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Coordination polymers of transition metal ions with polydentate imine ligands. Syntheses, materials characterization, and crystal structures of polymeric complexes of copper(I), silver(I) and zinc(II)

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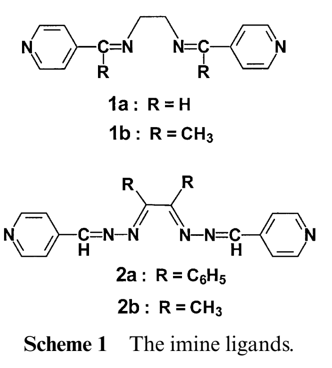
Received 21st September 2001, Accepted 5th February 2002
First published as an Advance Article on the web 26th February 2002

A series of new multidentate imine building blocks [$NC_5H_4(R)C{=}NCH_2CH_2N{=}C(R)C_5H_4N$ (R = H **1a**, R = Me **1b**) and $NC_5H_4CH{=}N{-}N{=}C(R){-}C(R){=}N{-}N{=}CHC_5H_4N$ (R = Ph **2a**, R = Me **2b**)] have been synthesized, aiming at the formulation of extended coordination polymers with various transition metal ions. Formation of the corresponding metal–ligand complexes has been monitored and characterized by chemical and spectroscopic techniques. X-Ray diffraction analysis of the available single crystals revealed diverse polymeric patterns of the hybrid organic–inorganic supramolecular systems. Complexation of Cu(I) with **1a** and **2a** yielded one-dimensional and two-dimensional polymers, respectively, with tetrahedral geometry around the metal centers. Similar reactions of Ag(I) with **1b** and with **2a** led to three-dimensional and two-dimensional arrays, respectively. The former contains silver ions with tetrahedral as well as square-planar coordination environments, while in the latter case the metal species bind to the ligands in a tetrahedral manner. Related syntheses of coordination compounds between **2a** and bivalent metal ions produced 1-D polymers with Cd(II) and 2-D polymeric networks with Zn(II), Co(II) and Mn(II).

Introduction

Construction of transition metal complexes with specific network topologies is one of the frontier areas of current research[1,2] because such complexes mimic zeolites[3,4] or other types of microporous solids,[5,6] and they afford functional materials with potentially controllable properties. These materials are used in molecular recognition and host–guest chemistry, catalytic applications, as well as optical, magnetic and electronic devices.[7] Tailored derivatives of 4,4′-bipyridyl ligands with various spacers between the bipyridyl functions are attractive molecular building blocks to this end, because they are very effective in the formation of diverse architectures such as one-dimensional chains,[8] and ladders,[9] two-dimensional grids[10] and three-dimensional dimantoids[11] with the metal ion connectors. These species can be either rigid or flexible, and the spacer's length between the two pyridyl rings can be varied readily. Their significance in the construction of hybrid organic–inorganic coordination polymers with interesting features has been demonstrated in a series of recent reports.[12–15] In this work we focus on a series of new 4,4′-bipyridyl-type organic ligands with added metal coordination functionality along the molecular backbone (Scheme 1), and demonstrate their assembly into diverse polymeric arrays with the aid of Cu(I), Ag(I) and Zn(II) (as well as other) metal ion auxiliaries. Detailed crystallographic characterization of the free ligands as well as of the extended polymeric arrays they form is also reported.



Scheme 1 The imine ligands.

Results and discussion

Synthesis and materials' characterization

Organic ligands containing unsaturated nitrogen atoms can be regarded as soft Lewis bases.[16] As such they may reveal high tendency to form stable coordination complexes with numerous transition metal ions, particularly those that can be regarded as soft Lewis acids [*e.g.*, Cu(I) and Ag(I)].[16] The poly-imine ligands **1a**, **1b**, **2a** and **2b** were chosen as suitable building blocks to this end (Scheme 1). The two former compounds are flexible about the central C–C bond, while the molecular framework of ligands **2a** and **2b** is more rigid. Each of these ligands contains four potential sites for coordination to metal ions, the peripheral pyridyl-N as well as the inner imino N-atoms. The latter can be active only if the relative disposition of the two halves of **1** and **2** with respect to the central C–C bond in them is *cis*.

The ligands **1a**[17,18] and **1b** are synthesized by condensing ethylenediamine (en) with 4-pyridinecarboxaldehyde or 4-acetylpyridine in anhydrous methanol. The Cu(I) complex of **1a**, [Cu(**1a**)(CH_3CN)]ClO_4 (**3**) has been prepared by reacting the ligand with [$Cu(CH_3CN)_4$]ClO_4 in anhydrous methanol under argon atmosphere in a 1 : 1 ligand to metal ratio. Complex **3** (yellow–orange) is stable in air in the solid state for 2–3 weeks. However, its stability in open solutions is solvent dependent; thus *e.g.*, **3** reveals considerably higher stability in CH_3CN (for approximately 6 h; after that the yellow–orange solution turns green) than in DMF (~1 h). Reaction of **1b** with $AgClO_4$ leads to the formation of [Ag(**1b**)](ClO_4)·$2H_2O$ (**4**). This material is stable in air in the solid state for 1–2 weeks, but it is

DOI: 10.1039/b108616b

light-sensitive and on prolonged standing in air it turns black. It is also stable in acetonitrile for about 6 h. The water composition of **4** was confirmed by thermogravimetric analysis. It shows weight loss of 6.80% (calcd. 7.06%) approximately at 60 °C, which represents the loss of two uncoordinated molecules of water.

