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Synthesis and crystal structures of a series of complexes based on a rigid angular ligand and the magnetic properties of the Cu(II) polymer

Hongwei Hou,* Lixia Xie, Gang Li, Tiezhu Ge, Yaoting Fan and Yu Zhu

Department of Chemistry, Zhengzhou University, Henan 450052, P. R. China.
E-mail: houhongw@zzu.edu.cn

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Treatment of 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpodz) with $AgNO_3$, $Cu(OAc)_2$, $CoSO_4$, CdI_2 or $MnSO_4$ afforded five complexes, the coordination polymers $[Ag(bpodz)(\mu\text{-}NO_3)]_n$ (**1**), $\{[Cu_2(bpodz)(\mu\text{-}OAc)_4](CH_3OH)_2\}_n$ (**2**), $\{[Co(bpodz)(SO_4)(H_2O)_3](CH_3OH)_2\}_n$ (**3**) and $[Cd(bpodz)_2(\mu\text{-}I)_2]_n$ (**4**), and the complex $[Mn(bpodz)_2(SCN)_2(H_2O)_2]$ (**5**). These compounds have been structurally characterized by X-ray single crystal diffraction. **1** is a 2-D network polymer constructed by ladder-like chains. In these chains, the nitrate anions are shared by two silver(I) to form a rhombic Ag_2O_2 plane. Polymer **2** is a 1-D wave-like chain in which the copper(II) atoms bridged by the acetate groups are separated by a distance of 2.623 Å. Polymer **3** shows a 1-D linear structure, in which interchain H-bonding interactions contribute to the final 2-D networks. Polymer **4** crystallizes as infinite CdI_2 chains in which cadmium(II) ions are doubly bridged by pairs of iodine atoms; the bpodz complete the octahedral coordination of the cadmium atoms, but act as monodentate ligands so do not to link the CdI_2 chains to form extended 2-D layers. Complex **5** is constructed into a 2-D stair-like structure through hydrogen bonds. Magnetic susceptibility data for polymer **2**, measured from 5 to 300 K, show strong antiferromagnetic coupling. These data were fitted to the appropriate equations derived from the Hamiltonian $H = -2JS_1S_2$, giving the parameter $-2J = 320\ \text{cm}^{-1}$.

Introduction

Over the past few years much progress has been made toward the building of supramolecular structures with organic and inorganic compounds, in which the organic components play a significant structural role in the control of the final structures.[1–4] At the same time, due to the incorporation of transition metals into organic systems, one of the appealing features in this field is the significant improvement in bulk properties such as thermal stability and dielectricity; the variable valences of metal ions can give rise to a variety of frameworks to fulfill special needs.[5] Thus, between organic and inorganic components there is a synergistic interaction, which provides a method for the design of novel materials.[6,7] Many strategies have been employed in the synthesis of polymeric compounds; one of the most fruitful choices consists in making good use of 4, 4′-bipyridine, which can complete the metal coordination and interconnect parallel chains.[1b,8] In the late sixties Musgraveand Mattson synthesized the first complexes of transition metals with 4,4′-bipyridine and suggested that these compounds were coordination polymers based on the infrared spectra data.[9] Since then, there has been a considerable amount of work on the preparation and structural characterization of similar types of compounds that contain bidentate ligands. Of the bidentate spacer ligands, those containing two pyridyl donor units represent an important class, which can afford variable lengths and linear or non-linear geometries.[10–12] In addition, this kind of polymers has attracted attention due to potential applications in the areas of catalysis,[13] conductivity,[14,15] magnetism,[16] and for their optical behavior.[17] Although a series of polymeric complexes containing bipyridyl-based ligands has been reported,[10–12,18,19] the remarkable coordination abilities of bipyridyl-based ligands have prompted us to design and synthesize new polymers containing pyridyl donor units. In contrast to the flexible bipyridyl-based ligands typically employed for crystal engineering with coordination compounds,[10f,18,19] the 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (bpodz) ligand that we employed here has a rigid molecular skeleton. To the best of our knowledge, only a few polymers constructed with bpodz have been reported.[20] Herein we report the synthesis and crystal structure analysis of the four bpodz containing coordination polymers, $[Ag(bpodz)(\mu\text{-}NO_3)]_n$ (**1**), $\{[Cu_2(bpodz)(\mu\text{-}OAc)_4](CH_3OH)_2\}_n$ (**2**), $\{[Co(bpodz)(SO_4)(H_2O)_3](CH_3OH)_2\}_n$(**3**) and $[Cd(bpodz)_2(\mu\text{-}I)_2]_n$ (**4**), and the complex $[Mn(bpodz)_2(SCN)_2(H_2O)_2]$ (**5**), as well as the magnetic properties of polymer **2**.

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Experimental

Materials and general methods

All reagents and chemicals were purchased from commercial sources and used as received. bpodz was synthesized according to the literature method[21] and was characterized by its ^{1}H NMR and IR spectra. (^{1}H NMR ($CDCl_3$): δ 8.88–8.90 (s, 4H), 8.02–8.03 (s, 4H); IR (KBr): ν/cm^{-1} 3450w, 3040w, 1062w, 1530s, 1482s, 1412s, 1322m, 1267m, 1221m, 976m, 834m, 708s.

Syntheses

$[Ag(bpodz)(\mu\text{-}NO_3)]_n$ (1). An acetonitrile solution (5 mL) of bpodz (11.2 mg, 0.05 mmol) was added into an acetonitrile solution (5 mL) of $AgNO_3$ (8.5 mg, 0.05 mmol). The solution was placed in the dark and kept at room temperature to allow for slow evaporation. Colorless crystals were gradually formed 3 days later in 40% yield. IR (KBr): ν/cm^{-1} 3048w, 1612m, 1565w, 1536m, 1483m, 1365s, 1302s, 1216m, 1059w, 1009w, 841m, 719m.

{[Cu_2(bpodz)(μ-OAC)$_4$](CH_3OH)$_2$}$_n$ (2). bpodz (11.2 mg, 0.05 mmol) in methanol (5 mL) was added into 4 mL of a methanol solution of $Cu(OAc)_2$ (10.0 mg, 0.05 mmol). The resultant green solution was filtered to give a clear solution. Dark-green crystals suitable for X-crystallography were obtained 4 days later (30% yield). IR (KBr): ν/cm^{-1} 3450w, 1624s, 1433s, 1274w, 1220w, 1059w, 843w, 721m, 686m, 628w.

