidazole). Both complexes are the first examples of ferromagnetically coupled one-dimensional polymeric compounds with a double end-to-end thiocyanate bridge [42]. The crystal structure of $[Ni(NCS)_2(HIm)_2]$ (Fig. 6) consists of a one-dimensional polymeric chain in which nickel(II) ions are bridged by two thiocyanate groups bonding in an end-to-end fashion in a *trans* arrangement. The Ni· · ·Ni distance is 5.557(1) Å. The crystal packing is determined by the intermolecular hydrogen bonds and ring-stacking interactions.

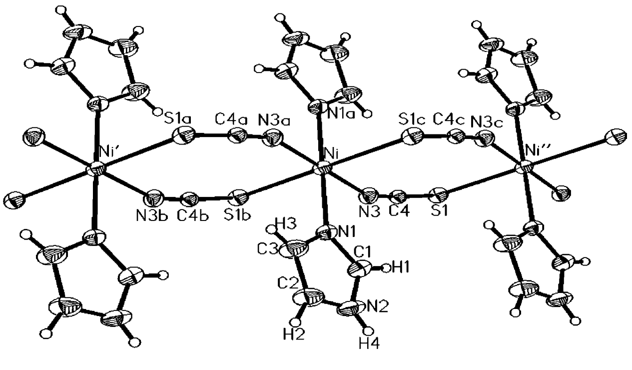


Fig. 6. Molecular structure of $[Ni(NCS)_2(HIm)_2]$ showing the atomic numbering. The Ni· · ·Ni distance is 5.557(1) Å, Ref. [42].

The variable temperature magnetic properties have been interpreted in terms of the De Neef expression [43], based upon the Hamiltonian of the equation:

$$H = -2J\sum_{i=1}(S_iS_{i+1}) - D\sum_{i=1}\left[(S_{iz})^2 - \frac{2}{3}\right] \qquad (1)$$

The best-fit parameters obtained by the least-squares fit through Eq. (1) are as follows: $2J = 8.0\ cm^{-1}$, $D = 0.2\ cm^{-1}$, $g = 2.18$.

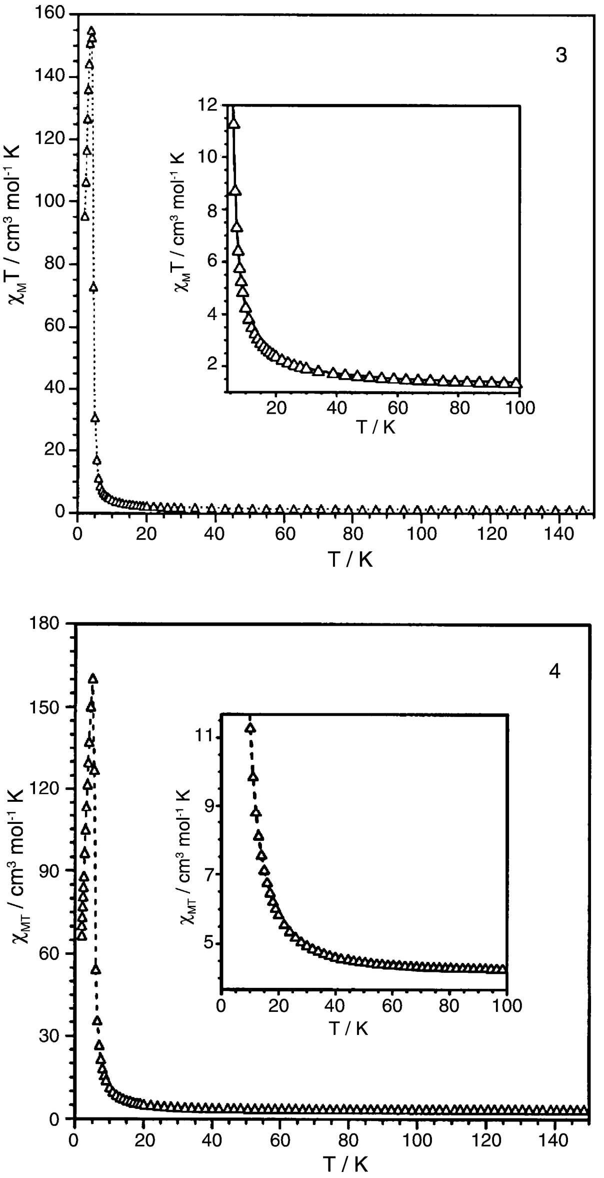


Fig. 7. Plot of $\chi_M T$ vs. T for complexes **3** and **4**. Experimental data are represented by triangles where the dotted line is an eye guide. The solid line in the insert of Fig. 7 for complex **3** is the best-fit curve down to 12 K through the De Neef equation (see text). The insert of Fig. 7 of complex **4** is included only for comparison purposes, Ref. [42].

As shown in the insert of Fig. 7 for **3**, the calculated curve matches the magnetic data very well from room temperature to temperatures near T_c. At lower temperatures, long-range magnetic ordering accounts for the deviation from one-dimensional magnetic behavior of **3**. The absence of a model for an $S = 3/2$ chain system precludes theoretical analysis of the magnetic data for complex **4**. Complex **3** is the first example of a ferromagnetically coupled nickel(II) chain with end-to-end thiocyanate bridges which exhibits long-range magnetic ordering ($T_c = 5.0$ K). Most likely, it is the hydrogen bonds which link the chains to each other and the ring-stacking interactions that provide an exchange pathway for this magnetic ordering.

The decrease of $\chi_M T$ in the very low temperature range is due to the saturation of magnetization as shown by the field cooled (FC) curves for **3** and **4** in Fig. 8. Both compounds exhibit a three-dimensional magnetic ordering with values of T_c equal to 5.0 (**3**) and 5.5 K (**4**), these values being determined from the field cooled magnetization (FCM) and zero field cooled magnetization (ZFCM) (see Fig. 8), as well as ac measurements (see Fig. 8, inserts). Neither frequency nor amplitude dependence was observed for in-phase and out-of-phase signals. Finally, the field dependence of the magnetization at 1.9 K for **3** and **4** (Fig. 9) provides additional evidence for the occurrence of ferromagnetic coupling in both compounds although no saturation of magnetization was reached up to 5 T. At 1.9 K, complex **4** exhibits a hysteresis loop of a soft magnet (Fig. 9, insert **4**), the values of the remanent magnetization and coercive field being 1.0 BM and 110 G, respectively.

In the case of complex **3**, no hysteresis was detected under our experimental conditions (see Fig. 9, insert **3**). The ferromagnetic exchange was confirmed by a magnetization study as a function of field at 1.9 K. The compounds exhibit long-range magnetic ordering with T_c equal to 5.0 and 5.5 K for **3** and **4**, respectively.

