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Heteronuclear, mixed-metal Ag(I)–Mn(II) coordination polymers with bridging *N*-pyridinylisonicotinohydrazide ligands: synthesis, crystal structures, magnetic and photoluminescence properties†

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Mixed-metal dicyanoargentate-bridged coordination polymers of Ag(I)–Mn(II) have been prepared and their structure and magnetic properties were determined. Reaction of manganese(II) chloride and potassium dicyanoargentate(I) with (X)(pyridin-2-ylmethylene)isonicotinohydrazide ligands (HL^1 X = Ph, HL^2 X = Me, HL^3 X = H) produced the coordination polymer 2D-$[Mn(\mu\text{-}L^1)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (**1**), 1D-$\{[Mn(L^2)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]CH_3OH\}_n$ (**2**) and $[Mn(L^3)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (**3**) in good yields. Trinuclear $\{Mn(\mu\text{-}L^1)Mn(\mu\text{-}L^1)Mn\}$ and $[Ag(CN)_2]^-$ building units form a two-dimensional slab in **1** and 1D strands in **2**. Variable temperature magnetic susceptibility measurements showed that despite the long distance among the high spin Mn(II) ions [10.4676(12) Å and 10.522(1) Å, for **1** and **2**, respectively], weak antiferromagnetic coupling takes place through the long NC–Ag–CN bridge. The best fit parameters to the model led to the magnetic coupling constant of $J = -0.1$ and $J = -0.47$ cm^{-1} for **1** and **2**, respectively. The photoluminescence behaviour of compounds **1** and **2** was studied. The spectrum of compound **1** shows a broad emission centered at about 450 nm and two excitation maxima at 270 and 310 nm.

Introduction

The design and synthesis of novel coordination polymers and metal–organic frameworks (MOFs) have attracted great attention in the fields of inorganic and coordination chemistry.[1] This is mainly due to the structural diversity of coordination polymers and their potential application as functional materials in fields such as catalysis,[2] separation,[3] gas storage,[4] sensor technology,[5] energy conversion,[6] medicine,[7] drug delivery[8] and magnetic materials.[9] On the other hand, heteronuclear complexes have attracted great attention in the field of coordination chemistry because of their applications in mimicking the active site of some metalloenzymes,[10] preparing multifunctional catalysts[11] and they are interesting materials for studying magnetic exchange when they embrace paramagnetic cores.[12] Controlled preparation of mixed-metal (heterometallic) coordination polymers with pre-formed secondary building units is a timely challenge in the field of coordination polymers or metal–organic frameworks.[13–15]

Several effective synthetic strategies have been employed to construct mixed-metal coordination polymers with diversified topological structures and interesting properties.[16] The more successful strategies for the synthesis of mixed-metal coordination polymers are to use multitopic organic bridging ligands having additional donor atoms, *i.e.* metal-binding pockets or to use chelate ligands with pendant donor groups to yield 'chelate complex ligands'.[14,15,17] Another strategy is to use metallate ions as metalloligands. The metallate ions can be derived from the binding of halides or pseudohalides like N_3^-, SCN^-, OCN^-, CN^- to metal ions, yielding particularly stable

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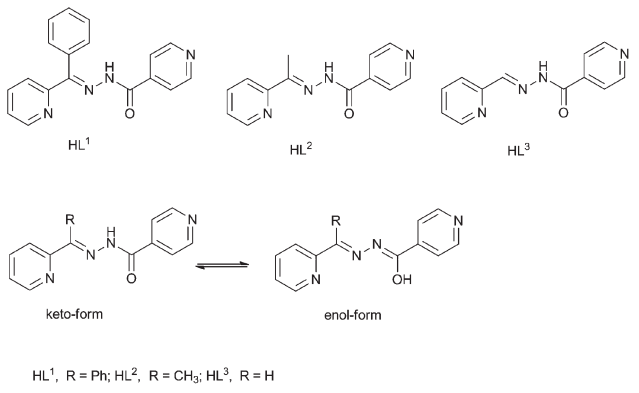
entities like $[Ni(CN)_4]^{2-}$ (found in Hofmann-type clathrates),[18] $[Cu(CN)_4]^{3-}$,[19] $[Ag(CN)_2]^-$,[20] $[Au(CN)_2]^-$,[21] and $[Au(CN)_4]^-$ (ref. 22) which then act as bridging metalloligands. The cyanide group is one of the most famous simple linkages and plays an important role, especially for the heterometallic magnetic systems in the Prussian blue series.[23] The bidentate cyanide ligand is able to bridge different metal atoms through its soft C and hard N donor atoms while the topological structures and the magnetic, optical and electronic properties of the corresponding compounds can be controlled.[24] Moreover, the cyanide group can stabilize a variety of transition metal centers and oxidation states with or without the peripheral ligands, offering relatively spacious room for the selection of cyanide-containing building blocks. As a result, a large number of cyanide-bridged complexes with various structure types have been successfully designed and synthesized thus far.[25] The majority of the heterometallic cyano-bridged complexes were prepared using cyanometalate $[M(CN)_x]^{n-}$ building blocks in conjunction with a transition metal complex.[26] The dicyanoargentate $[Ag(CN)_2]^-$ anion is a dual-purpose compound. $[Ag(CN)_2]^-$ can act as a bridging group for heterometallic compounds and as a magnetic coupling group. $[Ag(CN)_2]^-$ has been utilized widely as the bridging group (building block) to form a variety of bimetallic coordination networks with interesting magnetic and optical properties. When the $[Ag(CN)_2]^-$ anion is combined with paramagnetic metal atoms, it acts as a magnetic coupler[27] and transfers spin-crossover properties.[28] Several studies have been conducted on photoluminescence properties of $[Ag(CN)_2]^-$ bridged polymers[29] which indicate that materials containing this group are good candidates for optical studies.

Besides, hydrazone ligands obtained from the condensation of 4-pyridine carboxylic acid hydrazide {Py–C(O)–NH–NH_2} with aldehydes/ketones bearing an *ortho*-pyridine ring can act as ditopic ligands *via* two different donor sites (a tridentate N,N,O coordination pocket and the 4-pyridine moiety) and show the potential to form mono- and multi-nuclear structures (Scheme 1).[30] Applications of manganese complexes as model systems for metalloenzymes[31] and their exciting magnetic properties[32] prompted us to employ ditopic *N*-arylideneisonicotinhydrazide ligands together with $[Ag(CN)_2]^-$ to form new bimetallic Ag–Mn coordination networks which are reported here.