Ligands **2a** and **2b** are the 1 : 2 condensates of benzil dihydrazone or diacetyl dihydrazone with 4-pyridinecarboxaldehyde. The polymeric complexes $[Cu(\mathbf{2a})_2]ClO_4{\cdot}2CH_3CN{\cdot}1/2C_2H_5OC_2H_5$ (**5**), $[Ag(\mathbf{2a})_2]ClO_4{\cdot}2CH_3CN{\cdot}C_6H_5CH_3$ (**6**) and $[Zn(\mathbf{2a})_2(CH_3CN)_2](ClO_4)_2{\cdot}2CH_3CN{\cdot}C_2H_5OC_2H_5$ (**7**) were obtained (as acetonitrile–diethyl ether and acetonitrile–toluene solvates) by the reaction of Cu(I), Ag(I) and Zn(II) salts with **2a** in metal to ligand molar ratio of either 1 : 1 or 2 : 1. Similar crystalline complexes of Co(II) and Mn(II) with **2a**, $[Co(\mathbf{2a})_2(H_2O)_2](ClO_4)_2{\cdot}CH_3OH{\cdot}H_2O$ (**8**), $[Mn(\mathbf{2a})_2(CH_3CN)_2](PF_6)_2$ (**9**) could be also prepared, although they showed lesser crystallinity. As opposed to the *bis*-complexes described above, reaction of $Cd(ClO_4)_2$ with **2a** gives a 1 : 1 metal–ligand complex, $[Cd(\mathbf{2a})(CH_3CN)_2(H_2O)_2](ClO_4)_2$ (**10**). As in the previous examples referred to above, the polymeric complexes **5**–**10** are more stable in the solid state than in solutions.

The complexation process has been monitored by IR and by UV/Vis absorption spectroscopy. The absorption spectra of **1a** and **1b** in methanol show charge transfer bands at 235 nm and 230 nm with intensities of $\varepsilon(dm^3mol^{-1}cm^{-1})$ 27300 and 22700, respectively. In complexes **3** and **4**, these intra-ligand charge-transfer bands appear at slightly shifted wavelengths, 228 nm and 226 nm, respectively. Ligands **2a** and **2b** also show charge transfer absorptions at 305 nm ($\varepsilon/dm^3mol^{-1}cm^{-1}$ 41400) and 290 nm ($\varepsilon/dm^3mol^{-1}cm^{-1}$ 32500). As before, these bands are shifted by 5–15 nm in the metal complexes of **2a**. Furthermore, in the IR spectra of **1a** and **1b** the C=N stretching frequencies appear at 1648 cm^{-1} and 1642 cm^{-1}; in **2a** and **2b** these frequencies appear with slightly lower energies at 1618 cm^{-1} and 1612 cm^{-1}. On the other hand, ν(C=N) signals in complexes **3** and **4** appear at 1633 cm^{-1} and 1635 cm^{-1}, at somewhat lower energies than in the free ligands. Lowering of the C=N stretching frequencies by 8–14 cm^{-1} is detected also in the various metal complexes **5**–**10** in relation to those observed for **2a**. These variations on moving from the free ligands to their metal complexes should presumably be attributed to π back bonding between the metal and the ligand moieties.

Structural description

The structures of the ligands **1a**, **1b**, **2a**, and of their coordination polymers **3**–**7** have been determined precisely by X-ray crystallography (Table 1). Very fast deterioration of, and severe structural disorder in, crystals **8**–**10** allowed derivation of approximate structural models for these compounds only. No single crystals of adequate quality could be obtained for **2b** or for its complexes with transition metal ions.

Fig. 1a shows the molecular structure of the free ligand **1a**. It is characterized by an extended conformation with an *anti* conformation about the central C–C bond (in the crystal **1a** is located on the center of inversion and the N–C–C–N torsion angle is 180°). Identical symmetry and conformational features characterize the dimethyl derivative **1b** (Fig. 1b). The two pyridyl nitrogens are excellent coordination sites to transition metal ions. In addition, upon an induced *anti* ⟶ *syn* transformation about the central C–C bond, the two inner N-atoms are placed on the same side of the molecular backbone and may form another effective (bi-dentate) binding site. This phenomenon is illustrated nicely in the crystal structure of **3** $\{[Cu(\mathbf{1a})(CH_3CN)]ClO_4\}$, formed in a reaction of **1a** with the tetrahedral $[Cu(CH_3CN)_4]ClO_4$ complex (Fig. 2).

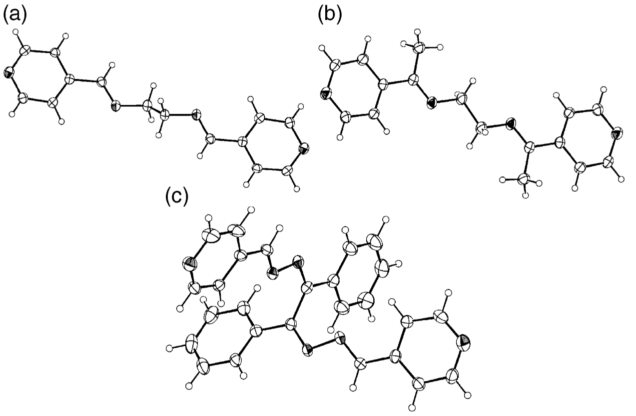


Fig. 1 Molecular structures of the free ligands (a) **1a**, (b) **1b** and (c) **2a**. The nitrogen atoms are marked by darkened ellipsoids. The N–C–C–N torsion angles about the central C–C bond are 180, 180 and 100.3° in **1a**, **1b**, and **2a**, respectively. Ellipsoids (darkened for the N-atoms) are shown at the 50% probability level at 110 K.

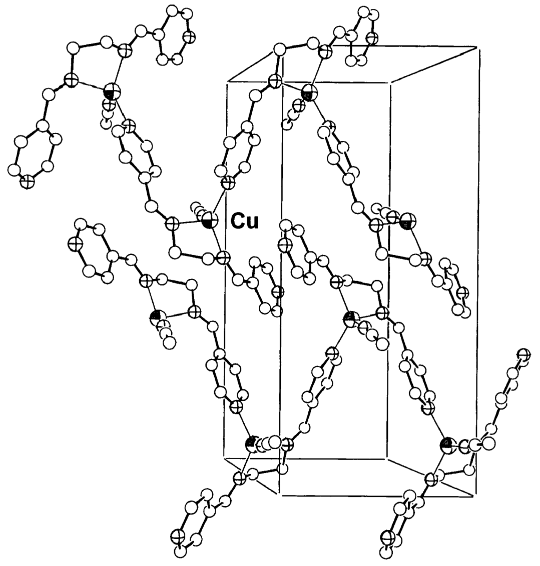


Fig. 2 Crystal structure of the 1-D polymer **3**, viewed approximately down the *a*-axis of the crystal (*c* is horizontal and *b* is vertical). Relative disposition of two neighboring polymeric entities is shown. In this and the following figures of the metal complexes all the N-sites are marked by crossed circles, while the metal ion is denoted by darkened circles.