In any case, an inspection of the magneto-structural data of the double end-to-end thiocyanate-bridged nickel(II) complexes studied, which are listed in Table 1, shows that (i) the magnetic coupling is always weakly ferromagnetic; (ii) it is not necessary to have the Ni–N–C and Ni–S–C angles very close to 180° and 90°, respectively, for quasi-orthogonality of the molecular orbitals; (iii) the value of the magnetic

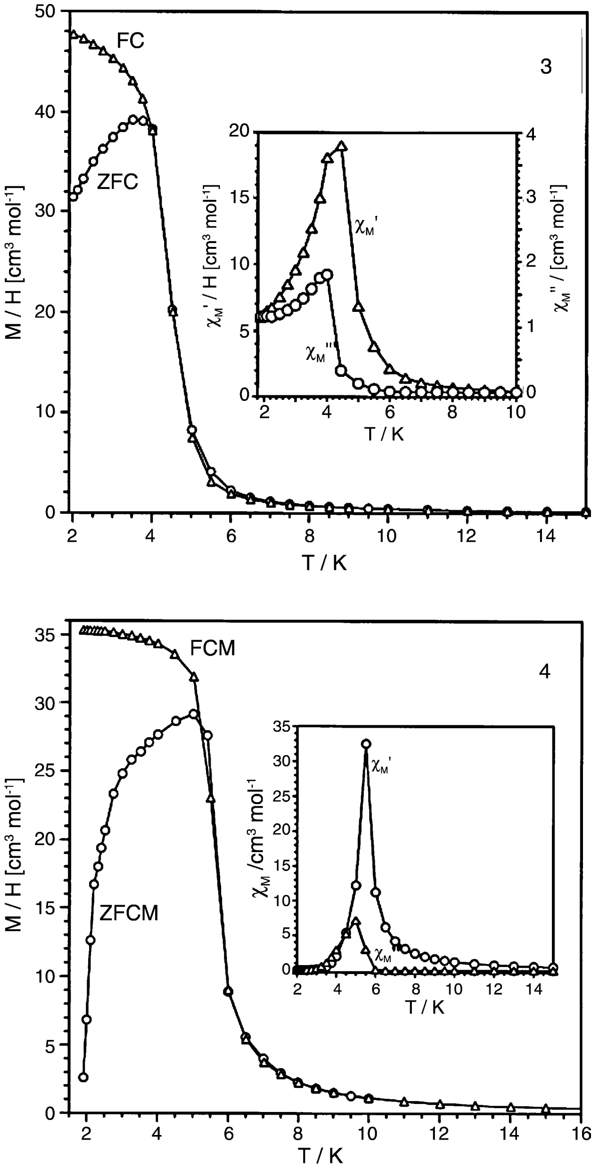


Fig. 8. Temperature dependence of the field cooled (FC, △) and zero field cooled (ZFC, ○) of the M/H quotient for complexes **3** and **4**. The insert shows the temperature dependence of both the in-phase (χ'_M) and out-of-phase (χ''_M) components of the ac molar magnetization at 1 G for both complexes, Ref. [42].

Table 1
Selected magneto-structural data for double end-to-end thiocyanato-bridged nickel(II) complexes

Compound[a]	Nuclearity	Ni–N–C (°)	Ni–S–C (°)	Ni–N (Å)	Ni–S (Å)	J (cm^{-1})	D (cm^{-1})	d[b] (Å)	Ref.
$[Ni_2(en)_4(\mu\text{-}NCS)_2]I_2$	Dimmer	167.0	100.0	2.04	2.61	4.5	−3.3	0.05	[35]
$[Ni_2(tren)_2(\mu\text{-}NCS)_2](BPh_4)_2$	Dimmer	167	100	2.04	2.61	2.4	−0.4	0.05	[37]
$[Ni_2(terpy)_2(NCS)_2(\mu\text{-}NCS)2]\cdot 2H_2O$	Dimmer	159.0	100.0	2.04	2.62	4.9	−4.3	0.56	[38]
$[Ni_2(2\text{-}mepn)_3(NCS)_2(\mu\text{-}NCS)_2]$	Dimmer	165.2	100.7	2.06	2.55	4.3	−2.0	0.84	[39]
		142.4	105.8	2.10	2.64			0.42	
$[Ni_2(2\text{-}mepn)_4(NCS)_2(\mu\text{-}NCS)_2](PF_6)_2$	Dimmer	166.7	96.2	1.93	2.83	6.3	−2.0	0.16	[39]
$[Ni(HIm)_2(\mu\text{-}NCS)_2]$ (**1**)	Chain	158.2	99.5	2.03	2.59	4.0	0.2	0.61	[42]

[a] en: ethylenediamine, tren: tris(2-aminoethyl)amine, terpy: 2,2′:6′2″-terpyridine, 2-mepn: 1,2-diamino-2-methylpropane and HIm: imidazole.

[b] d = Ni-mean $(NCS)_2$ plane distance.

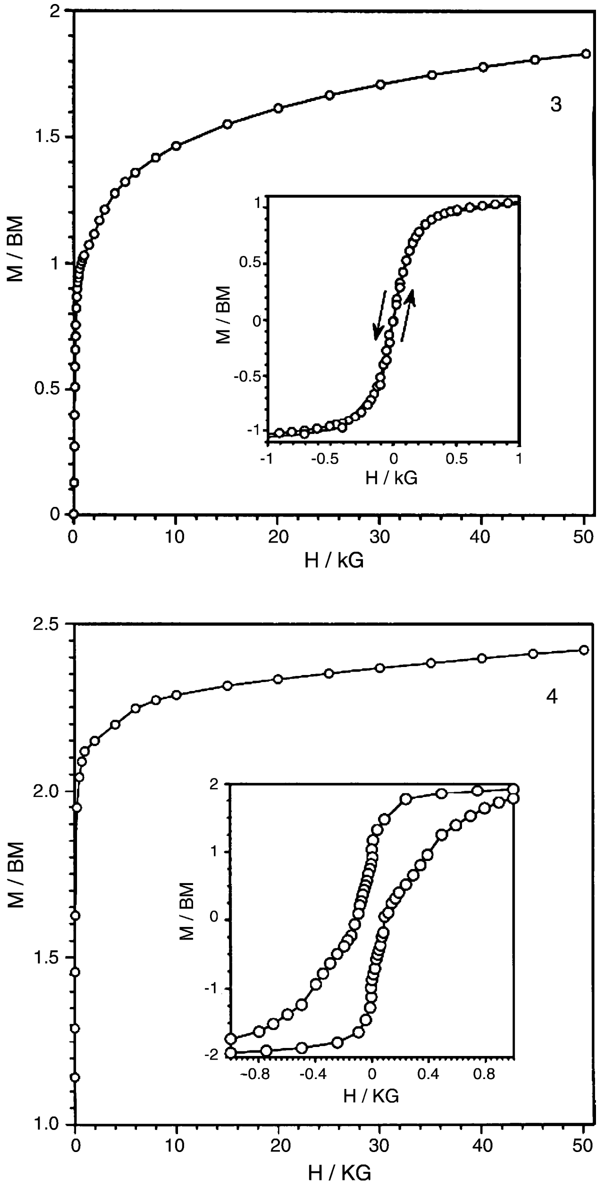


Fig. 9. Field dependence of the dc molar magnetization (○) for **3** and **4** at 1.9 K. The insert shows the magnetic hysteresis loop at 1.9 K. The solid line is an eye quide, Ref. [42].

coupling of **3** correlates well with those observed in the parent complexes in spite of presenting the greatest deviation from planarity.