Scheme 1 *N*-pyridinylisonicotinohydrazide ligands used in this study.

Results and discussion

Syntheses of compounds and spectroscopy

The reaction of 4-pyridinecarboxylic acid hydrazide with 2-pyridine-aldehyde/ketones in methanol gave the potentially tetradentate Schiff base ligands, HL^1, HL^2 and HL^3, in good yield and purity (Scheme 1). The analytical and spectroscopic data confirmed syntheses of the ligands. Compounds $[Mn(L^1)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (**1**), $\{[Mn(L^2)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]CH_3OH\}_n$ (**2**) and $[Mn(L^3)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (**3**) were synthesized by treatment of HL^{1-3}, $MnCl_2{\cdot}4H_2O$ and $KAg(CN)_2$ in molar ratios 1 : 2 : 2 in methanol. The compounds were characterized using microanalyses, and spectroscopic and thermal studies. The microanalytical results are in good agreement with the formulations given for **1–3**. ^{1}H-NMR, ^{13}C-NMR and IR spectroscopy confirmed that the ligands HL^{1-3} are in the keto-form in solution and solid state (*cf.* Scheme 1). In the ^{1}H-NMR spectra of HL^{1-3}, the signals at δ 12.1–14.8 ppm were assigned to the hydrazide N–H group, which was consistent with a rapid loss of this signal when D_2O was added to the solution. Existence of free ligands in keto form was confirmed by a very strong band in the range 1668–1691 cm^{-1} due to the amidic C=O stretching vibrations in the IR spectra of ligands. The infrared spectra of the compounds show a very broad O–H band (about 3400 cm^{-1}) for the coordinated methanol and so does not allow for any conclusion on Schiff base N–H deprotonation in the compounds. On complexation the absence of the aforementioned strong carbonyl band, shifts in the azomethine (–C=N–) band from 1628 to 1669 cm^{-1} and the appearance of a >C=N–N=C< band at 1612–1617 cm^{-1} support the coordination of the hydrazone ligands in the enol form as monoanionic $(L^{1-3})^-$ ligands in the compounds. The IR spectra of **1**, **2** and **3** show the characteristic stretching vibration bands of the CN bridging ligand in the range 2147–2165 cm^{-1} and thereby the presence of the $Ag(CN)_2^-$ moiety in the structure. The shift to higher wavenumbers of the CN stretching vibration in **1**, **2** and **3** when compared to $KAg(CN)_2$ (2133 cm^{-1}) is consistent with the bridging coordination of the CN group between the Ag(I) and Mn(II) ion. The observed IR bands are in agreement with the literature data for bridged $Ag(CN)_2^-$.[33]

The electronic spectra of the solution species from the dissolved compounds **1–3** (light orange) and HL^{1-3} (colourless) in MeOH solution are shown in Fig. S1 and S2,† respectively. Note that dissolution of a coordination polymer leads to disintegration and formation of free ligands, solvated metal ions and mono- to oligomeric metal–ligand complexes, which then give the signals in any solution spectrum. The hydrazone ligands display strong bands at 215–218, 270–290 and 325–365 nm. Based on their extinction coefficients they are assigned to intraligand π→π* (215–218 and 270–290 nm) and

n→π* (325–365 nm) transitions. Shifts of the bands in dissolved and disintegrated **1–3** relative to HL^{1-3} bands suggest the coordination of the ligand to the Mn(II) ion in solution. For such a solution complex the higher energy band at ~370 nm with a high extinction coefficient is then due to the ligand to metal charge transfer (LMCT) transition. The other higher energy intense transitions in the range 211–216 nm and 275–280 nm are intraligand π→π* and n→π* charge transfer transitions.

X-ray structures of 1 and 2

The structures of compounds **1** and **2** contain two different manganese(II) atoms and one silver(I) metal atom (Fig. 1). The silver atom is part of a monoanionic dicyanoargentate(I), $[Ag(CN)_2]^-$ group which bridges the two crystallographically different Mn atoms. Manganese atom Mn1 is five-coordinated in a close to square-pyramidal arrangement (τ = 0.06 in compound **1**, τ = 0.33 in compound **2**)[34] by the three chelating donor atoms of the mono-anionic pyridyl-hydrazonato ligand, a chlorido ligand and the N-atom of the $[Ag(CN)_2]^-$ bridge. The manganese atom Mn2 with an octahedral geometry sits on an inversion center and is coordinated by two N-atoms of two *trans* $[Ag(CN)_2]^-$ bridges, two *trans* methanol ligands and two N-atoms from pyridyl groups of two *trans* hydrazonato ligands. The *trans* position of the same ligands is, of course, due to the inversion symmetry of the Mn2 coordination sphere. Each pyridylhydrazonato ligand bridges Mn1 and Mn2 with the isonicotino part. The crystal lattice of compound **2** contains a methanol molecule per formula unit which is hydrogen-bonded to the hydrazone oxygen atom (O1 in Fig. 1b, Table 1).

In compound **1** the coordination at the silver atom in the $[Ag(CN)_2]$ group is close to linear (C1–Ag1–C2 = 172.8(2)°). In compound **2** the angle between the two cyanido groups is only 158.5(1)°. The reason is a long Ag···Cl contact (2.8612(7) Å) which distorts the NC–Ag–CN group from almost linear to trigonal (Fig. 1b). This long Ag···Cl contact organizes the packing of adjacent strands in **2** (*cf.* Fig. 5).