Here, in order to optimize the coordination scheme, the ligand molecule adopts a converging *syn* structure with a N–C–C–N torsion angle of 56.9(2)°. Every copper(I) ion in this structure coordinates simultaneously to two imino nitrogen atoms of one ligand and to a pyridyl N-site of another **1a** species. The coordination sphere around the metal ion is supplemented by a molecule of acetonitrile, and is characterized by a distorted tetrahedral geometry. The corresponding coordination distances are Cu–N(acetonitrile) 1.945(2) Å, Cu–N(pyridyl) 2.043(2) Å, and Cu–N(imine) 2.052(2) and 2.122(2) Å. The N–Cu–N angles vary from 84.87(6)° to 124.48(7)°, the lower value involving the two converging imino nitrogens. The second pyridyl group of the ligand species remains uncoordinated. The above coordination scheme yields one-dimensional polymeric chains of the hybrid organometallic entity, which has a zig-zag shape. Side packing of these arrays in the crystal is stabilized by van der Waals forces, including π-stacking between the aryl fragments of adjacent chains. The large distance between the Cu(I) ions in this structure precludes any direct interaction between them.

Reaction of **1b** with silver perchlorate leads, however, to the formation of a more complexed three-dimensional coordination polymer **4** $\{[Ag(\mathbf{1b})](ClO_4)\}$ which crystallized as a dihydrate. The Ag-reactant lacks a robust coordination shell of its own, and readily interacts with the N-sites provided by the organic ligand. In the crystal structure of this material (Fig. 3)

Table 1 Crystal and experimental data

	1a[a]	**1b**[a]	**2a**	**3**	**4**[b c]	**5**	**6**	**7**
Empirical formula	$C_{14}H_{14}N_4$	$C_{16}H_{18}N_4$	$C_{26}H_{20}N_6$	$C_{16}H_{17}N_5$-$CuClO_4$	$C_{16}H_{22}N_4$-$AgClO_6$	$C_{58}H_{51}N_{14}$-$CuClO_{4\ 1/2}$	$C_{63}H_{54}N_{14}$-$AgClO_4$	$C_{64}H_{62}N_{16}$-$ZnCl_2O_9$
Formula weight	238.29	266.34	416.48	442.34	509.70	1115.12	1214.52	1335.57
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$Pnn2$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	5.9900(3)	7.3740(5)	9.5290(5)	9.8940(10)	11.5400(5)	13.6180(7)	12.6820(3)	10.2480(2)
b/Å	7.0300(3)	10.9250(9)	11.2180(7)	21.3850(4)	11.5400(7)	21.5640(9)	12.8320(3)	21.2640(4)
c/Å	7.8110(4)	8.9120(9)	11.4780(6)	9.2910(2)	14.9430(5)	18.8540(10)	21.3680(5)	30.5870(7)
α/°	100.901(2)	90.0	76.320(4)	90.0	90.0	90.0	75.006(1)	90.0
β/°	99.006(2)	110.490(3)	85.512(4)	112.235(1)	90.0	92.419(2)	73.078(1)	92.371(1)
γ/°	106.180(2)	90.0	67.003(3)	90.0	90.0	90.0	64.3650(1)	90.0
V/Å^3	302.46(3)	672.54(10)	1097.3(1)	1819.64(6)	1989.98(16)	5531.7(5)	2963.55(12)	6659.6(2)
Z	1	2	2	4	4	4	2	4
D_c/g cm^{-3}	1.308	1.315	1.261	1.615	1.701	1.339	1.361	1.332
2θ range/°	3–55	3–55	2–55	2–56	2–56	2–51	2–56	2–56
No. unique reflections	1266	1419	4562	4294	2438	9806	12725	14007
No. refined parameters	82	92	289	245	256	699	757	896
$R1$ ($I > 2\sigma$)	0.050	0.066	0.079	0.035	0.042	0.088	0.047	0.073
$wR2$ (all data)	0.147	0.188	0.193	0.087	0.109	0.248	0.131	0.202
$\lvert\Delta\rho\rvert_{max}$ e Å^{-3}	0.32	0.30	0.33	0.47	0.88	0.84	1.22	0.78

[a] Molecules are located on centers of inversion. [b] Orthorhombic rather than tetragonal symmetry was indicated unequivocally by intensity distribution in the diffraction pattern, and later confirmed by the structure determination. [c] Molecules are located on twofold rotation axes.

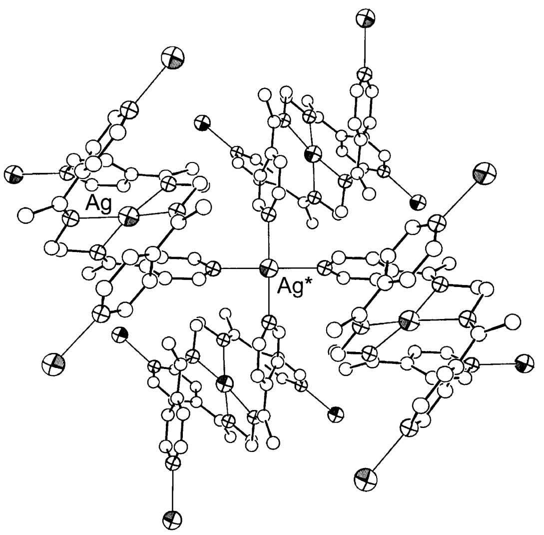


Fig. 3 Coordination geometry of the the two silver ions in polymer **4**. Ag has a distorted tetrahedral environment, while Ag* has a square-planar neighborhood, giving rise to a 3-D polymer. The perchlorate anions and solvent molecules are omitted for clarity. The peripheral pyridyl groups are coordinated in the crystal structure to the Ag*-silver ions of adjacent units (as shown), thus creating continuous three-dimensional arrays.