2.4. Superexchange magnetic interaction in heterometallic copper(II)–rhenium(IV) compounds with macrocyclic ligands

The search for new materials showing useful magnetic and magneto-optical properties is one of the main goals of molecular magnetism [44]. They can also be built with molecular precursors, specially chosen to achieve a three-dimensional covalent bonding network between spin–bearing species [9]. However, until now, study of the interaction between magnetic centers has been generally restricted to metal ions belonging to the first transition series.

The magnetic properties of related complexes containing second and third series transition elements, which induce larger spin–orbit coupling effects and a greater degree of covalence, are much less known. This is the case for the rhenium(IV) complexes, where the $5d^3$ ion usually forms octahedral compounds. Numerous types of hexachloro-, hexabromo- and hexaiodorhenate complexes have previously been investigated in great detail [45–49]. The study of magnetic properties of mononuclear hexahalogeno complexes revealed the occurrence of an intermolecular antiferromagnetic interaction, whose magnitude depends on the size of the organic cation (bulk effect). The exchange of the two chloride ions by an oxalato ligand in the rhenium coordination sphere allows the synthesis of new heterodinuclear $Re^{IV}-Cu^{II}$ complexes. The analysis of literature data [50–52] suggests that quite strong coupling should be obtained if the ligand is coordinated in a symmetric bidentate way with two short Cu^{II}–O bonds. For this reason, it seemed interesting to examine macrocyclic copper(II) complexes CuL_{α} and CuL_{β} (where L_{β} = *N*-DL-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and L_{α} = *N*-DL-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene) in order to obtain heterometallic systems bridged by oxalato groups. The square planar macrocyclic complexes with two vacant coordination sites at the metal atom play the role of the so–called "building blocks".

The two rhenium(IV)–copper(II) heterometallic complexes $[CuL_{\beta}]$ $[ReCl_4(ox)]$ DMF (**5**) and $[(CuL_{\alpha})_2Cl]$ $[ReCl_4(ox)]$ Cl (**6**) were synthesized and the crystal structures of both compounds were determined at 173(2) K [53]. The CuL_{β} macrocycle cation is approximately planar and coordinated from above and below by $[ReCl_4(ox)]^{2-}$ units via the bis(bidentate) oxalato ligands. It features an oxalato-bridged heterometallic Re^{IV}–Cu^{II} zigzag chain, the shortest intrachain metal–metal distances being Re···Cu = 5.568(2) and 5.870(2) Å in direction of the *b*-axis (Fig. 10).

The crystal structure of **6** consists of dinuclear complex cations $[(CuL_{\alpha})_2Cl]^{3+}$ with $[ReCl_4ox]^{2-}$ and isolated Cl^- as counter anions. Cu atoms in CuL_{α} are only five-fold coordinated in a square pyramidal surrounding and the cations $[CuL_{\alpha}]^{2+}$ are connected in pairs by chloride. The intramolecular Cu···Cu separation is 4.885(3) Å, the shortest Re···Cu distance is 7.612(3) Å (Fig. 11).

Our results show, that the magnitude of magnetic coupling between Re^{IV} and Cu^{II} in these compounds can be tuned by changing the coordination geometry around the copper(II) ions. This coordination depends on the position of the methyl groups around the equatorial nitrogen atoms of the ligands. In the case of the nearly square planar coordinated $[CuL_{\beta}]^{2+}$, a one-dimensional ferrimagnetic chain compound was obtained. Each $[ReCl_4(ox)]^{2-}$ ion is bound by the two long Cu^{II}–O bonds to the two macrocyclic fragments. Magnetic measurements indicate weak antiferromagnetic interactions between the Re^{IV} and Cu^{II} metal ions

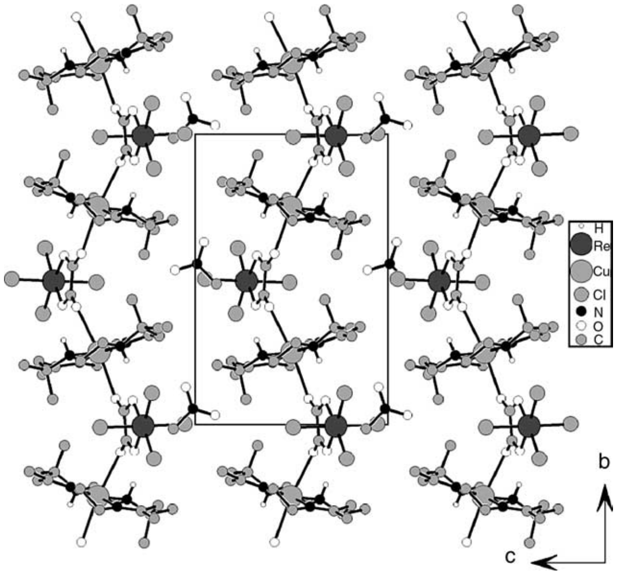


Fig. 10. Crystal structure of **5** (view axis *a*; H atoms bound to C have been omitted for clarity), Ref. [49].

within the chains. The magnetization temperature dependency reveals a transition from a one-dimensional ferrimagnetic system to three–dimensional magnetic ordering. In the case of a non-planar coordination sphere around Cu^{II}, the complex cation is open for coordination only on one side. This position is then occupied by a bridging chloro ligand, which connects two Cu^{II} macrocycle units and the isolated anion $[ReCl_4(ox)]^{2-}$ and is responsible for the charge balance. Strong antiferromagnetic interaction is not expected in the bimetallic Re^{IV}–Cu^{II} macrocyclic compounds **5** and **6** because of the poor overlap of the magnetic orbitals.

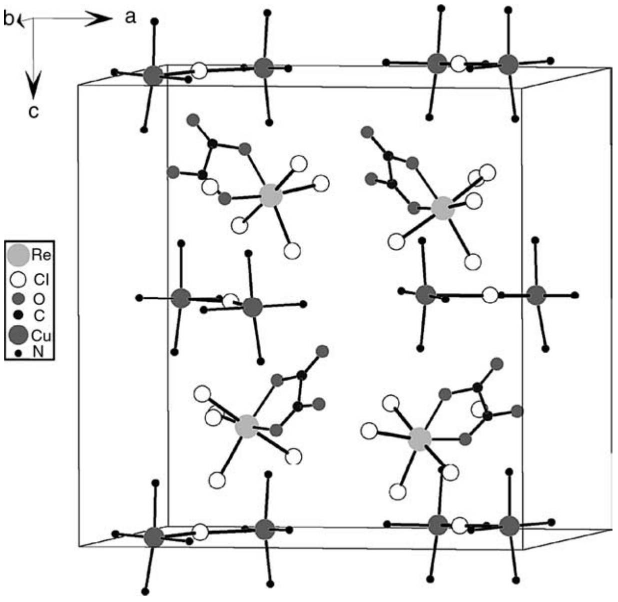


Fig. 11. Unit cell of **6** (C and H atoms of the macrocycle have been omitted for clarity), Ref. [49].