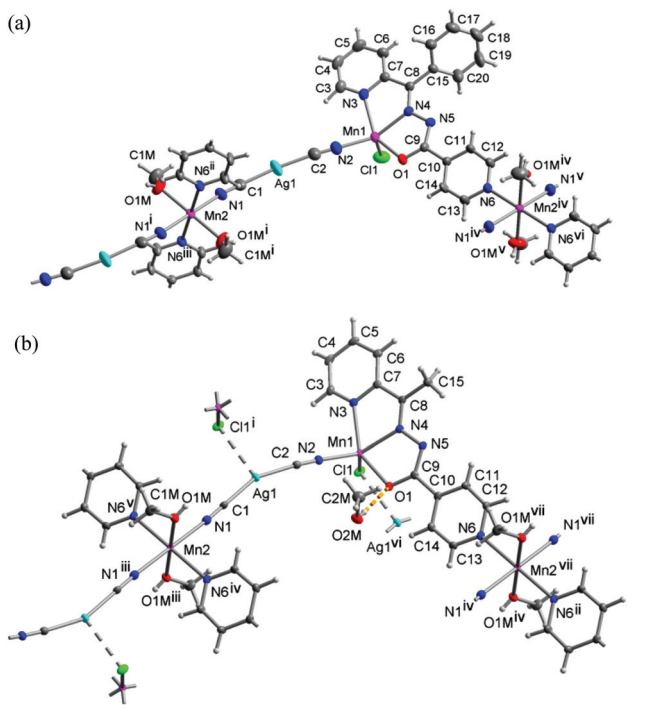


Fig. 1 (a) Extended asymmetric unit of compound **1** (50% probability ellipsoids, 296 K), with full coordination spheres of the metal atoms. Symmetry transformations: i = –*x*, –*y* + 1, –*z* + 3; ii = –*x* + 1, *y* + 1/2, –*z* + 5/2; iii = *x* – 1, –*y* + 1/2, *z* + 1/2; iv = –*x* + 1, *y* – 1/2, –*z* + 5/2; v = 1 + *x*, 0.5 – *y*, –0.5 + *z*; vi = 2 – *x*, –*y*, –*z*; vii = –*x* + 1, *y* + 1/2, –*z* + 1/2; viii = –*x*, –*y* + 1, –*z* + 1. (b) Extended asymmetric unit of compound **2** (50% probability ellipsoids, 96 K), with full coordination spheres of the metal atoms. Symmetry transformations: i = *x* + 1, *y*, *z*; ii = –*x*, –*y* + 1, –*z* + 1; iii = –*x* + 4, –*y* + 3, –*z* + 1; iv = –*x* + 2, –*y* + 2, –*z* + 1; v = *x* + 2, *y* + 1, *z*; vi = *x* – 1, *y*, *z*; vii = *x* – 2, *y* – 1, *z*.

Table 1 Selected bond lengths (Å) and angles (°) in **1** and **2**[a]

Compound **1**			
Ag1–C2	2.057(7)	O1–Mn1–N3	141.53(13)
Ag1–C1	2.061(6)	N4–Mn1–N3	71.22(13)
Mn1–N2	2.086(5)	N2–Mn1–Cl1	104.40(13)
Mn1–O1	2.155(3)	O1–Mn1–Cl1	102.19(10)
Mn1–N4	2.168(4)	N4–Mn1–Cl1	109.33(11)
Mn1–N3	2.289(4)	N3–Mn1–Cl1	101.49(10)
Mn1–Cl1	2.3855(16)	$N1^{i}$–Mn2–N1	180
Mn2–N1	2.180(4)	N1–Mn2–O1m	91.70(17)
Mn2–O1m	2.208(4)	N1–Mn2–$O1m^{i}$	88.30(17)
Mn2–$N6^{ii}$	2.272(4)	O1m–Mn2–$O1m^{i}$	180
C2–Ag1–C1	172.8(2)	N1–Mn2–$N6^{ii}$	91.03(15)
N2–Mn1–O1	107.92(16)	O1m–Mn2–$N6^{ii}$	91.60(15)
N2–Mn1–N4	145.39(17)	N1–Mn2–$N6^{iii}$	88.97(15)
O1–Mn1–N4	72.52(13)	O1m–Mn2–$N6^{iii}$	88.40(15)
N2–Mn1–N3	94.90(16)	$N6^{ii}$–Mn2–$N6^{iii}$	180
Compound **2**			
Ag1–C1	2.089(3)	N2–Mn1–Cl1	115.55(6)
Ag1–C2	2.093(3)	O1–Mn1–Cl1	101.30(5)
Ag1–$Cl1^{i}$	2.8612(7)	N4–Mn1–Cl1	120.46(6)
Mn1–N2	2.108(2)	N3–Mn1–Cl1	98.88(6)
Mn1–O1	2.1592(17)	C9–O1–Mn1	113.76(15)
Mn1–N4	2.166(2)	C2–N2–Mn1	177.1(2)
Mn1–N3	2.267(2)	C3–N3–Mn1	125.64(18)
Mn1–Cl1	2.3480(7)	C7–N3–Mn1	115.74(16)
Mn2–O1 m	2.1904(19)	C8–N4–Mn1	122.78(16)
Mn2–N1	2.195(2)	N5–N4–Mn1	118.58(15)
Mn2–$N6^{v}$	2.283(2)	O1m–Mn2–$O1m^{iii}$	180
Cl1–$Ag1^{vi}$	2.8612(7)	O1m–Mn2–$N1^{iii}$	92.26(8)
C1–Ag1–C2	158.50(10)	O1m–Mn2–N1	87.74(8)
C1–Ag1–$Cl1^{i}$	101.30(7)	$N1^{iii}$–Mn2–N1	180
C2–Ag1–$Cl1^{i}$	99.49(7)	O1m–Mn2–$N6^{iv}$	90.30(7)
N1–C1–Ag1	178.2(2)	N1–Mn2–$N6^{iv}$	90.03(8)
N2–C2–Ag1	174.2(2)	O1m–Mn2–$N6^{v}$	89.70(7)
Mn1–Cl1–$Ag1^{vi}$	91.77(2)	N1–Mn2–$N6^{v}$	89.97(8)
N2–Mn1–O1	100.49(8)	$N6^{iv}$–Mn2–$N6^{v}$	180
N2–Mn1–N4	123.91(8)	C1m–O1m–Mn2	126.96(18)
O1–Mn1–N4	72.16(7)	C1–N1–Mn2	174.9(2)
N2–Mn1–N3	97.38(8)	C12–N6–$Mn2^{vii}$	120.03(17)
O1–Mn1–N3	143.84(7)	C3–N6–$Mn2^{vii}$	122.72(17)
N4–Mn1–N3	71.77(8)		

[a] Symmetry operations for **1**: i = –*x*, –*y* + 1, –*z* + 3; ii = –*x* + 1, *y* + 1/2, –*z* + 5/2; iii = *x* – 1, –*y* + 1/2, *z* + 1/2; iv = –*x* + 1, *y* – 1/2, –*z* + 5/2. Symmetry operations for **2**: i = *x* + 1, *y*, *z*; ii = –*x*, –*y* + 1, –*z* + 1; iii = –*x* + 4, –*y* + 3, –*z* + 1; iv = –*x* + 2, –*y* + 2, –*z* + 1; v = *x* + 2, *y* + 1, *z*; vi = *x* – 1, *y*, *z*; vii = *x* – 2, *y* – 1, *z*.