two different coordination environments of the Ag atom are observed. One ion coordinates the pyridyl rings of four neighboring ligands, forming a four-coordinate square planar structure. Another ion has a distorted tetrahedral environment by binding to the four imino nitrogens of two different ligands. The Ag–N distances within the latter are 2.325(6) and 2.337(6) Å, while the N–Ag–N angles (involving a given ligand) are 75.3(2)°. To facilitate this interaction the organic ligand adopts a *syn* conformation about the central C–C bond [the inner N–C–C–N torsion angle is 57.0(9)°], and two such molecules converge on the metal ion in a staggered fashion. Within the square-planar assembly the Ag–N distances are 2.382(6) and 2.386(6) Å and N–Ag–N angles are 91.9(2) and 92.0(2)°. The resulting molecular organization is pseudo-tetragonal, with the two silver ions located on twofold rotation axes that extend parallel to the *c*-axis of the crystal. The perchlorate anion and two molecules of water are located in interstitial voids formed in this polymeric structure. As in the previous example, the metal ions are surrounded by the organic ligand and do not interact with one another.

In the crystal structure of free **2a** (Fig. 1c), the torsion angles about the central carbon–carbon bond are N=C–C=N 100.3(4)° and C–C–C–C 97.2(4)°. This pseudo-*syn* conformation is consistently preserved in its complexes with metal ions as well (see below), and represents the preferred structural feature (as opposed to the alternative extended *trans* conformation) of this ligand in the crystalline phase. The four individual substituent groups branching off the central C–C bond have delocalized π electrons and are planar, and may play an important role in directing by π–π stacking the intermolecular organization in crystals. Moreover, it has been anticipated that the imino nitrogens in this system will not take part in metal ion coordination due to the steric hindrance introduced to the central part of the ligand by the phenyl groups. The reaction of **2a** with $[Cu(CH_3CN)_4]ClO_4$ to yield the coordination polymer **5** {$[Cu($**2a**$)_2]ClO_4$} provides a suitable example. In fact, compound **5** represents an infinite 2-D square-type grid polymer sustained by coordination of Cu(I) to the pyridyl sites of the ligand (Fig. 4). Every metal ion is coordinated to four ligands in this way, and the coordination geometry around it resembles roughly a regular tetrahedron. The Cu–N(pyridyl) coordination distances are within the range of 2.002(6)–2.080(6) Å; the respective N–Cu–N vary between 99.3(2)° and 125.2(2)°. In the crystal (formed as an acetonitrile–diethyl ether solvate), adjacent polymeric arrays are related to each other by inversion and are held together by van der Waals forces. The perchlorate counter ions, as well as the partly disordered solvent molecules of diethyl ether and acetonitrile are trapped between them. The ligand conformation around the central bond in **5** is nearly the same as in the free ligand, the corresponding N=C–C=N and C–C–C–C torsion angles in the two crystallographically independent ligand species lying within 93.2(7)–98.2(8)°.

The reaction of **2a** with $AgClO_4$ leads to a coordination polymer **6** {$[Ag($**2a**$)_2]ClO_4$} with similar features. This includes the formation of two-dimensional polymeric networks sustained by the coordination of the silver ion auxiliary to four surrounding ligand moieties in a tetrahedral manner (Fig. 5a). The larger size of the metal ion is reflected in this case in longer metal–ligand bonds and smaller coordination angles. Thus, the

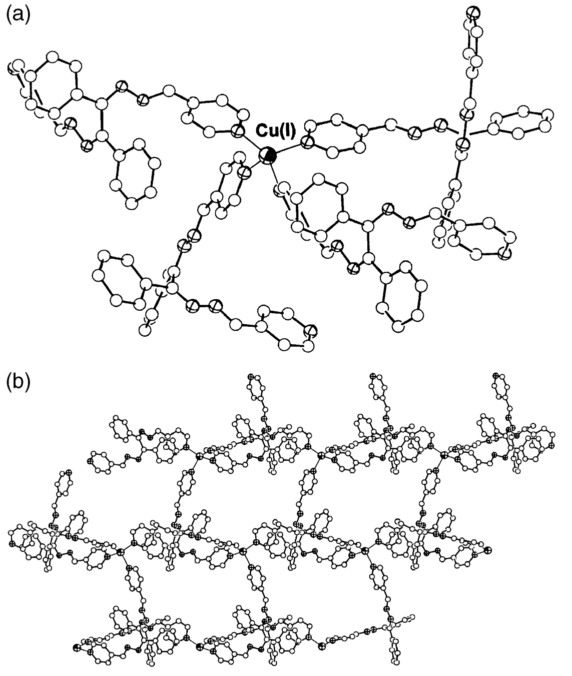


Fig. 4 Coordination polymer **5**. (a) Tetrahedral coordination around the Cu(I) bridging auxiliary. (b) Illustration of the 2-D square-grid-type array that forms involving all pyridyl sites of the ligand. The intermolecular voids are occupied by the perchlorate anions and solvent molecules.