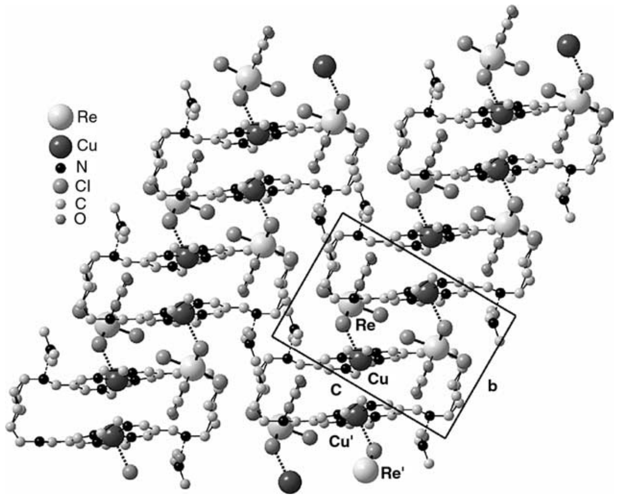


Fig. 12. Crystal structure of $[5CuCuL][ReCl_4(ox)]_2 \cdot 2DMF$ (view axis *a*, H atoms have been omitted for clarity), Ref. [54].

During the next step of our work we used the Cu(II) bis-macrocyclic complex to obtain new heterometallic systems. In a previous paper [53] we reported the study of magnetic and electrochemical properties of a new type of highly unsaturated bis-macrocyclic face-to-face transition metal complexes interacting with a guest molecule via strong π–π interactions. As a result one observes an increased communication between the metal centers reflected in the values of the conproportionation constants higher than in the parent bis-macrocyclic complexes.

Reaction of the rhenium(IV) compound, $[Bu_4N]_2[ReCl_4(ox)]$ with the unsaturated tetraazabis-macrocyclic copper(II) complex cation $[5CuCuL]^{4+}$ (L = 6,13-bis (dodecylaminomethylidene)-1,4,8,11-tetrazacyclotetradeca-4,7,11,14-tetraene) produced a new kind of binuclear compound: $[5CuCuL][ReCl_4(ox)]_2 \cdot 2DMF$ in which $[ReCl_4(ox)]^{2-}$ [54] anions and $[5CuCuL]^{4+}$ cations are held united by electrostatic forces. The crystal structures of this compound were determined at 173(2) K (Fig. 12).

The complex behaves as a ferrimagnetic Cu^{II}–Re^{IV} bimetallic, pseudo-one-dimensional chain with two weak intrachain antiferromagnetic magnetic coupling parameters through the chlorine atom ($J = -21\,cm^{-1}$) and through the oxalate-oxygen atom ($j \approx -9\,cm^{-1}$). over the temperature range 1.7–300 K.

Summing up the molecular magnet research carried out in recent years; many new antiferro and ferromagnetic molecular materials of d-electron metals were synthesized [55–64]. Their crystalline, electron and molecular structures were identified, as well as their physicochemical properties, and especially their low-temperature magnetism. The effect of structural factors on the possible existence of antiferro-, ferri- and ferromagnetic compounds was also discussed. This was proven with the example of the group of Cu^{II} tricyanomethanide complexes of the type $M\{C(CN)_3\}_2L_2$, in which the metallic centres are bonded by bidentate pseudohalogenic ligands $-C(CN)_3$. The magnetic centres displayed both ferro- and antiferromagnetic coupling in the crystalline lattice [65–73]. Many new linear ferri- and ferromagnets coupled together through the effect of antiferromagnetic exchange were synthesized and investigated [74–78].

An important accomplishment is also the realization of new single molecule magnets (SMM) using polymeric or tetrameric complexes of d- and f-electron metals [79]. The idea of single molecule magnets synthesis belongs to the most current research trends.

3. Inorganic Materials Research Group (M. Nicolaus Copernicus University, Toruń)

Magnetochemistry originated in Nicolaus Copernicus University in Toruń with the first seed sown by Prof. Antoni Grodzicki and his collaborator M.Sc. Michał Chrząszcz. Inspiration came from University of Wrocław and now diversified research is being pursued in the many fields of coordination chemistry and magnetochemistry.

3.1. Magnetism of d-electron metal coordination compounds

The research topics are related to synthesis, structure, spectroscopy, thermal and magnetic properties of new transition-metal complexes, especially homobimetallic copper(II) complexes with carboxylato bridges and heterobimetallic complexes with thiocyanato bridges [80–84].

The spectroscopic, magnetic and thermal properties of a large number of heteropolynuclear complexes were investigated [85–92]. In particular, properties of copper(II)–chromium(III) bimetallic complexes [85,86,89,90–92], nickel(II)–chromium(III) [87,89,90,92] and cobalt(II)–chromium(III) [90] systems have been studied. Hexaisothiocyanatochromate(III), which can form bridges with different metal ions via the sulfur atoms, was used in these complexes as the anionic building block. Coordinatively unsaturated copper(II), nickel(II) and cobalt(II) complexes, mainly with various diamines and imidazoles, served as cationic units. Most of the complexes synthesized have the following composition, $[ML_2]_3[Cr(NCS)_6]_2 \cdot nH_2O$.

3.2. Antiferro- and ferromagnetic heteropolynuclear compounds

In the these heterpolynuclear complexes the metal(II) and chromium(III) ions are antiferromagnetically coupled. Sometimes the overall magnetic interactions are negligible due to the balance between antiferro- and ferromagnetic pathways. Thiocyanato bridges transmit antiferromagnetic interactions more efficiently in the nickel(II)–chromium(III) heterocomplexes than in copper(II)–chromium(III) heterocomplexes, probably as a result of a longer *M*–*S* distance and also because for electronic reasons.

An X-ray crystal structure of $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ has shown the one-dimensional structure of the anionic heterobimetallic unit with the thiocyanato bridges, –NCS–Ni–SCN–Cr–NCS–Ni–Cr– [89]. To the best of our knowledge, $[Ni(en)_3]_n[\{Ni(en)_2Cr(NCS)_6\}_{2n}]$ represents is not only the first structurally characterized nickel(II)–chromium(III) system exhibiting intermetallic connections through thiocyanato bridges, but also one of the few examples of a thiocyanato bridged one-dimensional heterobimetallic compound. The magnetic behavior of this complex has been explained as a sum of cationic and anionic parts. The former shows simple Curie behavior of the nickel(II) ion, whereas the latter was treated as a Heisenberg linear chain with spin alternation. The intrachained nickel(II) and chromium(III) ions are antiferromagnetically coupled ($J \sim 20\,\mathrm{cm}^{-1}$). The structural features related to thiocyanato-bridged units being in *cis* positions at both metallic centers are responsible for moderate antiferromagnetic interactions.