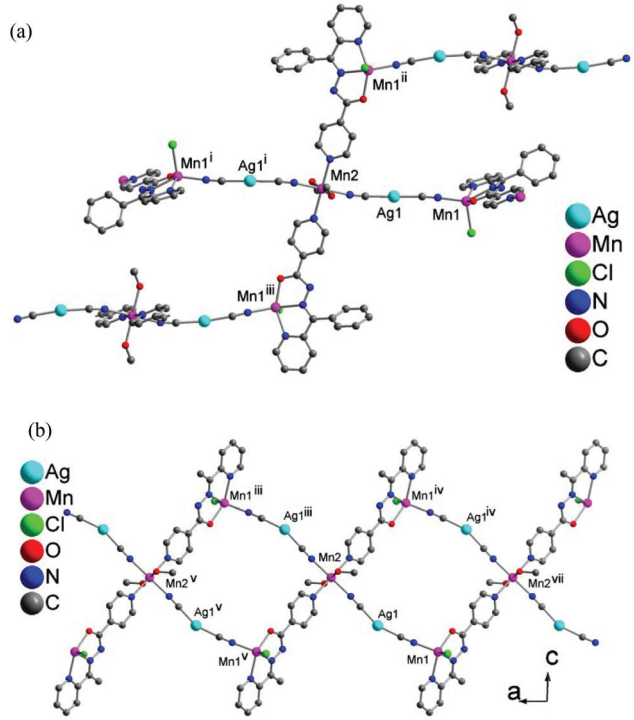


Fig. 2 Trinuclear manganese building unit with bridging $[Ag(CN)_2]^-$ groups in (a) compound **1**. Symmetry transformations: i = $-x$, $-y + 1$, $-z + 3$; ii = $-x + 1$, $y + 1/2$, $-z + 5/2$; iii = $x - 1$, $-y + 1/2$, $z + 1/2$. (b) Compound **2**. Symmetry transformations: iii = $-x + 4$, $-y + 3$, $-z + 1$; iv = $-x + 2$, $-y + 2$, $-z + 1$; v = $x + 2$, $y + 1$, z; vii = $x - 2$, $y - 1$, z.

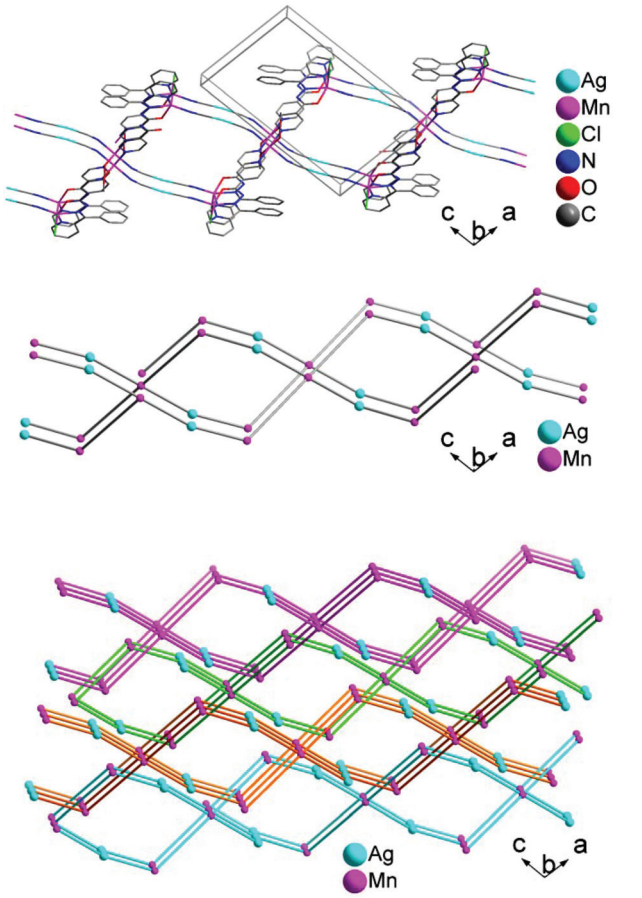


Fig. 3 Two-dimensional slab constructed from the trinuclear manganese building block and bridging $[Ag(CN)_2]^-$ groups parallel to the [101]-plane in the structure of **1**. Top: wire-frame model. Middle: schematic representation of a single slab showing only the Mn and Ag atoms and their topological connecting lines. Bottom: interdigitation and packing of stack of four neighboring slabs which are differentiated by differently colored topological lines.

Two Mn1 atoms, with two bridging hydrazonato ligands and one central Mn2 atom, can be observed to form a trinuclear manganese unit (Fig. 2). In **1** four bridging $[Ag(CN)_2]^-$ groups, two to each side, connect each trinuclear unit to four neighboring trinuclear units which are tilted by 90° (Fig. 2a). In **2** the four bridging $[Ag(CN)_2]^-$ groups, two to each side, connect the middle trinuclear unit to two adjacent trinuclear units which run parallel (Fig. 2b).

This way, in **1** the trinuclear manganese units and the $[Ag(CN)_2]^-$ groups form a two-dimensional slab parallel to the [101] plane (Fig. 3). Neighboring slabs pack by interdigitation which is driven by π-stacking between symmetry-related metalloaromatic[35] Mn–O1–C15–N5–N4 chelate rings and between pyridyl rings of the hydrazonato ligands (Fig. 4).[36]

In compound **2** the trinuclear manganese building unit and bridging $[Ag(CN)_2]^-$ groups form 1D strands which run along the *a* direction (Fig. 2b). These strands stack along *b* with a translational shift of one-unit cell along *a* (Fig. 5). The stacking along *b* is mediated by the long Ag···Cl contacts.