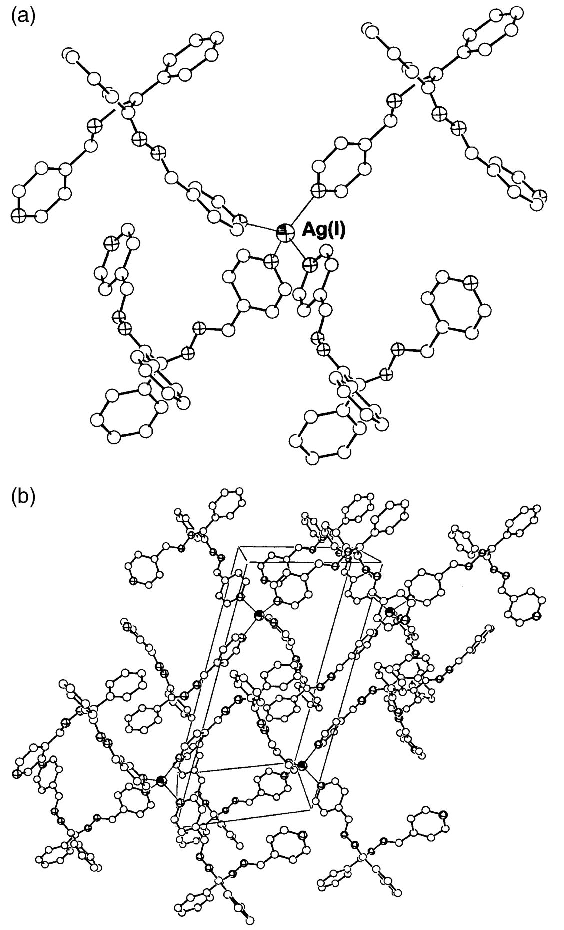


Fig. 5 Coordination polymer **6**. (a) Tetrahedral coordination environment around the Ag(I) metal ion. (b) Crystal packing of the 2-D polymeric arrays viewed approximately down the *b*-axis of the crystal (*a* is horizontal and *c* is roughly vertical). Two inversion-related layers extending perpendicular to the *c* axis, that interact with one another by van der Waals forces and π–π stacking between neighboring phenyl groups are shown. Anions and solvent molecules are omitted for clarity.

Ag–N(pyridyl) coordination distances vary within 2.268(2)–2.362(2) Å, while the respective N–Ag–N range from 83.1(3)° to 90.3(3)°. Fig. 5b illustrates the 2-D networks that form in **6**. All 2 : 1 ligand–metal ion units involved in them are related by pure lattice translations. In the crystal, every such polymeric 2-D array is approached from above and below by similar arrays related by inversion, entrapping in between the perchlorate anion along with molecules of acetonitrile and toluene as a solvate.

Another interesting variant of this system involves the Zn(II) complex with **2a** {**7**; [Zn(**2a**)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$}. The zinc ion has high propensity for forming either four-coordinate tetrahedral or five-coordinate square-pyramidal complexes with organic ligands. Yet, somewhat surprisingly, it is characterized in **7** by an octahedral coordination environment. Thus, as shown in Fig. 6, the Zn(II) ion coordinates in this structure to four equatorial pyridyl donors and two axial acetonitrile ligands. The Zn–N(py) coordination distances are 2.124, 2.150, 2.172 and 2.203(3) Å, while those of Zn–N(acetonitrile) are 2.212 and 2.245(4) Å. All the N–Zn–N coordination angles correspond to a nearly ideal octahedral geometry, and the N=C–C=N and C–C–C–C torsion angles about the central bond are preserved within 85.9(5)–93.1(5)°. Due to this twisting of the ligand the resulting structure consists of two-dimensional arrays of interconnected species, which are aligned parallel to the *ab*-plane of the crystal. The zinc ions lie in the center of such layers. In the surrounding ligands the pyridyl ends turn inward, while the phenyl substituents turn outward and are in contact with the neighboring layers.

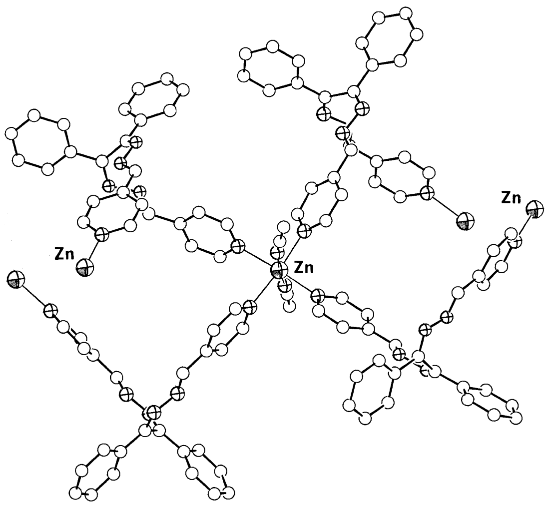
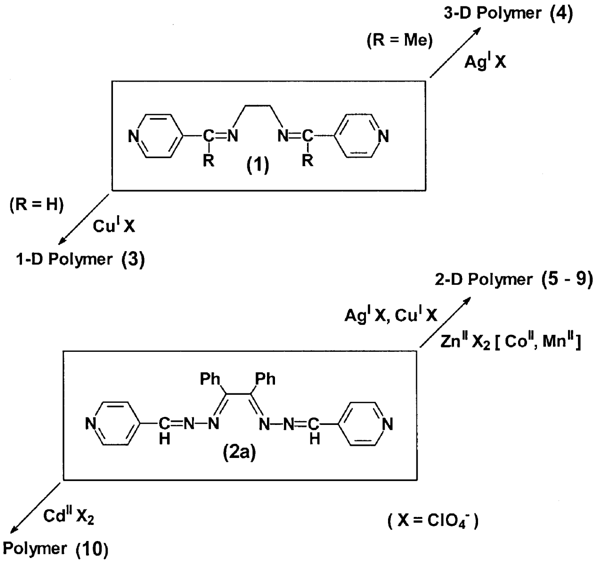


Fig. 6 Octahedral coordination around the Zn(II) ion in coordination polymer **7**, with square-planar coordination of the pyridyls and axial coordination of two acetonitrile ligands. The peripheral pyridyl groups are coordinated in the crystal structure to the zinc ions of adjacent units (as shown), thus creating continuous two-dimensional arrays (as in **5** and **6**) aligned parallel to the *ab* plane of the crystal.

Isomorphous coordination polymerization has been observed in the 2 : 1 complexes formed between **2a** and Co(ClO$_4$)$_2$·6H$_2$O {**8**; [Co(**2a**)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$} and with the hexafluorophosphate salt of Mn(II) {**9**; [Mn(**2a**)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$}, the detailed structure of which could not be precisely determined. As in **7**, the coordination environment around the cobalt (with two external axial molecules of water) and manganese (with two axial acetonirile ligands) is octahedral, and the coordination polymers formed have an extended double chain structure. On the other hand, reaction of **2a** with cadmium perchlorate yielded a 1 : 1 one-dimensional zig-zag shaped polymeric array {**10**; [Cd(**2a**)(CH$_3$CN)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$} similar to those observed in **3**. The coordination sphere of the cadmium ions remains octahedral. Yet, in this case, only two *cis*-related sites are occupied by pyridyl rings of two different **2a** ligands. The octahedral environment around the metal is completed by other ligating species, two molecules of acetonitrile and two molecules of water. Structures **8**–**10** contain also considerable amounts of disordered crystallization solvent.