{[Co(bpodz)(SO_4)(H_2O)$_3$](CH_3OH)$_2$}$_n$ (3). bpodz (11.2 mg, 0.05 mmol) in 5 mL methanol was added dropwise into a methanol solution (5 mL) of $CoSO_4 \cdot 7H_2O$ (14.1 mg, 0.05 mmol) to give a clear solution. Red crystals suitable for X-ray diffraction were obtained after 2 weeks by slow evaporation of the methanol solution at room temperature (50% yield). IR (KBr): ν/cm^{-1} 3370s, 1613m, 1508m, 1505m, 1497m, 1420m, 1130s, 848m, 716s, 509m.

[Cd(bpodz)$_2$(μ-I)$_2$]$_n$ (4). bpodz (11.2 mg, 0.05 mmol) in tetrahydrofuran (4 mL) was added into a tetrahydrofuran solution (4 mL) of CdI_2 (18.3 mg, 0.05 mmol). Evaporation at room temperature over several days yielded a white powder. The resultant solid was dissolved in *N*,*N*-dimethylformamide (3 mL), from which bright colorless crystals of X-ray quality were obtained 3 weeks later (31% yield). IR (KBr): ν/cm^{-1} 3086w, 1614w, 1568m, 1537m, 1486m, 1421m, 1226w, 837m, 716s.

[Mn(bpodz)$_2$(SCN)$_2$(H_2O)$_2$] (5). A solution of $MnSO_4$(8.5 mg, 0.05 mmol) in water (3 mL) was added into a solution of bpodz (11.2 mg, 0.05 mmol) in methanol (5 mL), and then a solution of KSCN (7.5 mg, 0.05 mmol) in 2 mL water was slowly added to the preceding mixture. The resulting solution was left for 3 days at room temperature as bright yellow crystals were gradually formed in 50% yield. IR (KBr): ν/cm^{-1} 2066s, 1615s, 1537s, 1485s, 1415s, 1221m, 1003m, 838s, 718s.

Crystal structure determination

Single crystals suitable for X-ray determination were mounted on glass fibers. All data were collected at room temperature on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed using SHELXL-97 crystallographic software package.[22] Table 1 shows selected crystallographic crystal data and processing parameters for the complexes **1**, **2**, **3**, **4** and **5**. Selected bond lengths and bond angles are listed in Table 2.†

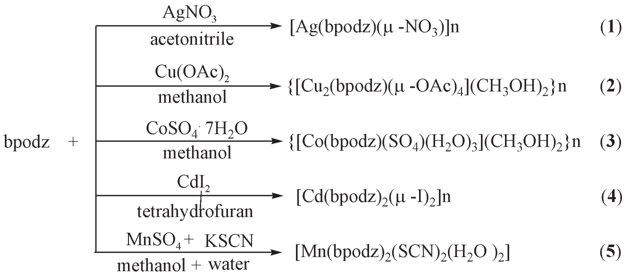
Magnetic measurements

Variable-temperature magnetic susceptibility data were obtained on a SQUID susceptometer (Quantum Design, MPMS-5) in the temperature range of 5–300 K with an applied field of 500 G. All data have been corrected for diamagnetism by using Pascal's constants.[23]

Results and discussion

Preparation of the compounds (Scheme 1)

It should be pointed out that placing the mixture of $AgNO_3$ with bpodz in the dark is an effective route for preparation of polymer **1**; in light a black powder was formed whose composition could not be identified. We presume that $AgNO_3$ undergoes decomposition first, making the subsequent reactions complicated.



Scheme 1

The reaction of bpodz with $Cu(OAc)_2$ in methanol (metal-to-ligand molar ratio 1:1) yielded the new dicopper 1-D polymer **2** {[Cu_2(bpodz)(μ-OAc)$_4$](CH_3OH)$_2$}$_n$, which is different from the mononuclear complex [Cu(bpodz)$_2$(OAc)$_2$(H_2O)](H_2O)$_2$(CH_3OH)[20] (metal-to-ligand molar ratio 1:2 in methanol–water). Significant changes between the two methods involve both the solvent and metal-to-ligand molar ratio. Although a detailed study is still needed, the differences in the structures may be caused by the different metal-to-ligand molar ratios used in the reactions. When a metal-to-ligand molar ratio of 1:2 is used, Cu(II) is easy coordinated by two pyridyl nitrogen atoms from two ligands. The presence of excess bpodz may drive the coordination of the uncoordinated pyridyl nitrogen atoms. Fig. 1 shows the experimental X-ray powder diffraction pattern and the simulated pattern calculated from single-crystal X-ray diffraction data for polymer **2**.[24] The two patterns correspond.

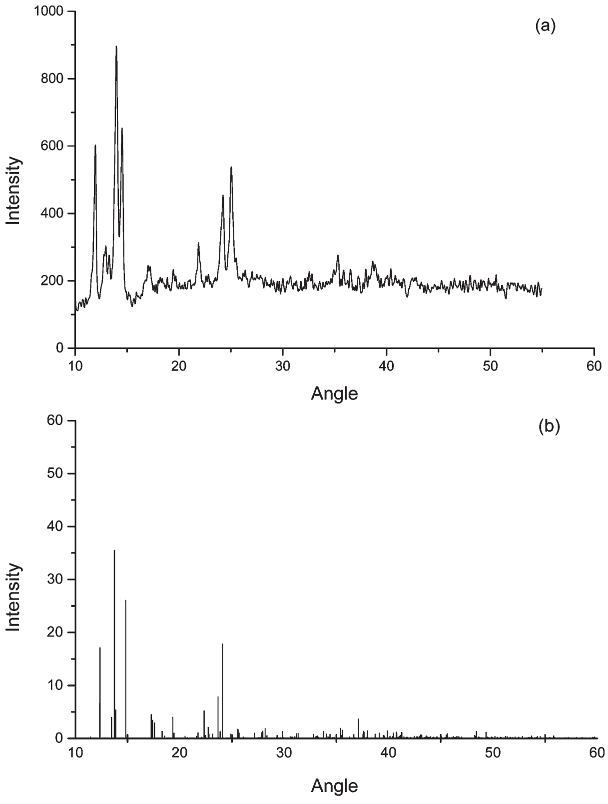


Fig. 1 (a) The experimental X-ray powder diffraction pattern and (b) the simulated pattern calculated from the single-crystal X-ray diffraction data.

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† CCDC reference numbers 213496–213500 for compounds **1**–**5**, respectively. See http://www.rsc.org/suppdata/nj/b3/b307384j/ for crystallographic data in .cif or other electronic format.