XRD patterns of the compounds **1**–**3** are compared in Fig. S5–S7 in the ESI.†

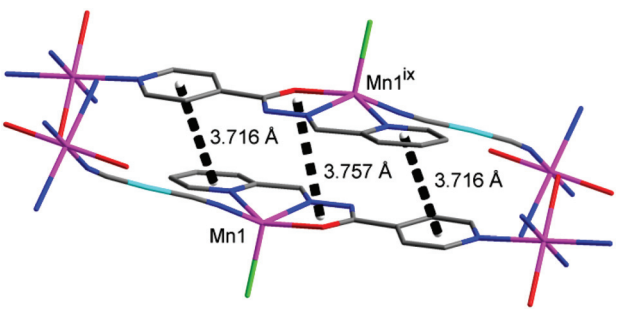


Fig. 4 π-Stacking interactions between hydrazonato-manganese fragments from neighboring slabs. The phenyl ring from the hydrazonato ligand is not shown for clarity. Symmetry transformation ix = $1 - x$, $1 - y$, $-z$.

Magnetic studies

Fig. 6 shows the temperature dependence of the $\chi_M T$ product for compounds **1** and **2**. The values observed at room temperature, 6.52 and 6.35 emu mol^{-1} K, respectively, are somewhat lower than the spin only values for 1.5 high spin Mn(II) ions (4.337 emu mol^{-1} K per Mn^{2+}).[37] On lowering temperature, the $\chi_M T$ product remains almost constant up to 50 K, for compound **1**, and then decreases more rapidly at lower temperatures.

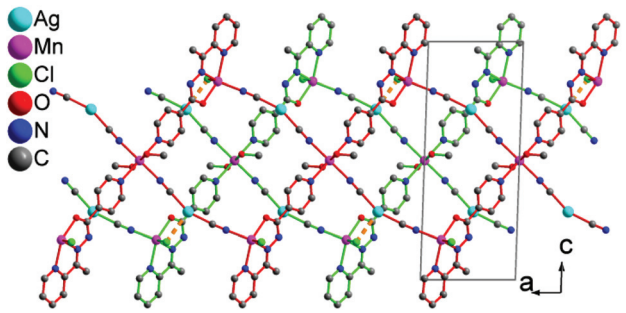


Fig. 5 Section of the packing in **2** showing two of the 1D strands (differentiated by red and green bond color) which run along the *a* axis. The two strands stack along the *b* axis and are connected by long Ag···Cl contacts (shown as orange broken lines).

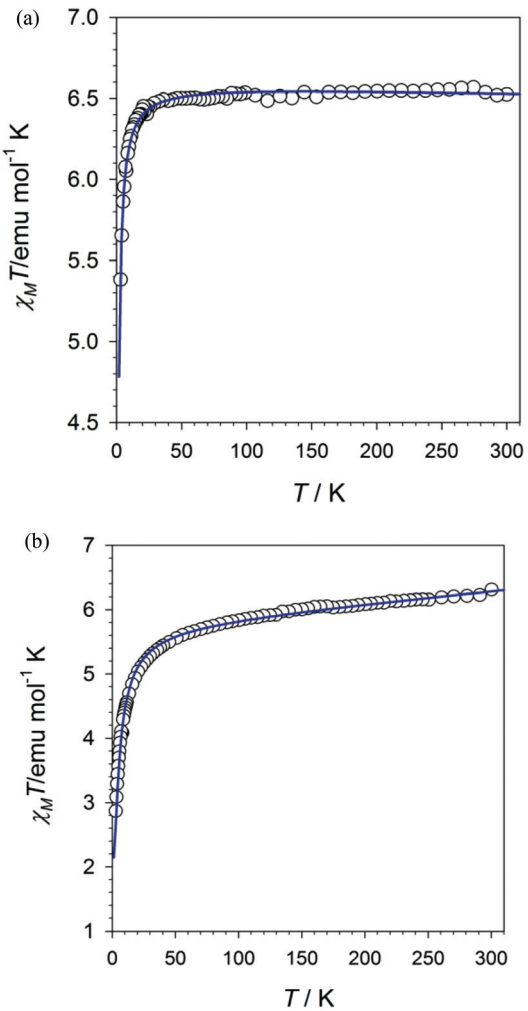


Fig. 6 Temperature dependence of the $\chi_M T$ product for compounds **1** (a) and **2** (b). The solid lines correspond to the best fit to the model, see text.

Similarly for compound **2**, the $\chi_M T$ product slowly decreases at temperatures above 50 K and then more rapidly at lower temperatures. This behaviour is indicative of weak antiferromagnetic interactions in both compounds which are to some degree stronger in **2**. The *M vs*. *H* plots at 2 K are also consistent with this weak antiferromagnetic coupling (see Fig. S3 in ESI†).

The structures of **1** and **2** show the Mn(II) ions linked by $[Ag(CN)_2]^-$ and pyridyl-hydrazonato bridges yielding networks of different topologies. Previous studies have shown the dicyanoargentate(I) linker to mediate some magnetic coupling among Mn(II) ions.[38,39] On the other hand the coupling through the pyridyl-hydrazonato link is expected to be much weaker, therefore only the topology given by the former linker has to be considered for the analysis of the magnetic exchange interactions. Under this approach, we can explain the magnetic properties of both compounds by means of the Heisenberg–Dirac–Van Vleck Hamiltonian for a linear trinuclear compound $\hat{H} = -J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) - j(\hat{S}_1\hat{S}_3)$ (Scheme 2).[40]

For the case of compounds **1** and **2** the Mn1···Mn1a interaction can be neglected because of the long Mn1···Mn1a distance (20.935 Å and 21.049 Å, for **1** and **2**, respectively). Then the magnetic susceptibility numerical expression can be obtained applying the Van Vleck formula for three $S = 5/2$ spins. The exchanges through the pyridyl-hydrazonato link have been introduced as a Weiss parameter in the magnetic susceptibility equation (mean molecular field approximation). The best fit parameters to the model are $g = 1.97$, $J = -0.1$ cm^{-1}, $\Theta = 0.08$ K, $R = 1.74\ 10^{-5}$ and $g = 1.96$, $J = -0.47$ cm^{-1}, $\Theta = 0.1$ K and $R = 4.82 \times 10^{-5}$, for **1** and **2**, respectively. R is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\sum[(\chi_M T)_{obs}(i)]^2$. We observe a good match between the theoretical and the experimental plots which support the model employed.