This study demonstrates the versatile modes by which organic ligands and metal ion auxiliaries can self-assemble into robust hybrid organic–inorganic arrays (Scheme 2). It illustrates also several facile synthetic procedures that can be utilized in the supramolecular construction of such coordination polymers. We are currently screening the reaction and crystallization conditions in these as well as in similar systems in order to be able in the feature to *a priori* target the formulation of a desired polymer type.



Scheme 2 Composition of the coordination polymers **3**–**10**: [Cu(**1a**)(MeCN)]ClO_4 **3**; [Ag(**1b**)]ClO_4 **4**; [Cu(**2a**)$_2$]ClO_4 **5**; [Ag(**2a**)$_2$]ClO_4 **6**; [Zn(**2a**)$_2$(MeCN)$_2$]$(ClO_4)_2$ **7**; [Co(**2a**)$_2$(H_2O)$_2$]$(ClO_4)_2$ **8**; [Mn(**2a**)$_2$(MeCN)$_2$]$(PF_6)_2$ **9**; [Cd(**2a**)(MeCN)$_2$(H_2O)$_2$]$(ClO_4)_2$ **10**. Crystals of the above compounds (with the exception of **3**) contain additional molecules of crystallization solvent (see Experimental).

Experimental

General

The complex $[Cu(CH_3CN)_4]ClO_4$ was synthesized by a reported procedure.[19] All other reagents were procured commercially. Microanalyses were performed by a Perkin–Elmer 2400II elemental analyzer and CE instrument model no. EA110. Copper was estimated gravimetrically as CuSCN. The melting point was determined by an electro-thermal IA9000 series digital melting point apparatus and is uncorrected. IR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV–VIS spectra on a Shimadzu UV-160A spectrophotometer, ^1H and ^{13}C NMR spectra by a Brucker DPX200 spectrometer and EI (electron impact) mass spectra on a VG Autospec M-250 instrument. Thermogravimetric and differential analyses were taken on TA Instruments module SDT 2960 under argon atmosphere up to 100 °C with a heating rate of 5 °C min^{-1}.

Syntheses

1a. 1 ml (15 mmol) of distilled ethylenediamine and 2.86 (30 mmol) of freshly distilled 4-pyridinecarboxaldehyde were refluxed in 50 ml of anhydrous methanol for 6h. On evaporating the solvent a slight yellow semi-solid was obtained which on re-crystallization from *n*-hexane gave colorless needles suitable for X-ray analysis. Yield, 2.18 g (61%); mp 125–128 °C. Anal. found (calc. for $C_{14}H_{14}N_4$): C, 70.43 (70.56%); H, 5.76 (5.92%); N, 23.62 (23.52%). EI–MS: *m*/*z* 238.1 (M^+, 40%), 119.1 ($M^+/2$, 95%). FTIR/cm^{-1} (KBr): 1648vs (C=N). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.66 (d, J = 4 Hz, 4 H), 8.25 (s, 2 H), 7.53 (d, J = 4 Hz, 4 H), 4.03 (s, methylene, 4 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 160.84, 150.42, 142.63, 121.83, 61.27. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (CH_3OH): 235 (27 300).

1b. This ligand was prepared by a procedure exactly the same as that for **1a** by starting with 1 ml (15 mmol) of distilled ethylenediamine and 3.32ml (30 mmol) of freshly distilled 4-acetylpyridine to obtain colorless microcrystals. Yield, 2.30 g (58%); mp 173–175 °C. Anal. found (calc. for $C_{16}H_{18}N_4$): C, 72.29 (72.14%); H, 6.92 (6.82%); N, 20.97 (21.04%). EI–MS: *m*/*z* 267.1 (MH^+, 90%), 237.1 (MH^+ − $2CH_3$, 12%). FTIR/cm^{-1} (KBr): 1642vs (C=N). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.64 (d, J = 4 Hz, 4 H), 7.60 (d, J = 4 Hz, 4 H), 3.94 (s, methylene, 4 H), 2.28 (s, methyl, 6 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 164.54, 150.14, 147.74, 121.19, 53.35, 15.66. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 230 (22 700).

[Cu(1a)(CH_3CN)]ClO_4 (3). Solid $[Cu(CH_3CN)_4]ClO_4$ (0.33 g, 1 mmol) was added to 30 ml anhydrous degassed methanol solution of 0.24 g (1 mmol) of **1a** under argon atmosphere and stirred for 3h maintaining dry conditions. The orange yellow compound was precipitated out, filtered off, washed with 2 ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.22 g (50%). Single crystals were grown by direct diffusion of toluene into a moderately concentrated acetonitrile solution of the complex. Anal. found (calc. for $C_{16}H_{17}N_5CuClO_4$): C, 43.27 (43.42%); H, 3.92 (3.88%); N, 15.82 (15.83%); Cu, 14.30 (14.37%). FTIR/cm^{-1} (KBr): 1633vs (C=N); 1100vs, 1085vs, 630m (ClO_4). ^1H NMR (200 MHz, $(CD_3)_2SO$, TMS): δ 8.51 (s, 2 H), 7.76 (d, J = 4 Hz, 4 H), 7.48 (d, J = 4 Hz, 4 H), 3.30 (s, 4 H), 2.99 (s, 3 H). UV–VIS λ_{max}/nm (CH_3OH): 228.