In an attempt to obtain metal cobalt(II) polymers, we tried the reaction of $Co(NO_3)_2$ with bpodz in CH_3CN, which yielded poorly crystalline products not suitable for single-crystal X-ray analysis. However, on changing the counter anion from nitrate to divalent sulfate the 2-D network polymer **3** was obtained.

It is worth noting that when $MnSO_4$ reacted with bpodz, only colorless crystals of bpodz were formed. After KSCN was added, SCN^- acted as the counter anion, instead of SO_4^{2-}, and yellow crystals of **5** were obtained. The IR spectrum revealed that there was no absorption of SO_4^{2-} around 1125 cm^{-1} in **5**, while an IR absorption band around 2066 cm^{-1} could be ascribed to SCN^-, indicating that SCN^- is mono-coordinated to the metal ion.[25]

Crystal structures

[Ag(bpodz)(μ-NO$_3$)]$_n$(1). Polymer **1** is composed of $Ag_2(bpodz)_2(\mu\text{-}NO_3)_2$ units in which two bpodz bridge four Ag atoms to form a polymeric chain, while two oxygen atoms of the nitrate anions are shared by two Ag(I) centers to give rise to a rhombic Ag_2O_2 plane with an Ag···Ag distance of 3.588 Å(Fig. 2). The Ag1B–N4A and Ag1B–N1B bond lengths are not equal; the average value is 2.233 Å. The Ag1B–O2B and Ag1B–O2E distances are 2.515 and 3.003 Å, respectively. The N1B–Ag1B–N4A and N4A–Ag1B–O2B bond angles are 140.06° and 130.07°, respectively. The dihedral angles between the Ag_2O_2 plane and the two pyridyl ring planes (N4A–C12A and N1B–C5B) are 102.2° and 104.4°, respectively. This reveals that the two pyridyl ring planes are almost parallel with a dihedral angle of 8.6°. Nitrate anions are coordinated in a bridging monodentate fashion through oxygen atoms to Ag(I), one of the five coordinating modes of nitrate anions reported in coordination polymers (Chart 1).[26–30] The more important feature of polymer **1** is that infinite molecular ladders are formed in which bridging nitrate anions can be considered as the rungs of the ladders and bpodz as the siderails. The Ag(I) ions form bonds to the oxadiazole nitrogen atom of adjacent ladders (Ag1C–N3A, 3.004 Å) (Fig. 3) to lead to a 2-D network polymer. The distance of 3.437 Å between the two parallel pyridyl rings indicates that π–π interactions serve to stabilize the network.

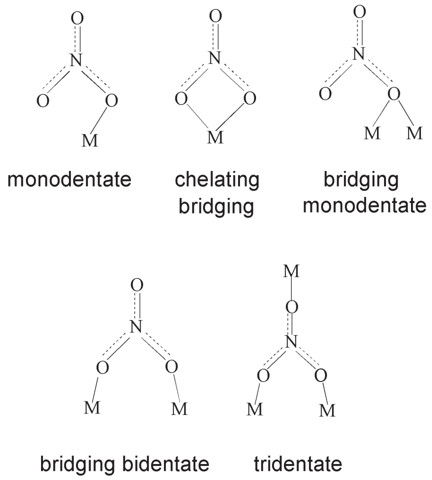

Chart 1

As far as silver(I) polymers are concerned, the reported structures consist of sinusoidal chain,[31] helical chain,[31] 1-D W-type chain,[32] 1-D ladder chain,[32] 1-D zigzag chain,[27] 1-D double chain,[33] 2-D pleated sheet,[34] 3-D cubic framework,[35] 3-D enantiomorphic framework,[36] 3-D helical framework,[37] diamond-like networks,[38] and 3-D network consisting of molecular ladders and hydrogen bonds.[39] The ladder-like chains in polymer **1** are reminiscent of $[Ag_3(CF_3CO_2)_3]\cdot(dpbd)$ (dpbd = 1,4-diphenyl-1,3-butadiene),[32] which exhibits a similar 1-D ladder-like chain. However, some differences arising from the properties of these ligands and anions exist between **1** and $[Ag_3(CF_3CO_2)_3]\cdot(dpbd)$. For instance, in polymer **1**, nitrate anions only act as the rungs of the ladder. Therefore, the formation of the ladder-like chains is mainly due to bpodz, while the 1-D ladder chain formed in $[Ag_3(CF_3CO_2)_3]\cdot(dpbd)$ results from the bridging trifluoroacetate groups, which act as both the rungs and the siderails. In addition, polymer **1** exhibits distinct features, for example, the bridging monodentate nitrate anions and interactions between Ag(I) and the nitrogen atoms of 1,3,4-oxadiazole. The latter contribute to the final 2-D network.

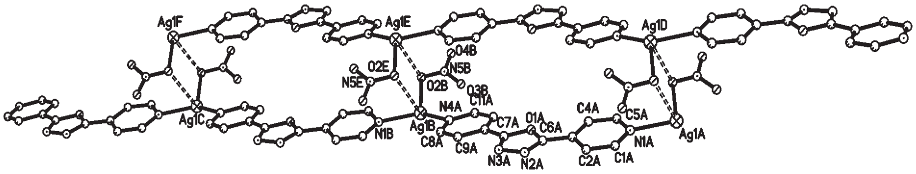

Fig. 2 ORTEP drawing of **1** with the atom numbering scheme, showing the ladder-like chain. The Ag–O bond distance of more than 3.0 Å is shown as double dashed lines.

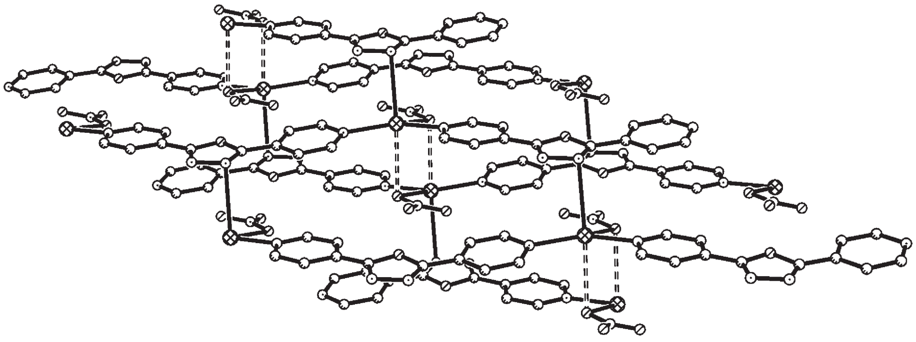

Fig. 3 The 2-D network structure of **1**. Adjacent ladder-like chains are connected by Ag–N interactions.