We have also studied copper(II) complexes with tertiary phosphites and perfluorinated carboxylates as potential precursors for chemical vapor deposition (CVD) of metal or oxide layers [93–95]. The spectroscopic, magnetic and EPR data indicate the formation of polymeric species via carboxylic and hydroxyl bridges with the rarely reported Cu(II)–P(III) bond.

Some research has been carried out through collaboration with Dr. Zdeněk Smékal and Dr. Pavel Kopel from the Department of Inorganic and Physical Chemistry, Palacký University, Olomouc, Czech Republic. The structure and magnetic properties of dimeric oxalato bridged copper(II) complexes with chelating diamines were established [96,97]. Copper(II) ions in these compounds are antiferromagnetically coupled with $J = -157$ to $-175\,\mathrm{cm}^{-1}$ ($H = -2JS_1S_2$). Copper(II), cobalt(II) and nickel(II) complexes of trithiocyanuric acid were also characterized [98].

In addition, the magnetic properties of copper(II) diantipyrylmethane complexes [99,100] have been investigated. Both weak antiferromagnetic and ferromagnetic interactions, between the copper(II) ions were noted depending on the anion used. Spectroscopic, magnetic, EPR and structural data have been reported for dimeric copper(II) chloroacetate complexes with 5,7-dimethyl- and 5,7-diphenyl-1,2,4-triazolo-[1,5-α]-pyrimidine [101]. A strong antiferromagnetic interaction was observed, compared and discussed with the literature data for similar copper(II) chloroacetate compounds with different N-donor axial ligands.

Furthermore, the isomerism of iron(III)-complexed dyes based on 1,5-diaryl-3-cyanoformazanes was investigated with the use of IR, UV–vis, FAB-MS and magnetic methods [102]. A strong antiferromagnetic interaction was found in the brown form of the dyes studied and the authors proposed a dimeric structure with double oxygen bridges. The violet form showed magnetic behavior typical for a monomeric low-spin iron(III) species which had been observed for other Fe(III) compounds with formazane derivatives.

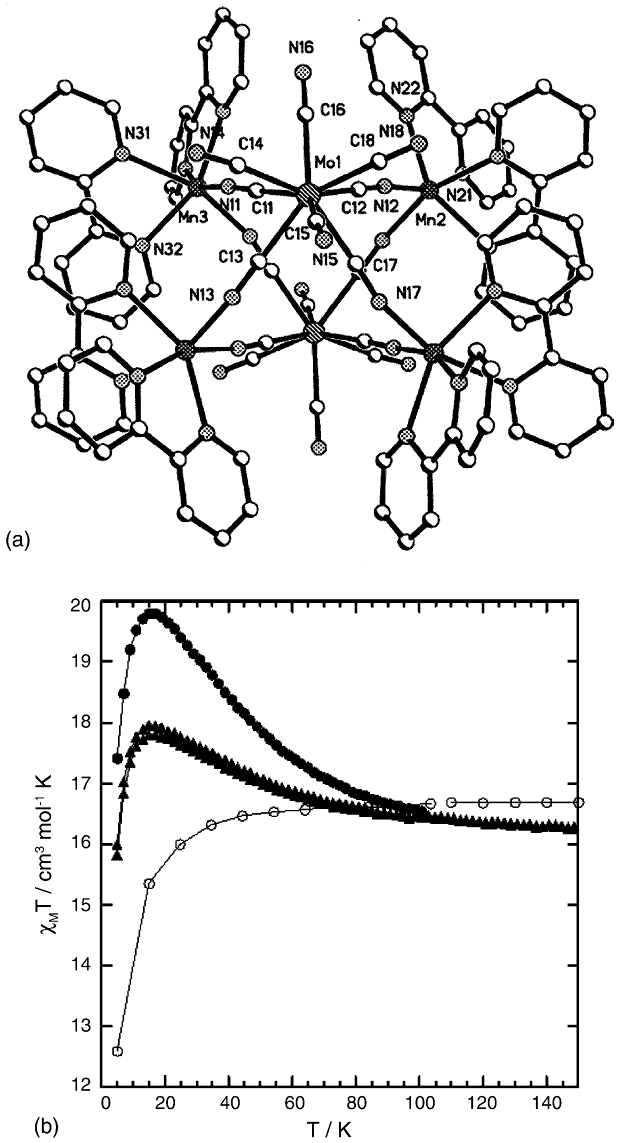


Fig. 13. The $\{[Mn(bpy)_2]_4[Mo(CN)_8]_2\}\cdot 8H_2O$ compound: (a) the molecular structure of hexamer Mn_4Mo_2; (b) photomagnetic properties of $Mn_4^{II}M_2^{IV}$ clusters: (a) $\chi_M T$ vs. $f(T)$ before and after (○) irradiation at 336–356 nm (●), and after irradiation followed by thermal heating at 300 K (▲) for $Mn_4^{II}Mo_2^{IV}$, Ref. [103].

A strong antiferromagnetic interaction was found in the brown dimeric form of the dyes studied, whereas the violet form showed typical low-spin iron(III) magnetic behavior.

The elucidation of the magneto-structural correlations for heteropolymetallic complexes is still an important goal of modern magnetochemistry.