[Ag(1b)](ClO_4)·$2H_2O$ (4). 0.27 g (1 mmol) of **1b** was dissolved in 25 ml of acetonitrile. To this solution 0.21 g (1 mmol) of solid $AgClO_4$ was added and dissolved with stirring. The colorless reaction mixture was kept in the refrigerator overnight. Colorless crystals which were also suitable for X-ray analysis were deposited, filtered off, washed with 5 ml of methanol and dried *in vacuo* under fused $CaCl_2$. Yield, 0.24 g (47%). Anal. found (calc. for $C_{16}H_{22}N_4AgClO_6$): C, 37.56 (37.68%); H, 4.39 (4.35%); N, 10.89 (10.99%). FTIR/cm^{-1} (KBr): 1635vs (C=N); 1143vs, 1115vs, 1084vs, 630s (ClO_4). ^1H NMR (200 MHz, $(CD_3)_2SO$, TMS): δ 8.50 (br, 4 H), 7.61 (d, 4 H), 3.58 (s, 4 H), 2.31 (s, 6 H). UV–VIS λ_{max}/nm (CH_3OH): 226. TGA/DTA: water loss, 6.80% (calcd. 7.06%).

2a. Benzil dihydrazone (1.87 g, 7.86 mmol), synthesized by a reported procedure,[20] was dissolved in 30 ml of anhydrous methanol. To this colorless solution, 1.50 ml (15.72 mmol) of freshly distilled 4-pyridinecarboxaldehyde was added. The resulting yellowish mixture was refluxed for 8h, maintaining a dry atmosphere. Then it was slowly cooled to room temperature to yield yellowish crystalline solid, which was filtered off and dried in air. Crystals suitable for X-ray analysis were obtained by slow evaporation of *n*-hexane solution. Yield, 2.45 g (75%); mp 119–121 °C. Anal. found (calc. for $C_{26}H_{20}N_6$): C, 74.82 (74.97%); H, 4.84 (4.84%); N, 19.98 (20.18%). EI–MS: *m*/*z* 417.2 (MH^+, 100%). FTIR/cm^{-1} (KBr): 1618vs (C=N). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.57 (d, J = 4 Hz, 4 H), 8.38 (s, 2 H), 7.88 (d, J = 4 Hz, 4 H), 7.51–7.26 (m, 10 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 165.99, 157.87, 150.33, 140.89, 133.44, 131.47, 128.90, 127.85, 122. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 305 (41 400).

2b. Diacetyl dihydrazone (0.90 g, 7.86 mmol), synthesised by a reported procedure[20] was dissolved in 40 ml anhydrous methanol. To this solution 1.50 ml (15.72 mmol) of freshly distilled 4-pyridinecarboxaldehyde was added. The resulting slight yellow mixture was refluxed for 6h maintaining dry conditions, then cooled to room temperature. A yellowish solid separated out, which was filtered off and dried in air. Yield, 1.79 g (78%), mp 166–168 °C. Anal. found (calc. for $C_{16}H_{16}N_4$): C, 65.55 (65.72%); H, 5.62 (5.52%); N, 28.97 (28.76%). EI–MS: 293.2 (MH^+, 53%). FTIR/cm^{-1} (KBr): 1612vs (C=N). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.73 (d, $J = 4$ Hz, 4 H), 8.11 (s, 2 H), 7.68 (d, $J = 4$ Hz, 4 H), 2.30 (s, methyl, 6 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 163.12, 153.42, 150.54, 141.12, 122.15, 13.25. UV–VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 290 (32 500).

[Cu(2a)$_2$]ClO$_4$·2CH$_3$CN·1/2C$_2$H$_5$OC$_2$H$_5$ (5). 0.42 g (1 mmol) of **2a** was dissolved in 25 ml of anhydrous degassed acetonitile to which 0.33 g (1 mmol) of freshly prepared $[Cu(CH_3CN)_4]ClO_4$ was added under argon atmosphere. The reaction mixture was stirred for 3h. The reddish yellow precipitate was filtered, washed with methanol (5 ml) and stored *in vacuo* over fused $CaCl_2$. Yield, 0.34 g (30%) (in terms of metal). Single crystals suitable for X-ray analysis were grown by direct diffusion of diethyl ether into an acetonitrile solution of the complex. Anal. found (calc. for $C_{56}H_{46}N_{14}CuClO_4$): C, 62.24 (62.37%); H, 4.38 (4.30%); N, 18.05 (18.19%), Cu, 5.82 (5.90). (The diethyl ether molecule might be lost during the drying process). FTIR/cm^{-1} (KBr): 1608vs (C=N); 1099vs, 632m (ClO_4). UV–VIS λ_{max}/nm (CH_3OH): 300.

[Ag(2a)$_2$]ClO$_4$·2CH$_3$CN·C$_6$H$_5$CH$_3$ (6). 0.21 g (0.5 mmol) of **2a** was dissolved in 25 ml of acetonitrile. To this yellowish solution 0.10 g (0.5 mmol) of solid $AgClO_4$ was added and dissolved with stirring. To this clear solution toluene was added dropwise with stirring until the solution became turbid. The reaction mixture was kept in the refrigerator for overnight, yielding a yellow crystalline compound, which was a filtered off, washed with 5 ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.19 g (32%). Single crystals suitable for X-ray analysis were grown by direct diffusion of toluene into a dilute acetonitrile solution of the complex. Anal. found (calc. for $C_{52}H_{40}N_{12}AgClO_4$): C, 59.93 (60.02%); H, 4.04 (3.88%); N, 15.98 (16.16%). (The acetonitrile molecules and the toluene molecule might be lost during the drying process). FTIR/cm^{-1} (KBr): 1608vs (C=N); 1088vs, 621s (ClO_4). UV–VIS λ_{max}/nm (CH_3OH): 290.

[Zn(2a)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$·2CH$_3$CN·C$_2$H$_5$OC$_2$H$_5$ (7). To a 30 ml acetonitrile–water (5 : 1 v/v) solution of 0.21 g (0.5 mmol) of **2a**, 0.19 g (0.5 mmol) of solid $Zn(ClO_4)_2·6H_2O$ was added and dissolved with stirring. To the yellowish solution diethyl ether was added dropwise with constant stirring until the solution became turbid. The reaction mixture was kept in the refrigerator for overnight, and the precipitated light yellow compound was filtered off and washed with 5 ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.25 g (38%). Single crystals suitable for X-ray analysis were grown by direct diffusion of diethyl ether into an acetonitrile solution of the complex. Anal. found (calc. for $C_{56}H_{46}N_{14}ZnCl_2O_8$): C, 56.85 (57.00%); H, 4.10 (3.93%); N, 16.48 (16.63%). (The diethyl ether molecule and part of the acetonitrile molecules might be lost during the drying process). FTIR/cm^{-1} (KBr): 1604vs (C=N); 1100vs, 630m, split (ClO_4). UV–VIS λ_{max}/nm (CH_3OH): 296.