Table 1 Crystal data and structure refinement parameters for complexes **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_{12}H_8AgN_5O_4$	$C_{22}H_{28}Cu_2N_4O_{11}$	$C_{14}H_{22}CoN_4O_{10}S$	$C_{18}H_{16}CdIO_2$	$C_{26}H_{20}MnN_{10}O_4S_2$
FW	394.10	651.56	497.35	814.65	655.58
T/K	291(2)	291(2)	291(2)	291(2)	291(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P-1	$C2/c$	$P2(1)/n$	$P2(1)/c$	P-1
a/Å	8.949(2)	29.829(6)	7.4061(15)	4.1122(8)	7.9571(16)
b/Å	9.856(2)	13.139(3)	10.725(2)	13.463(3)	8.6740(17)
c/Å	8.358(2)	8.5558(17)	26.453(5)	23.674(5)	11.326(2)
α/°	102.12(3)	90	90	90	94.31(3)
β/°	110.50(3)	105.95(3)	96.11(3)	91.69(3)	110.17(3)
γ/°	74.78(3)	90	90	90	94.66(3)
U/Å^3	660.5(2)	3224.1(11)	2089.2(7)	1310.1(4)	726.9(3)
Z	2	4	4	2	1
μ/mm^{-1}	1.554	1.373	0.980	3.229	0.650
Collected reflect.	2263	3234	5345	3589	2127
Unique reflect.	2263	1922	3237	2089	2127
R_1 [$I > 2\sigma(I)$]	0.0421	0.0678	0.0547	0.0644	0.0594
$wR_2{}^a$ [$> 2\sigma(I)$]	0.0884	0.1490	0.1232	0.1569	0.1722
R_1 (all data)	0.0529	0.1342	0.0885	0.0783	0.0690
$wR_2{}^a$ (all data)	0.0918	0.1692	0.1340	0.1850	0.1821
R_{int}	0.0000	0.0592	0.0530	0.0813	0.0000

[a] For polymer **1**: $w = 1/[\sigma^2(F_o{}^2) + (0.0403P)^2 + 0.8090P]$. For polymer **2**: $w = 1/[\sigma^2(F_o{}^2) + (0.0843P)^2 + 0.0000P]$. For polymer **3**: $w = 1/[\sigma^2(F_o{}^2) + (0.0688P)^2 + 0.0000P]$. For polymer **4**: $w = 1/[\sigma^2(F_o{}^2) + (0.0746P)^2 + 8.5992P]$. For complex **5**: $w = 1/[\sigma^2(F_o{}^2) + (0.1399P)^2 + 0.0000P]$. For all complexes $P = (F_o{}^2 + 2F_c{}^2)/3$.

{[Cu_2(bpodz)(μ-OAC)$_4$](CH_3OH)$_2$}$_n$(2). In polymer **2**, polymeric binuclear units exist (Fig. 4). The two copper ions are located at equivalent sites. The copper–copper distance of 2.623 Å is short enough to allow a degree of metal–metal bonding character and strong magnetic properties. Each copper atom has an octahedral coordination environment, with four oxygen atoms from four bridging acetate groups, forming a equatorial plane, one pyridyl nitrogen atom and another Cu. The Cu–O distances are in the range of 1.954 to 1.975 Å. The axial Cu–N distance is 2.202 Å. The coordination geometry around the Cu(II) ion can be regarded as a Jahn–Teller-distorted octahedron. The Jahn–Teller effect in the polymer manifests itself as an asymmetric elongation along the axial direction. In the structure of **2**, four acetate groups are bound to the Cu(II) atoms, thus forming a Cu(OAc)$_4$Cu paddle-wheel-type cage between two bpodz as the basis for the polymeric chain. It is clear from the structure that four oxygen atoms (O2, O4, O3A, O5A) are almost coplanar. In addition, the displacement of the Cu1 atom from this plane is only 0.0630 Å. Furthermore, the ring (O2, O3A, O2A, O3) is also coplanar and the displacement of Cu(II) from the ring plane is only 0.0025 Å. It can be seen that the two independent acetate groups form a good plane and the dihedral angle between the (O2, O3, O2A, O3A) and (O4, O5, O4A, O5A) rings is 84.3° (mean). The ring (O2, O3, O2A, O3A) and the pyridyl ring (N1–C5) are inclined at an angle of 1.8°. A highly organized self-assembly is achieved in the crystal chains of **2**, wherein the connectivity of two terminal coordinated bpodz forms a corrugated 1-D chain. The final wave-like polymeric chain results from the rigidity of bpodz. In the reported mononuclear complex [Cu(bpodz)$_2$(OAc)$_2$(H_2O)](H_2O)$_2$(CH_3OH), bpodz only acts as a mononuclear ligand;[20] moreover, the acetate groups do not serve as bridges. Obviously, if bridging ligands coordinate axially to dinuclear paddle-wheel units, polymeric structures can be obtained. Such structures have been reported with bridging pyrazine, *N,N'*-hexamethylenetetramine, 2-aminopyrimidine, and dioxane.[40–44]

{[Co(bpodz)(SO_4)(H_2O)$_3$](CH_3OH)$_2$}$_n$(3). The structural unit of polymer **3** is depicted in Fig. 5. Co(II) is octahedrally coordinated by two nitrogen atoms from bpodz and four oxygen atoms from three water molecules and one $SO_4{}^{2-}$ anion. The O6–Co1–O8 and O5–Co1–O7 bond angles are 179.87(18)° and 177.34(19)°, respectively. The O5–Co1–O6 and O7–Co1–O8 bond angles are 89.50(14)° and 91.3(2)°, respectively. Thus, the CoO_4 unit forms a quite ideal equatorial plane (the mean deviation from the plane is 0.0164 Å). Co1–O7 and Co1–O6 bond lengths (mean 2.082 Å) are shorter than the Co1–O5 and Co1–O8 bond lengths (mean 2.110 Å). The Co–N bond lengths are 2.167(4) and 2.182(4) Å, respectively. The pyridyl ring (N4A–C12A) is almost perpendicular to the equatorial plane to which it is attached, the dihedral angle being 87.1°. The dihedral angle between the pyridyl ring N4A–C12A and the oxadiazole ring O1A–C7A is 5.6°, indicating almost coplanarity. In addition, the N4A–C12A and N1–C5 rings in two bpodz are nearly parallel with a dihedral angle of 1.8°.