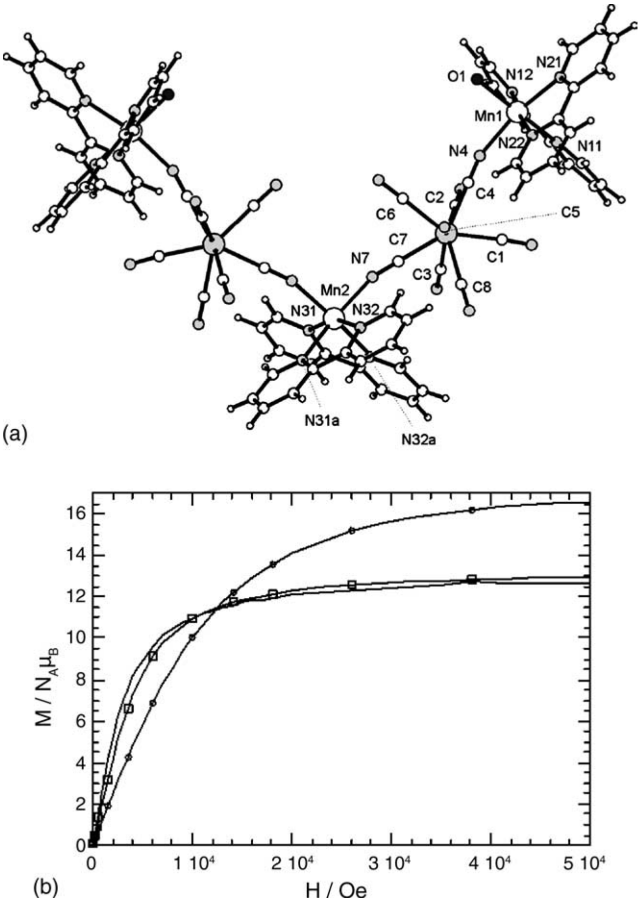


Fig. 14. The $\{[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\}\cdot 7H_2O$ compound: (a) the molecular structure of pentamer Mn_3W_2; (b) M(H) at $T = 2$ K: experimental (line), calculated Brillouin function for spin $S = 13/2$ (squares), the sum of Brillouin functions calculated for two independent spins $S = 1/2$ and three independent spins $S = 5/2$ (circles), Ref. [104].

4. Inorganic Molecular Materials Group (Jagiellonian University, Kraków)

The challenge of the Inorganic Molecular Materials Group is the construction of efficient crystalline materials with spin bistability, which can act as switches, detectors, or memory devices. Supramolecular heterobimetallic coordination networks based on electronically active cationic 3d-metal complexes and Mo and W octacyanometalate building blocks are especially suitable for these functions. The labile electronic configurations of the metal centers may be switched reversibly involving magnetic, optical and structural changes, usually stimulated by variation of temperature and/or pressure and by light irradiation.

Their interplay is illustrated by a wide range of architectures including zero-dimensional molecules, one-dimensional chains and two-dimensional layers based on $[M(CN)_8]^{3-/4-}$ ($M = Mo, W$) molecular building blocks and pre-organized 3d metal complexes [103].

4.1. New molecular magnets of molybdenium(IV, V) and tungsten(IV, V)

Zero-dimensional structures, resulting from the metal-directed self-assembly of *cis*-protected $[Mn(bpy)_2(H_2O)_2]^{2+}$ octahedral tecton and octacyanometalates and the synthesis of hexanuclear clusters $\{[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\}\cdot 8H_2O$

(M = Mo, W) and pentanuclear high-spin $\{[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\}\cdot 7H_2O$ [103,105] are among the most important achievements of this research group.

In the case of the $[M^{IV}(CN)_8]^{4-}$ building block, the hexanuclear cluster $\{[Mn^{II}(bpy)_2]_4[Mo^{IV}(CN)_8]_2\}\cdot 8H_2O$ has octahedral geometry (Fig. 13a) [103]. The molecule is formed from two, mutually perpendicular, $Mn_2{}^{II}Mo_2{}^{IV}$ squares sharing the Mo corners.

Photomagnetic measurements of solid $\{[Mn(bpy)_2]_4[M(CN)_8]_2\}\cdot 8H_2O$ (Fig. 13b) indicate that these clusters display irreversible photo-induced magnetic modifications.

Irradiation ($\lambda = 337$–357 nm) at 5 K in the SQUID results in formation of a $Mn_2{}^{I}Mn_2{}^{II}M_2{}^{V}$ photoproduct [104], while under ambient conditions, in the presence of O_2, photodecomposition of the cluster into $[Mn^{II}(bpy)_2(CN)_2]$ and $[M^{VI}(CN)_4(O_2)]$ takes place.

The self-assembly of *cis*-$[Mn^{II}(bpy)_2(H_2O)_2]^{2+}$ and $[W^{V}(CN)_8]^{3-}$ precursors results in the formation of the pentanucleark $\{[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\}\cdot 7H_2O$ [105]. The pentanuclear molecule has a slightly distorted V-shape with two tungsten(V) atoms linked by single cyano bridges to three manganese(II) centers in alternating sequence Mn–W–Mn–W–Mn (Fig. 14a). The complex exhibits intramolecular antiferromagnetic coupling between Mn(II) and W(V) centers consistent with a ground state spin of $S = 13/2$ (Fig. 14b) and a ferromagnetic long range transition at 0.66 K. The supramolecular architectures of $Mn_4{}^{II}Mo_2{}^{IV}$ and $Mn_3{}^{II}W_2{}^{V}$ lattices are controlled by CN-bridging, intra- and inter-molecular π–π stacking (face-to-face and edge-to-face) interactions and an extensive network of hydrogen bonds between terminal cyano ligands and the water molecules. The preference for the formation of zero-dimensional molecules in the self-assembly of *cis*-$[Mn^{II}(bpy)_2(H_2O)_2]^{2+}$ and $[W(CN)_8]^{3-/4-}$ is enforced by the electroneutrality of the resulting $\{[Mn^{II}(bpy)_2]_4[M^{IV}(CN)_8]_2\}\cdot 8H_2O$ and $\{[Mn^{II}(bpy)_2][Mn^{II}(bpy)_2(H_2O)]_2[W^{V}(CN)_8]_2\}\cdot 7H_2O$ products as