The values obtained for the coupling through the $[Ag(CN)_2]^-$ bridge are rather weak, as expected from the diamagnetic character of the Ag(I) ion and the large separation between the Mn(II) ions (more than 10 Å), but they are within the range of previous studies.[38,39] Also, it can be observed that the magnetic interaction is somewhat stronger in **2**, which can be explained in terms of some slight structural differences in the respective Mn(II)–NC–Ag–CN–Mn(II) magnetic exchange pathways. The magnetic coupling is an electronic property which is related to the overlap between the orbitals bearing the unpaired electrons of the paramagnetic centers with those of the bridge. In general, it is observed that the larger the overlap, the larger the antiferromagnetic coupling.[37] The dicyanoargentate is a linear bridge and the largest overlap occurs when all the atoms are in the same line with bonding angles close to 180°. The deviation from the linearity decreases the overlap, and therefore, the antiferromagnetic coupling. For compound **1** the CN–Mn angles are 165.2(5)° and 175.2(5)° whereas for **2** we have angles of 174.9(2)° and 177.1(2)°, these

Scheme 2 Magnetic coupling scheme in compounds **1** and **2**.

latter being closer to 180° and this is probably the explanation for the higher antiferromagnetic coupling in **2**. The small J value, which is comparable to those found in other cyanide-bridged Ag–Mn complexes,[41] suggests the overall weak magnetic coupling between the Mn(II) ions with a long separation.

The structure of **3** is not known, so an analysis of the magnetic properties cannot be done at the same level and just a Curie–Weiss fit can be performed. A Curie constant of C = 6.37 emu mol^{-1} K is obtained in agreement with 1.5 high spin Mn(II) ions per formula (Fig. S4†). A Weiss constant of −3.44 K indicates some antiferromagnetic interactions. However, this Weiss constant is not comparable to that of **1** and **2**, since here all the interactions are concentrated just in one parameter, while the analysis done for **1** and **2** only reflects the coupling through hydrogen bonding and/or through the pyridyl-hydrazonato bridge.

Photoluminescence study

In general, silver(I) complexes can emit weak photoluminescence at low temperature.[42] Several theoretical and experimental studies have reported that the $Ag(CN)_2^-$ group is photoluminescent, emitting at the border of the UV–Vis region.[43] The photoluminescence behavior of single crystals of $Tl[Ag(CN)_2]$ has been studied as a function of temperature.

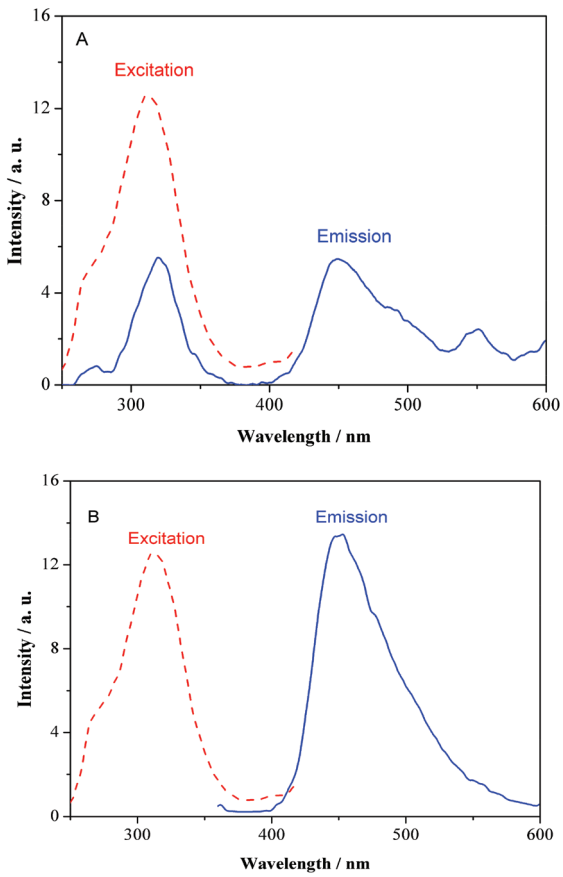


Fig. 7 Emission and excitation spectra for compound **1** with excitation at (A) 270 nm and (B) 310 nm.

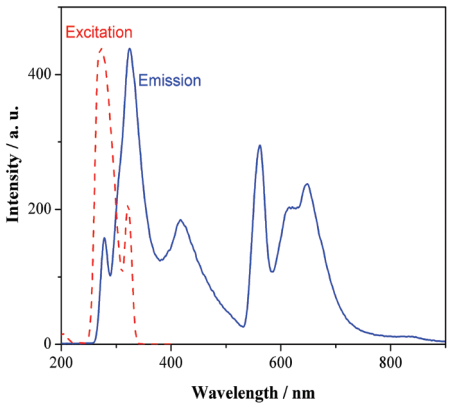


Fig. 8 Emission and excitation spectra for compound **2** with excitation at 272 nm.

The 10 K spectra show a broad emission centered at about 420 nm and two excitation maxima at 301 and 314 nm.[43d,e]

At ambient temperature, compound **1** shows photoluminescence with emission maxima at 320 and 450 nm upon excitation at 270 nm and emission maximum at 450 nm when excitation is at 310 nm (Fig. 7). The condensed polymeric materials may be good candidates for thermally stable and solvent-resistant blue fluorescent material. Compound **2** with excitation at 272 nm shows an emission maximum at 420 nm (Fig. 8). The emission bands of these compounds is due to the presence of the $Ag(CN)_2^-$ bridging group which can show photoluminescence properties. The emission bands can be due to MLCT or metal centred transitions of the type $4d^{10} \rightarrow 4d^9\ 5s^1$ and $4d^{10} \rightarrow 4d^9\ 5p^1$ on the silver(I) center (excited triplet to singlet states).[43a,g]

Conclusions

Three new coordination polymers of Mn(II) with dicyanoargentate anion and isonicotinohydrazone based ligands were synthesized and two of them fully characterized by X-ray diffraction and magnetic susceptibility measurement studies. Trinuclear $\{Mn(\mu\text{-}L^1)Mn(\mu\text{-}L^1)Mn\}$ and $[Ag(CN)_2]^-$ building units form a two-dimensional slab in **1** and 1D strands in **2**. Neighboring slabs pack by interdigitation which is driven by π-stacking between symmetry-related metalloaromatic chelate rings and between pyridyl rings of the hydrazonato ligands. Magnetic studies revealed that despite the large Mn(II)···Mn(II) separation and despite the diamagnetic character of the dicyanoargentate(I) bridge, weak antiferromagnetic coupling takes place through the long NC–Ag–CN bridge. This study revealed that ditopic *N*-arylideneisonicotinhydrazide ligands together with $[Ag(CN)_2]^-$ form new bimetallic Ag–Mn coordination networks which can be used as model systems for investigation on metalloenzymes and their exciting magnetic properties.