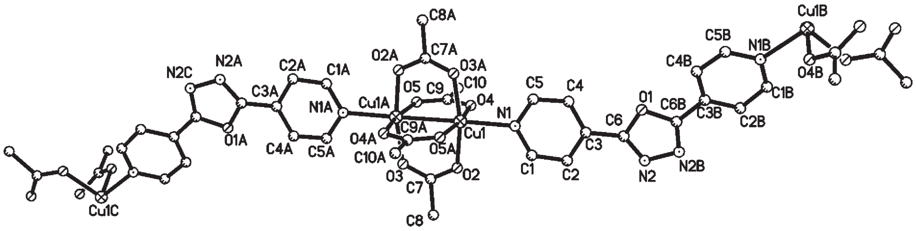

Fig. 4 ORTEP drawing of **2** with the atom numbering scheme, showing the molecular structure. Hydrogen atoms are omitted for clarity.

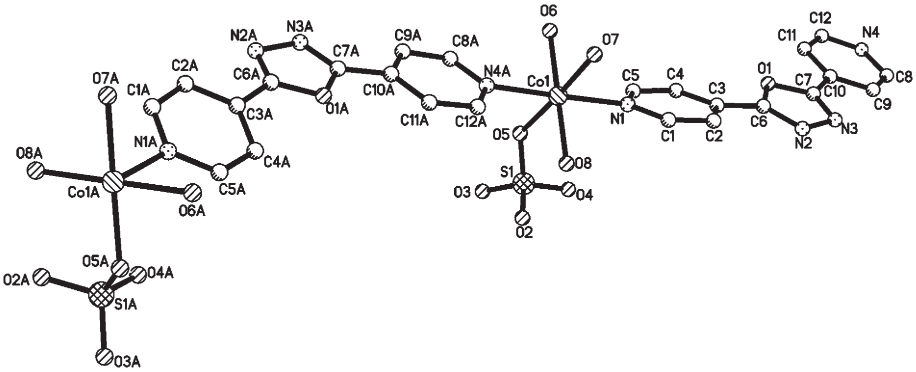

Fig. 5 ORTEP drawing of **3** with the atom numbering scheme. Hydrogen atoms are omitted for clarity.

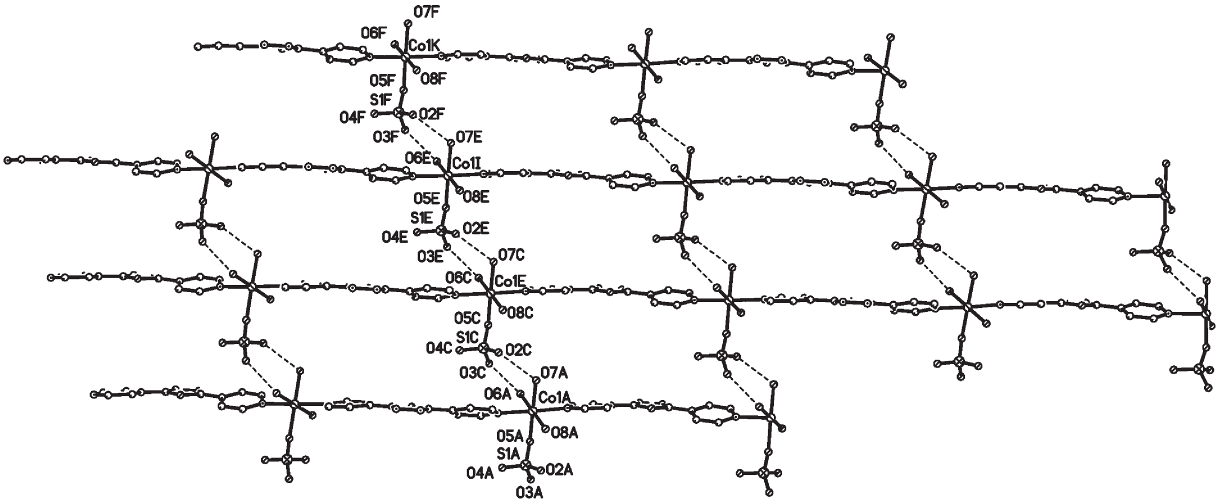

Fig. 6 The 2-D structure in **3** formed by hydrogen bonding. Hydrogen atoms are omitted for clarity.

In the solid state structure of **3**, infinite $\{[Co(bpodz)(SO_4)(H_2O)_3](CH_3OH)_2\}_n$ layers are formed by double hydrogen bonds (O–H···O). It can be seen from Fig. 6 that H atoms of coordinated water molecules from one chain interact with SO_4^{2-} units from adjacent chains, forming strong O–H···O hydrogen bonds (O7···O2 = 2.758 Å, O7–H7E···O2 = 173.19°; O6···O3 = 2.758 Å, O6–H6F···O3 = 170.94°). Through O–H···O hydrogen bonds, each $\{[Co(bpodz)(SO_4)(H_2O)_3](CH_3OH)_2\}_n$ chain joins neighboring chains to constitute the final 2-D layer structure.

$[Cd(bpodz)_2(\mu\text{-}I)_2]_n$ (4). The building block of polymer **4** is shown in Fig. 7. **4** crystallizes as infinite CdI_2 chains in which cadmium atoms are doubly bridged by pairs of iodine atoms; two bpodz complete the octahedral coordination of the cadmium atoms. The coordination geometry around the Cd(II) atom is a distorted octahedron with four iodine atoms arranged in a square-planar fashion and two pyridyl nitrogen atoms. The four iodine atoms can be separated into two kinds. The Cd–I bond length of the first kind is 2.912 Å, while the second Cd–I distance is 3.061 Å. Both of these are within the range of values for polymers in which cadmium atoms are bridged by iodine atoms [2.9(1) $Å_{mean}$; 2.741(1)–3.109(1) $Å_{range}$].[45] The Cd–N bond length of 2.433 Å is somewhat longer and approaches the upper limit of observed $Cd–N_{aromatic}$ values [2.36(6) $Å_{mean}$; 2.248(2)–2.448(6) $Å_{range}$].[46] The formation of CdI_2Cd connections between the units, rather than CdI_2 motifs, is consistent with the soft acid Cd(II) having a strong preference for the soft base I^-. However, it is unexpectedly interesting that bpodz only uses one terminal pyridyl group to coordinate to the Cd(II) atoms, while the other terminal pyridine group is uncoordinated. As a result, the structural units of polymer **4** are linked by two iodine atoms through the cadmium atoms to form novel infinite molecular chains. The chains are parallel and overlap (Fig. 8).