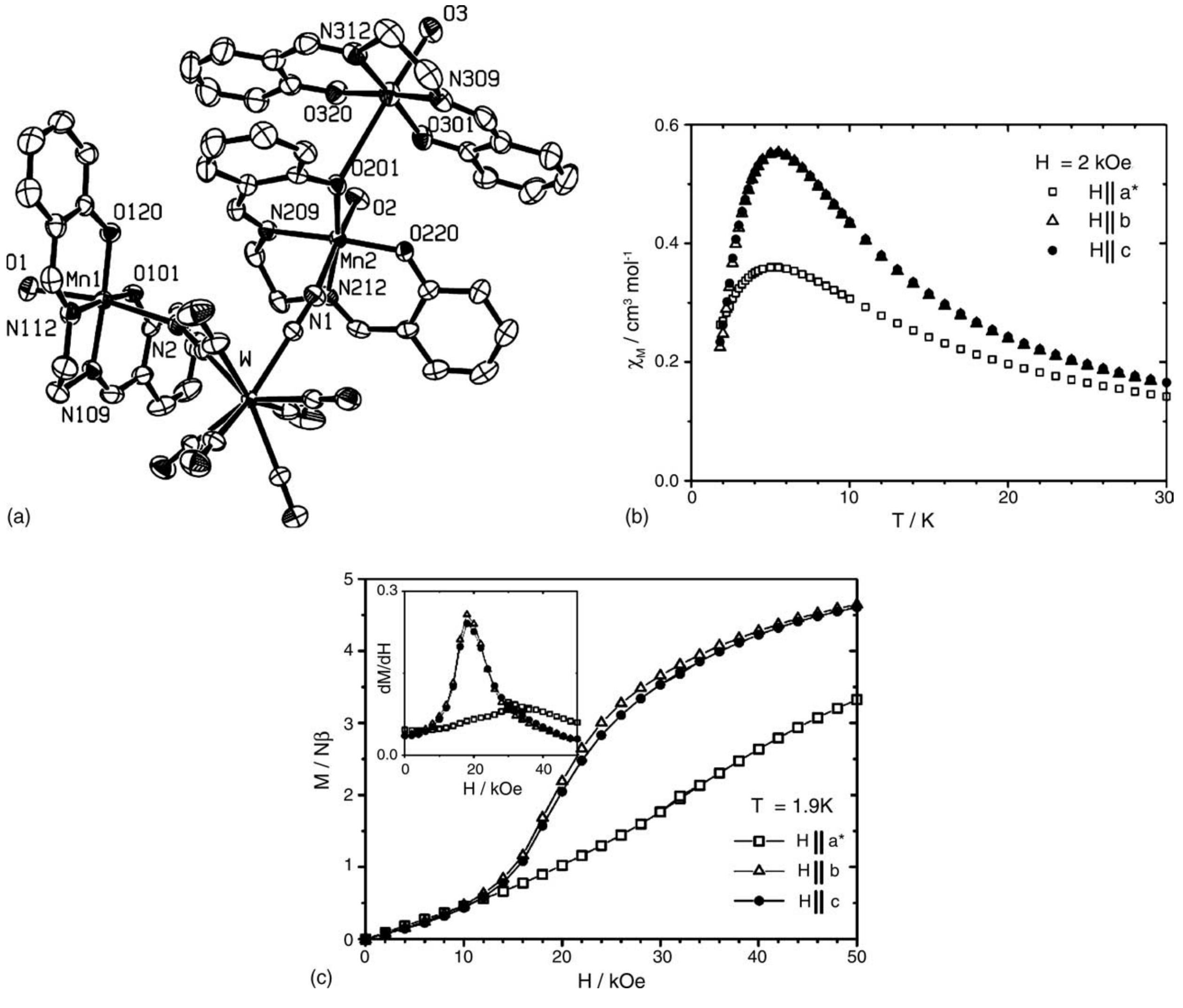


Fig. 15. The $[Mn^{III}(salen)H_2O]_3[W^{V}(CN)_8]\cdot H_2O$ compound: (a) molecular structure of tetramer $Mn_3{}^{II}W^{V}$; (b) thermal dependence of the magnetic susceptibility of a single crystal; (c) field-dependent magnetization of a single crystal at $T = 1.9$ K, Ref. [109].

well as by the π–π stacking of bpy ligands, which seems to prevent the growth of the larger structures. The reaction between $[Mn^{III}(salen)(H_2O)]^+$ [salen = the *N*,*N′*-ethylenebis(salicylideneaminato dianion)] and $[W^V(CN)_8]^{3-}$ in methanol resulted in the formation of $[Mn^{III}(salen)H_2O]_3[W^V(CN)_8]\cdot H_2O$ [106–109]. The structure consists of the asymmetric V-shape Mn–NC–W–NC–Mn–$O_{phenolate}$–Mn molecules, where the W(V) coordinates [Mn(salen)H_2O] and singly phenolate-bridged $[Mn(salen)H_2O]_2$ moieties through the neighboring cyano bridges (Fig. 15a). The

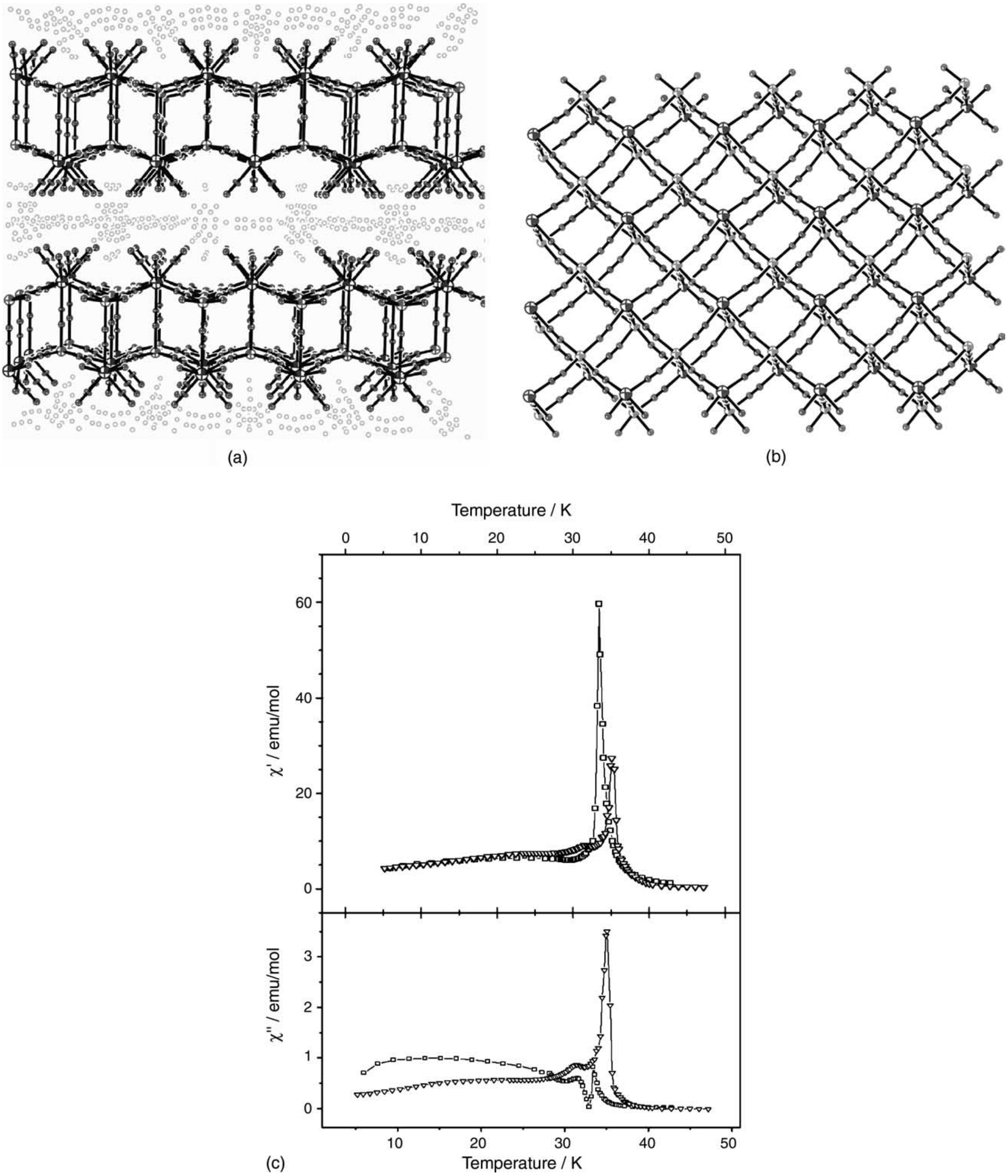


Fig. 16. Crystal structure of $\{(LH_n)Cu_n^{II}[M^V(CN)_8]_n\cdot xH_2O\}_\infty$: (a) the projection showing alternatively stacked anionic double-layers $\{Cu^{II}[M^V(CN)_8]^-\}_n$ and layers of LH_n^{n+} cations and water molecules (yellow); (b) the view showing the square grid patterns in double layer; (c) example of in-phase χ' and out-of-phase χ'' components of ac susceptibility vs. T (f = 140 Hz, H_{ac} = 5 Oe, H_{dc} = 0), Refs. [110,111].

magnetic studies reveal antiferromagnetic intramolecular interactions through the CN and phenolate bridges and relatively weak intermolecular interactions.