[Co(2a)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·CH$_3$OH·H$_2$O (8). 0.21 g (0.5 mmol) of **2a** was dissolved in 25 ml of methanol. To this yellowish solution 0.185 g (0.5 mmol) of solid $Co(ClO_4)_2·6H_2O$ was added and dissolved with stirring, and the pink solution kept in the air for slow evaporation. After a few days a reddish yellow crystalline compound precipitated, which was filtered off, washed with 1 ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.265 g (45%). Single crystals were grown by slow evaporation of a dilute methanol solution of the complex. Anal. found (calc. for $C_{53}H_{50}N_{12}CoCl_2O_{12}$): C, 54.38 (54.07%); H, 4.25 (4.28%); N, 14.32 (14.28%). FTIR/cm^{-1} (KBr): 1610vs (C=N); 1104vs, 622m (ClO_4).

[Mn(2a)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ (9). To a 20ml acetonitrile solution of 0.21 g (0.5 mmol) **2a**, 0.18 g (0.5 mmol) of solid $Mn(ClO_4)_2·6H_2O$ was added and dissolved by stirring. To this reaction mixture 5ml water solution of 0.10 g (0.62 mmol) sodium hexafluorophosphate was added with stirring, and left in the air. After few days a pink crystalline compound precipitated, which was filtered off, washed with water and dried *in vacuo* over fused $CaCl_2$. Yield, 0.26 g (42%). Single crystals were grown by slow evaporation of a dilute acetonitrile solution of the complex. Anal. found (calc. for $C_{56}H_{46}N_{14}MnP_2F_{12}$): C, 53.19 (53.37%); H, 3.76 (3.68%); N, 15.48 (15.56%). FTIR/cm^{-1} (KBr): 1608vs (C=N); 837 (PF_6).

[Cd(2a)(CH$_3$CN)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (10). 0.21 g (0.5 mmol) of **2a** was dissolved in 25 ml of acetonitrile, into which solution 0.15 g of solid $Cd(ClO_4)_2·XH_2O$ was added and dissolved with stirring. Within 5 min a yellow compound precipitated out which was filtered, washed with 5ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.27 g (64%). Single crystals were grown by slow evaporation of an acetonitrile solution of the complex. Anal. found (calc. for $C_{30}H_{30}N_8CdCl_2O_{10}$): C, 42.64 (42.57%); H, 3.75 (3.58%); N, 13.17 (13.24%). FTIR/cm^{-1} (KBr): 1610vs (C=N); 1104vs, 628m (ClO_4).

All reactions were carried out using uniformly 1 : 1 stoichiometry of metal and ligand. Correspondingly, in the case of 1 : 2 metal–ligand complexes **5**–**9** the excessive metal starting material remained unreacted and separated out. Moreover, improved yields of the products could be obtained in these reactions when a 1 : 2 metal–ligand ratio was applied.

CAUTION! Though while working with the perchlorate compounds described here we have not met with any incident, care should be taken in handling them as perchlorates are potentially explosive. These should not be prepared and stored in large amounts.

Crystallography

The diffraction measurements were carried out on a Nonius KappaCCD diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å). The crystalline samples of the analyzed compounds were covered with a thin layer of light oil and cooled to 110 K in order to minimize loss of solvent, structural disorder and thermal motion effects, and increase the precision of the results. The crystal and experimental data for **1a**, **1b 2a**, and **3**–**7** are summarized in Table 1. These structures were solved by direct (SHELXS-86, SIR-92)[21,22] and Patterson methods (DIRDIF-96),[23] and refined by full-matrix least-squares on F^2 (SHELXL-97).[24] All non-hydrogen atoms were refined anisotropically. The hydrogens were located in idealized positions (the methyls being treated as rigid groups), and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2\ U_{ij}$ (eq.) for the atom to which they are bonded]. Ligand **1** and **2** differ significantly in their shapes and packing efficiency of their polymeric complexes with metal ions. Thus, complexes **3** and **4** are characterized by relatively high density of the solid material. On the other hand, complexes **5**–**7** of the bulkier ligand, crystallized with a high content of uncoordinated solvent and the resulting materials have a considerably lower density.

Similar crystallographic analyses of compounds **8**–**10** elucidated clearly the coordination modes in these materials. However, due to poor quality of the corresponding crystals and severe disorder of the component species therein (which severely diminished high-angle diffraction), they could yield atomic parameters of limited precision only and thus should be regarded as preliminary results to be refined in the future when suitable crystals become available. Crystal data identifying these structures are: **8**: $C_{53}H_{50}N_{12}CoCl_2O_{12}$, formula weight 1176.88, monoclinic, space group $P2_1/n$, a = 18.8590(5), b = 10.2760(3), c = 29.3990(10) Å, β = 105.460(1)°, V = 5491.2(3) Å^3, Z = 4. **9**: $C_{56}H_{46}N_{14}MnP_2F_{12}$, formula weight 1259.31, monoclinic, space group $P2_1/n$, a = 10.6400(5), b = 30.286(2), c = 21.985(2) Å, β = 92.508(5)°, V = 7077.7(8) Å^3, Z = 4. **10**: $C_{30}H_{30}N_8CdCl_2O_{10}$, formula weight 845.65, monoclinic, space group $P2_1/c$, a = 10.8750(8), b = 18.910(1), c = 19.720(1) Å, β = 98.009(3)°, V = 4015.8(5) Å^3, Z = 4. (These crystals contain additional molecules of heavily disordered solvent.)

CCDC reference numbers 171379–171386.

See http://www.rsc.org/suppdata/dt/b1/b108616b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This research was supported in part by the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities, as well as by Grant No. 1999082 from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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