$[Mn(bpodz)_2(SCN)_2(H_2O)_2]$ (5). Single-crystal X-ray analysis revealed a new complex of Mn(II) ions. Coordination to the Mn(II) center in **5** is provided by the pyridine groups of two bpodz ligands and two N-linked isothiocyanate ions, resulting in an almost square-planar arrangement. The remaining coordination sites are completed by two water molecules, modifying the coordination geometry to an octahedral environment (Fig. 9). The Mn–O bond distances are 2.214(3) Å. The N_{py}–Mn and $N_{SCN}{}^-$–Mn distances are 2.345(3) and 2.142(3) Å, respectively, showing that SCN^- coordinates to copper much more strongly than does the pyridine nitrogen atom. The deviation of the manganese(II) ion from the best equatorial plane defined by the N1, N1A, N5, N5A atoms is 0 Å. In addition, the rigid bpodz has the expected angular geometry, and is monodentate ligand as well as that in polymer **4**. The N–C–S angles are 178.7(4)°. The C–N–Mn angles are 165.9(4)°.

Neighboring units are connected through O–H···N hydrogen bonds (Fig. 9) involving the oxygen atoms of coordinated water molecules and the nitrogen atoms of oxadiazole and pyridine (O2D···N2AA = 2.892 Å; O2D···N4AB = 2.795 Å). The resulting 2-D structure contains almost rectangular holes and shows a stair-like configuration (Fig. 10), in which bpodz form the steps while the hydrogen bonds are the rise of the stairs.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–5**[a]

1			
Ag(1)–N(4)#1	2.215(4)	Ag(1)–O(2)	2.515(5)
Ag(1)–N(1)	2.251(4)	N(1)–C(1)	1.327(6)
N(4)–Ag(1)#2	2.215(4)		
N(4)#1–Ag(1)–N(1)	140.06(15)	C(1)–N(1)–Ag(1)	121.1(3)
N(4)#1–Ag(1)–O(2)	130.07(14)	C(5)–N(1)–Ag(1)	120.9(3)
N(1)–Ag(1)–O(2)	87.83(14)	C(8)–N(4)–Ag(1)#2	119.5(3)
N(5)–O(2)–Ag(1)	104.1(3)	C(12)–N(4)–Ag(1)#2	123.0(3)
2			
Cu(1)–O(5)#1	1.954(6)	O(1)–C(6)	1.377(10)
Cu(1)–O(2)	1.955(6)	O(1)–C(6)#2	1.377(10)
Cu(1)–O(3)#1	1.958(7)	O(2)–C(7)	1.241(11)
Cu(1)–O(4)	1.975(6)	O(3)–C(7)	1.245(12)
Cu(1)–N(1)	2.202(7)	O(3)–Cu(1)#1	1.958(7)
Cu(1)–Cu(1)#1	2.623(2)	O(4)–C(9)	1.264(10)
O(5)–C(9)	1.253(10)	O(5)–Cu(1)#1	1.954(6)
O(6)–C(11)	1.81(4)		
O(5)#1–Cu(1)–O(2)	89.5(3)	O(5)#1–Cu(1)–Cu(1)#1	83.01(18)
O(5)#1–Cu(1)–O(3)#1	88.9(3)	O(2)–Cu(1)–Cu(1)#1	84.38(18)
O(2)–Cu(1)–O(3)#1	168.4(2)	O(3)#1–Cu(1)–Cu(1)#1	83.97(19)
O(5)#1–Cu(1)–O(4)	168.6(2)	O(4)–Cu(1)–Cu(1)#1	85.58(18)
O(2)–Cu(1)–O(4)	89.1(3)	N(1)–Cu(1)–Cu(1)#1	178.9(2)
O(3)#1–Cu(1)–O(4)	90.2(3)	C(6)–O(1)–C(6)#2	102.8(10)
O(5)#1–Cu(1)–N(1)	96.1(3)	C(7)–O(2)–Cu(1)	122.1(7)
O(2)–Cu(1)–N(1)	95.0(3)	C(7)–O(3)–Cu(1)#1	122.3(6)
O(3)#1–Cu(1)–N(1)	96.6(3)	C(9)–O(4)–Cu(1)	121.0(6)
O(4)–Cu(1)–N(1)	95.3(3)	C(9)–O(5)–Cu(1)#1	125.3(6
C(5)–N(1)–Cu(1)	122.6(7)	C(1)–N(1)–Cu(1)	120.4(6)
3			
Co(1)–O(7)	2.071(5)	Co(1)–O(6)	2.094(4)
Co(1)–O(5)	2.109(3)	Co(1)–O(8)	2.111(4)
Co(1)–N(1)	2.167(4)	Co(1)–N(4)#1	2.182(4)
S(1)–O(4)	1.458(4)	S(1)–O(3)	1.470(3)
S(1)–O(2)	1.481(4)	S(1)–O(5)	1.487(3)
O(7)–Co(1)–O(6)	88.6(2)	O(7)–Co(1)–O(5)	177.34(19)
O(6)–Co(1)–O(5)	89.50(14)	O(7)–Co(1)–O(8)	91.3(2)
O(6)–Co(1)–O(8)	179.87(18)	O(5)–Co(1)–O(8)	90.62(15)
O(7)–Co(1)–N(1)	89.18(18)	O(6)–Co(1)–N(1)	86.66(16)
O(5)–Co(1)–N(1)	92.55(13)	O(8)–Co(1)–N(1)	93.29(15)
O(7)–Co(1)–N(4)#1	88.97(18)	O(6)–Co(1)–N(4)#1	93.17(16)
O(5)–Co(1)–N(4)#1	89.30(14)	O(8)–Co(1)–N(4)#1	86.88(15)
N(1)–Co(1)–N(4)#1	178.15(14)	S(1)–O(5)–Co(1)	131.7(2)
C(5)–N(1)–Co(1)	122.8(3)	C(1)–N(1)–Co(1)	120.6(3)
C(8)–N(4)–Co(1)#2	121.0(3)	C(12)–N(4)–Co(1)#2	121.1(3)
4			
Cd(1)–N(1)#1)	2.433(9)	Cd(1)–N(1)	2.433(9)
Cd(1)–I(1)	2.9117(11)	Cd(1)–I(1)#1	2.9117(11)
Cd(1)–I(1)#2	3.0612(11)	Cd(1)–I(1)#3	3.0612(11)
I(1)–Cd(1)#4	3.0612(11)		
N(1)#1–Cd(1)–N(1)	180.000(4)	N(1)#1–Cd(1)–I(1)	92.6(2)
N(1)–Cd(1)–I(1)	87.4(2)	N(1)#1–Cd(1)–I(1)#1	87.4(2)
N(1)–Cd(1)–I(1)#1	92.6(2)	I(1)–Cd(1)–I(1)#1	180.0
N(1)#1–Cd(1)–I(1)#2	89.7(2)	N(1)–Cd(1)–I(1)#2	90.3(2)
I(1)–Cd(1)–I(1)#2	86.98(2)	I(1)#1–Cd(1)–I(1)#2	93.02(2)
N(1)#1–Cd(1)–I(1)#3	90.3(2)	N(1)–Cd(1)–I(1)#3	89.7(2)
I(1)–Cd(1)–I(1)#3	93.02(2)	I(1)#1–Cd(1)–I(1)#3	86.98(2)
I(1)#2–Cd(1)–I(1)#3	180.0	Cd(1)–I(1)–Cd(1)#4	86.98(2)
5			
Mn(1)–N(5)	2.142(3)	Mn(1)–N(5)#1	2.142(3)
Mn(1)–O(2)	2.214(3)	Mn(1)–O(2)#1	2.214(3)
Mn(1)–N(1)#1	2.345(3)	Mn(1)–N(1)	2.345(3)
N(5)–Mn(1)–N(5)#1	180.00(18)	N(5)–Mn(1)–O(2)	89.48(13)
N(5)#1–Mn(1)–O(2)	90.52(13)	N(5)–Mn(1)–O(2)#1	90.52(13)
O(2)–Mn(1)–O(2)#1	180.00(12)	N(5)#1–Mn(1)–O(2) #1	89.48(13)
N(5)–Mn(1)–N(1)#1	89.74(14)	N(5)#1–Mn(1)–N(1) #1	90.26(14)
O(2)–Mn(1)–N(1)#1	90.61(12)	O(2)#1–Mn(1)–N(1) #1	89.39(12)
N(5)–Mn(1)–N(1)	90.26(14)	N(5)#1–Mn(1)–N(1)	89.74(14)
O(2)–Mn(1)–N(1)	89.39(12)	O(2)#1–Mn(1)–N(1)	90.61(12)
N(1)#1–Mn(1)–N(1)	180.00(9)		