Experimental

Materials and instrumentations

Manganese(II) chloride tetrahydrate, 4-pyridinecarboxylic acid hydrazide, 2-benzoylpyridine, 2-acetylpyridine, 2-pyridylcarboxaldehyde and potassium dicyanoargentate(I) ("potassium silver cyanide") were purchased from Aldrich and used as received. Solvents of the highest grade commercially available (Merck) were used without further purification. IR spectra were recorded as KBr disks with a Bruker FT–IR spectrophotometer. UV–Vis spectra of solution were recorded on a thermo spectronic, Helios Alpha spectrometer.

Photoluminescence spectra of the compounds were recorded on a PerkinElmer Luminescence Spectrometers (equipped with a xenon lamp) by absorption and emission modes. The spectra were recorded at room temperature in the range of 200–900 nm. ^{1}H and ^{13}C NMR spectra of the ligands in DMSO-d_6 solution were recorded on a Bruker spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane. Magnetic measurements were made on polycrystalline samples using a Vibrating Sample Magnetometer (CFMS, Cryogenic Ltd). The temperature dependence of the magnetization in the range between 2 and 300 K was recorded using a constant magnetic field of 0.10 T. Further measurements were done at 2 K in fields up to 12 T to saturate the samples. The experimental data have been corrected for the magnetization of the sample holder (gelatin) and for atomic diamagnetism.

Synthesis of (*E*)-*N*′-(phenyl(pyridin-2-yl)methylene)isonicotinohydrazide (HL^1). A methanol (10 ml) solution of 2-benzoylpyridine (0.30 g, 1.64 mmol) was added dropwise to a methanol solution (10 ml) of 4-pyridinecarboxylic acid hydrazide (0.23 g, 1.64 mmol) and the mixture was refluxed for 6 h. Then the solution was evaporated on a steam bath to 5 cm^3 and cooled to room temperature. The resulting light yellow precipitate was separated and filtered off, washed with 5 ml of cooled methanol and re-crystallized from hot methanol. Yield: 80% (0.40 g). Anal. Calc. for $C_{18}H_{14}N_4O$ (M_W = 302.33): C, 71.51; H, 4.67; N, 18.53. Found: C, 71.62; H, 4.73; N, 18.60. FT-IR (KBr, cm^{-1}): 3110 (N–H, w, br), 3062 (m), 2932 (w), 1691 (C═O, vs), 1669 (C═N, s), 1577 (m), 1548 (s), 1508 (m), 1490 (s), 1465 (s), 1444 (s), 1412 (m), 1319 (s), 1277 (s), 1216 (m), 1142 (s), 1084 (s), 1072 (w), 1141 (m), 992 (m), 927 (m), 895 (m), 847 (s), 807 (s), 768 (m), 744 (vs), 702 (vs), 678 (s), 652 (s), 615 (m), 449 (m). ^{1}H NMR (250.13 MHz, DMSO-d_6, TMS): δ = 14.81 (s, 1H, N–*H*), 8.93 (m, 3H), 7.94 (m, 2H), 7.73 (d, 2H, 4-pyr), 7.61 (m, 4H), 7.49 (d, 2H). ^{1}H NMR (250.13 MHz, DMSO-d_6 + D_2O): δ = 7.41–8.80 (aromatic) ppm. ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 121.5, 124.6, 127.1, 128.6, 131.1, 133.4, 136.4, 138.1, 140.7, 149.0, 150.6, 154.9, 164.4, 193.8 ppm. UV-Vis spectrum in CH_3OH [λ_{max}, (ε, L^3 mol^{-1} cm^{-1}), c = 5 × 10^{-5}]: 217 (27 340), 268 (26 460), 325 nm (12 660).

Synthesis of (*E*)-*N*′-(1-(pyridin-2-yl)ethylidene)isonicotinohydrazide (HL^2). Following the procedure for HL^1 compound HL^2 was obtained by the reaction of 2-acetylpyridine (0.242 g, 2.0 mmol) with 4-pyridinecarboxylic acid hydrazide (0.274 g, 2.0 mmol) in methanol. Yield: 80% (0.40 g). Anal. Calc. for $C_{13}H_{12}N_4O$ (M_W = 240.26): C, 64.99; H, 5.03; N, 23.32%. Found: C, 65.02; H, 5.01; N, 23.37%. FT-IR (KBr, cm^{-1}): 3420 (w), 3186 (N–H, m), 1670 (C═O, vs), 1623 (C═N, s), 1613 (s), 1581 (s), 1565 (s), 1551 (s), 1456 (m), 1419 (s), 1386 (vs), 1306 (s), 1221 (m), 1152 (s), 1124 (m), 1068 (m), 1013 (m), 991 (m), 848 (s), 785 (vs), 757 (s), 723 (s), 672 (s), 631 (m), 565 (m), 486 (w), 470 (w), 427 (m). ^{1}H NMR (250.13 MHz, DMSO-d_6, TMS): δ = 12.13 (s, 1H, N–*H*), 8.73 (d, 2H, 4-pyr, C*H*═N), 8.14 (d, 1H, 2-pyr, C*H*═N), 7.71 (d, 2H, 4-pyr), 7.57 (m, 2H, 2-pyr), 7.48 (d, 1H, 2-pyr), 2.32 (s, 3H, CH_3). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ = 162.2, 155.3, 150.1, 148.6, 140.7, 136.2, 131.4, 128.3, 123.8, 121.98, 12.5 ppm. UV-Vis spectrum in CH_3OH [λ_{max}, (ε, L^3 mol^{-1} cm^{-1}), c = 5 × 10^{-5}]: 215 (28 200), 240 (19 100), 293 (27 100), 365 nm (13 900).