The material becomes antiferromagnetically ordered below $T_N = 4.6$ K. The presence of the magnetic anisotropy is documented with the $M(H)$ measurements carried out both for polycrystalline and single-crystal (Fig. 15b and c). At $T = 1.9$ K a *spin-flop* transition is observed when a field of 18 kOe is applied to the sample (in parallel to the *bc* plane, which is the easy plane of magnetization). The field dependence of magnetization shows field-induced metamagnetic behavior from the antiferromagnetic ground state of $S_T = 3/2$ to the state of $S_T = 5/2$.

The construction of a higher dimensional network requires the use of weakly bonded metal-solvent complexes. The example of this strategy is the self-assembly of $[M(CN)_8]^{3-}$ and $[CuL]^{2+}$ in acidic aqueous solution to generate the two-dimensional family $\{(LH_n)Cu_n{}^{II}[M^V(CN)_8]_n{\cdot}xH_2O\}_\infty$ (M = Mo, W; L = tetren, $n = 5$, $x = 9$ or L = dien, $n = 3$, $x = 4$) compounds [110,111]. The $[CuL]^{2+}$ complex ion provides the pre-programmed bare Cu(II) centers formed by the release of the fully protonated polyamine ligand. The $\{(LH_n)Cu_n{}^{II}[M^V(CN)_8]_n{\cdot}xH_2O\}_\infty$ consist of alternatively stacked anionic double-layers $\{Cu^{II}[M^V(CN)_8]^-\}_n$ and layers of $LH_n{}^{n+}$ cations and water molecules, ensuring the charge balance of the network (Fig. 16a and b).

The $\{(LH_n)Cu_n{}^{II}[M^V(CN)_8]_n{\cdot}xH_2O\}_\infty$ systems exhibit soft ferromagnetic behavior with ordering temperatures T_c in the range of 28–37 K (Fig. 16c). The ferromagnetic coupling can be rationalized in terms of the interactions of unpaired electrons originating from the mutually orthogonal $3d_{x2-y2}$ orbital of Cu(II) and the mixture of $5d_{z2}$ and $5d_{x2-y2}$ ground state orbitals of the M(V) center of bicapped trigonal prism geometry along both types of Cu–NC–M bridge. The architecture of alternatively stacked coordination anionic and molecular cationic layers in $\{(LH_n)Cu_n{}^{II}[M(^VCN)_8]_n{\cdot}xH_2O\}_\infty$ is very interesting from the point of view of the cationic exchange.

A logical extension of the building-block approach is to combine the *pre-organized multinuclear supramolecular coordination compound* formed by 3d metal centers bridged by organic *spacer* ligands with the octacyanometalate moiety. In order to explore this idea we have chosen the predictable coordination polymer network of one-dimensional chains that are generated from the metal ions coordinated to linear bi-functional ligands such as 4,4′-bipyridine (4,4′-bpy). While these polymeric strands are usually cross-linked by hydrogen-bonded bridging 4,4′-bpy ligands, our new strategy consists in the cross-linking of $\{[M^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains by $[M(CN)_8]^{3-/4-}$ *spacers*. The novel two-dimensional coordination network $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})(DMF)]_2[W^V(CN)_8]_2{\cdot}2DMF{\cdot}2H_2O$ (Fig. 17a) has been obtained [112,113]. The structure consists of the expected 2-dimensional grid-type network, which is built of infinite $\{[Cu^{II}(\mu\text{-}4,4'\text{-bpy})]^{2+}\}_n$ chains cross-linked by octacyanotungstate units. The Cu^{II}–NC–W^V–CN–Cu^{II} linkage exhibits the topology of 3,2-chain. The magnetic properties correspond to a dominant ferromagnetic coupling within the $Cu_3{}^{II}W_2{}^V$ pentamer units ($J = +35(4)\ cm^{-1}$) and much weaker effective AF inter-unit coupling which includes both intra- and inter-3,2-chain interactions between pentamers ($J' = -0.05(1)\ cm^{-1}$) (Fig. 17b).

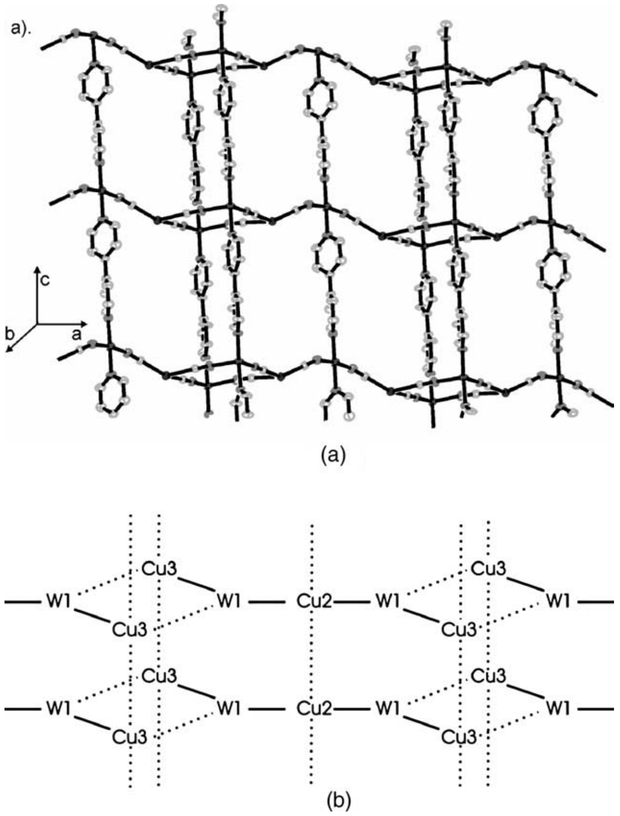


Fig. 17. The crystal structure and magnetic properties of $[Cu(\mu\text{-}4,4'\text{-bpy})(DMF)_2][Cu(\mu\text{-}4,4'\text{-bpy})(DMF)]_2[W^V(CN)_8]_2{\cdot}2DMF{\cdot}2H_2O$: (a) side view of two-dimensional layer; (b) the exchange interactions represented by J (solid lines) and J' (dotted lines), Refs. [112,113].

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