[a] Symmetry transformations used to generate equivalent atoms. For polymer **1**: #1 $x, y-1, z+1$; #2 $x, y+1, z-1$. For polymer **2**: #1 $-x+1/2, -y+3/2, -z$; #2 $-x, y, -z+1/2$. For polymer **3**: #1 $x+1/2, -y+1/2, z-1/2$; #2 $x-1/2, -y+1/2, z+1/2$. For polymer **4**: #1 $-x, -y+1, -z+1$; #2 $x-1, y, z$; #3 $-x+1, -y+1, -z+1$; #4 $x+1, y, z$. For complex **5**: #1 $-x, -y, -z$.

Magnetic properties

The magnetic susceptibility of polymer **2** was measured from 5 to 300 K. Fig. 11 shows a plot of $\chi_M T$ *versus* T. The value of $\chi_M T$ at 300 K is 0.754 cm^3 mol^{-1} K, which is smaller than that expected for two magnetically quasi-isolated spin doublets (*ca.* 0.8 cm^3 mol^{-1} K). The $\chi_M T$ value smoothly decreases to 0.0305 cm^3 mol^{-1} K at 5 K, indicating the occurrence of antiferromagnetic interactions between Cu ions.

It should be noted that polymer **2** exhibits two types of magnetic exchange interactions between two Cu(II) ions: one is through short bridges *via* the acetate groups and the other is through a long bridge *via* bpodz. Actually, because of the long organic bpodz fragment, the possibility of overlap of magnetic orbitals through the C and N atoms of bpodz is negligible.[20] Hence, the Cu(OAc)$_4$Cu paddle-wheel-type cage plays an important role in the magnetic properties of polymer **2**. For this type of structure the antiferromagnetic interaction is strong because unpaired electron density from both Cu ions is transferred to the same orbital of the bridging acetate. The solid curve in Fig. 11 is the best fit of the $\chi_M T$ data, assuming a dinuclear Cu(II) complex and applying the Bleaney–Bowers formula[47] ($H = -2JS_1S_2$). Magnetic parameters thus determined are $-2J = 320$ cm^{-1} and $g = 2.14$. The discrepancy factor $\sigma = [\Sigma(\chi_{\text{obs}} - \chi_{\text{calcd}})^2/\Sigma\chi_{\text{obs}}]^{1/2}$ in the least-squares fits was 2.3×10^{-4}, $\rho = 0.0025$. In contrast to the reported dinuclear copper(II) carboxylates, for example, Cu$_2$(C$_{10}$H$_9$O$_2$)$_4$-(C$_2$H$_5$OH)$_2$ ($-2J = 242$ cm^{-1}),[40a] [Cu(C$_7$H$_{15}$COO)$_2$]$_2$ ($-2J = 320$ cm^{-1}),[48] [Cu(C$_7$H$_{15}$COO)$_2$C$_2$H$_5$N]$_2$ ($-2J = 344$ cm^{-1})[48] and [Cu(C$_7$H$_{15}$COO)$_2$C$_6$H$_7$N]$_2$ ($-2J = 300$ cm^{-1}),[48] polymer **2** ($-2J = 320$ cm^{-1}) shows a considerably strong antiferromagnetic interaction. It is well-known that for the exchange interaction in these molecules a superexchange mechanism, rather than a direct metal-metal interaction, is an important factor, in which the electronic structure of the bridging O–C–O moiety determines the magnitude of the antiferromagnetic interaction.[40a] In the case of polymer **2**, the dihedral angle between Cu–O–O–Cu and the carboxyl moiety is only 1.3°, which would lead to a increase in $-2J$ due to increased overlap of the Cu d$_{x}2_{-y}2$ and the 2p$_x$ carboxylate oxygen orbitals in the symmetric HOMO.[49] This is a quite reasonable explanation.

Because Ag(I) and Cd(II) have no unpaired electrons, polymers **1** and **4** are expected to be diamagnetic. Polymer **3** shows negligible magnetic properties as well as {[Cu(bpodz)$_2$-(H$_2$O)$_2$](ClO$_4$)(OH)(H$_2$O)$_{2.5}$}$_n$ due to the long bpodz bridge.[20] Complex **5**, considering its hydrogen bonding interactions and the monodentate bpodz ligand between neighboring Mn(II) atoms, also exhibits very weak magnetic interactions.

Conclusion

A 2-D polymer [Ag(bpodz)(μ-NO$_3$)]$_n$ containing ladder-like chains, a 1-D wave-like polymer {[Cu$_2$(bpodz)(μ-OAc)$_4$]-(CH$_3$OH)$_2$}$_n$, a 2-D polymer {[Co(bpodz)(SO$_4$)(H$_2$O)$_3$]-(CH$_3$OH)$_2$}$_n$, a 1-D linear polymer [Cd(bpodz)$_2$(μ-I)$_2$]$_n$ and a complex [Mn(bpodz)$_2$(SCN)$_2$(H$_2$O)$_2$] have been synthesized and structurally characterized by X-ray diffraction analyses. Magnetic susceptibility data for polymer {[Cu$_2$(bpodz)(μ-OAc)$_4$](CH$_3$OH)$_2$}$_n$ show strong antiferromagnetic coupling. These data were fitted to the appropriate equations derived from the Hamiltonian $H = -2JS_1S_2$, giving the parameter $-2J = 320$ cm^{-1}.

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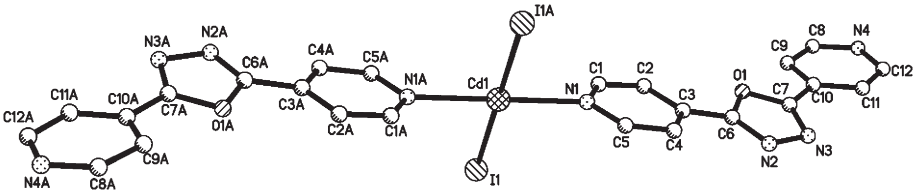

Fig. 7 ORTEP drawing of **4** with the atom numbering scheme. Hydrogen atoms are omitted for clarity.

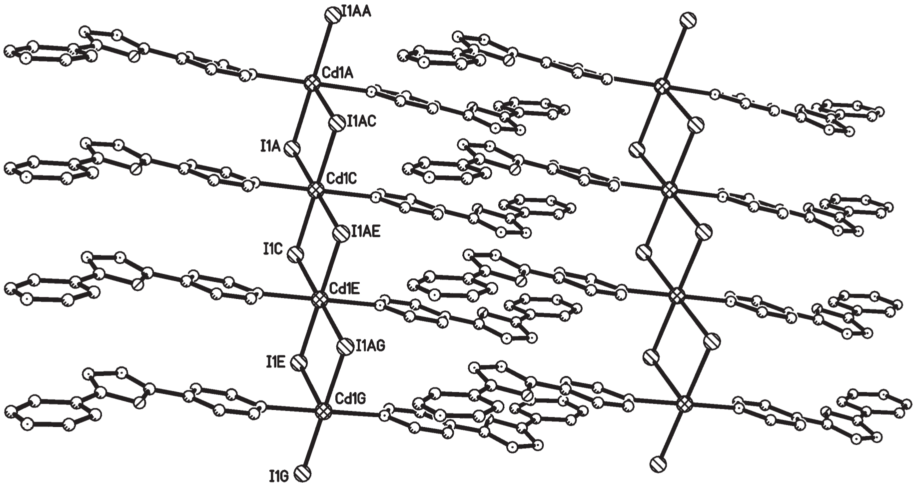

Fig. 8 A view of two adjacent units of polymer **4** showing the Cd(μ-I)$_2$Cd interactions.

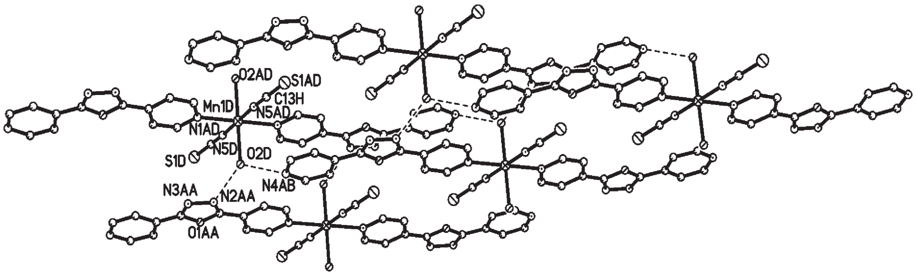

Fig. 9 The 2-D structure in **5** formed by hydrogen bonding. Hydrogen atoms are omitted for clarity.

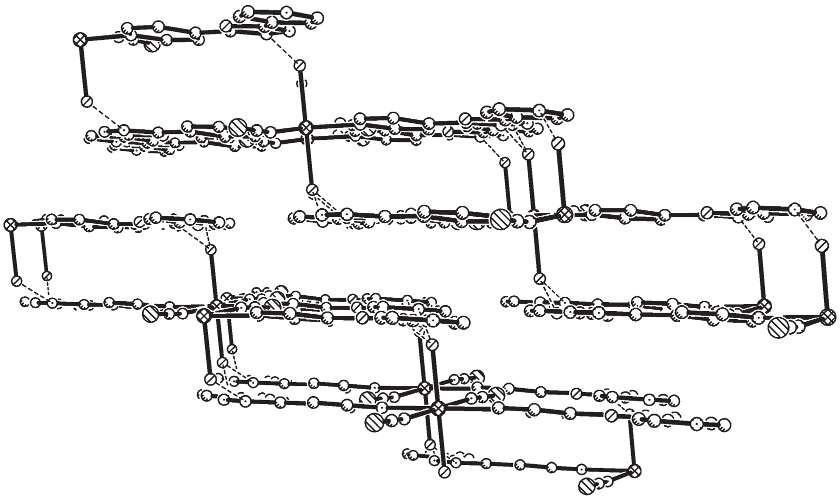

Fig. 10 The rectangular holes in complex **5**.

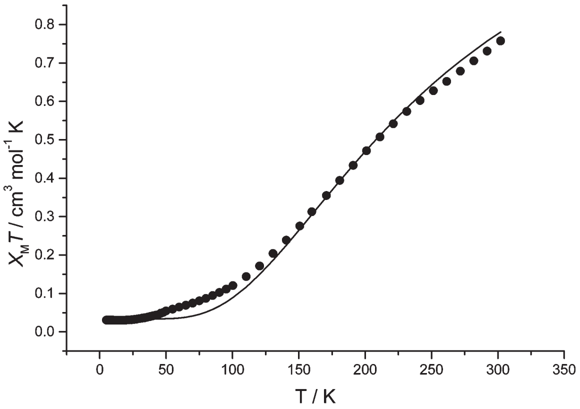

Fig. 11 Plot of $\chi_M T$ *vs.* T for **2**. The solid line is the theoretical curve obtained with $g = 2.14$ and $-2J = 320$ cm^{-1}.

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