Synthesis of (*E*)-*N*′-(pyridin-2-ylmethylene)isonicotinohydrazide (HL^3). Compound HL^3 was synthesized by a procedure similar to the synthesis of HL^1 with 2-pyridinecarbaldehyde (0.242 g, 2.0 mmol). Yield: 80% (0.40 g). Anal. Calc. for $C_{12}H_{10}N_4O$ (M_W = 226.23): C, 63.71; H, 4.46; N, 24.76%. Found: C, 63.74; H, 4.45; N, 24.78%. FT-IR (KBr, cm^{-1}): 3293 (N–H, m, br), 1668 (C═O, vs), 1595 (C═N, w), 1543 (vs), 1463 (s), 1439 (m), 1402 (s), 1343 (m), 1254 (vs), 1219 (s), 1145 (s), 1099 (w), 1063 (m), 992 (m), 951 (m), 849 (s), 784 (vs), 752 (s), 685 (vs), 595 (s), 449 (w). ^{1}H NMR (500 MHz, DMSO-d_6, TMS): δ = 12.26 (s, 1H, N–*H*), 8.81 (d, 2H, 4-pyr, C*H*═N), 8.64 (d, 1H, 2-pyr, C*H*═N), 8.51 (s, 1H, C*H*═N, azomethine), 8.00 (d, 1H, 2-pyr), 7.89 (t, 1H, 2-pyr), 7.82 (d, 2H, 4-pyr), 7.43 (t, 1H, 2-pyr). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 162.4, 153.4, 150.9, 150.6, 149.7, 140.7, 137.4, 125.1, 122.0, 120.6 ppm. UV-Vis spectrum in CH_3OH [λ_{max}, (ε, L^3 mol^{-1} cm^{-1}), c = 5 × 10^{-5}]: 218 (29 500), 273 (20 300), 303 nm (30 800).

Synthesis of $[Mn(L^1)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (1). $MnCl_2{\cdot}4H_2O$ (0.396 g, 2.0 mmol) and potassium dicyanoargentate(I) (0.398 g, 2.0 mmol) were added to a methanol (30 ml) solution of HL^1 (0.30 g, 1.0 mmol), and the resulting solution refluxed gently for 6 h. After cooling, the red solid was filtered off, washed with cooled methanol and dried at 60 °C. Single crystals of **1** were obtained by the thermal gradient method from methanol over 5 days. **Caution!** *Although we have not experienced any problem with the reported compounds in this work, cyanide complexes of metal ions are very toxic. Even a small amount of the product should be handled with care*. Yield: 88% (0.53 g). Anal. Calc. for $C_{21}H_{17}AgClMn_{1.5}N_6O_2$ (M_W = 611.13): C, 41.27; H, 2.80; N, 13.75; Ag, 17.65; Mn, 13.48. Found: C, 41.29; H, 2.81; N, 13.79; Ag, 17.61; Mn, 13.45. FT-IR (KBr, cm^{-1}): 3405 (m), 3275 (m, br), 2159 (vs), 1659 (m), 1612(s), 1596 (m), 1571 (s), 1556 (m), 1508 (vs), 1460 (vs), 1435 (m), 1361 (vs), 1325 (m), 1314 (s), 1196 (w), 1151 (w), 1103 (s), 1014 (vs), 852 (m), 791 (m), 759 (s), 695 (vs), 685 (s), 657 (m), 599 (w), 454 (w). UV-Vis spectrum in CH_3OH [λ_{max}, (ε, L^3 mol^{-1} cm^{-1}), c = 2.5 × 10^{-5}]: 211 (62 400), 240^{sh} (48 000), 278^{sh} (37 000), 369 (53 600), 378 nm (52 900).

Synthesis of $\{[Mn(L^2)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]\cdot CH_3OH\}_n$ (2). Compound **2** was synthesized by a procedure similar to that of compound **1** using HL^2. Dark-brown crystals

of this compound were obtained by the thermal gradient method from methanol over 6 days. Yield: 87% (0.505 g). Anal. Calc. for $C_{16}H_{15}AgClMn_{1.5}N_6O_2\cdot(CH_4O)\cdot(CH_4O)$ (M_W = 581.11): C, 35.14; H, 3.30; N, 14.46; Ag, 18.56; Mn, 14.18. Found: C, 35.12; H, 3.31; N, 14.48; Ag, 18.53; Mn, 14.20%. FT-IR (KBr, cm^{-1}): 3405 (m), 3200 (m, br), 2147 (vs), 1615 (m), 1605 (m), 1593 (s), 1568 (s), 1496 (vs), 1461 (vs), 1445 (s), 1363 (vs), 1310 (s), 1221 (w), 1161 (w), 1137 (m), 1101 (w), 1061 (s), 1044 (m), 1011 (s), 913 (w), 854 (m), 787 (s), 760 (m), 713 (m), 692 (vs), 636 (w), 564 (w), 435 (w). UV-Vis spectrum in CH_3OH [λ_{max}, (ε, L^3 mol^{-1} cm^{-1}), c = 2.5 × 10^{-5}]: 214 (57 400), 238^{sh} (36 200), 279 (21 900), 364 nm (60 100).

Synthesis of $[Mn(L^3)(Cl)(\mu\text{-}NCAgCN)Mn_{0.5}(CH_3OH)]_n$ (3). Compound **3** was synthesized by a procedure similar to that of compound **1** with HL^3 as the ligand. An orange-red precipitate was obtained over 10 days from methanol at 60 °C which was filtered off, washed with cooled methanol and dried at 60 °C. Yield: 76% (0.406 g). Anal. Calc. for $C_{15}H_{13}AgClMn_{1.5}N_6O_2$ (M_W = 535.03): C, 33.67; H, 2.45; N, 15.71; Ag, 20.16; Mn, 15.40. Found: C, 33.70; H, 2.44; N, 15.75; Ag, 20.14; Mn, 15.43%. FT-IR (KBr, cm^{-1}): 3415 (vs, br), 2923 (s), 2165 (vs), 1652 (m), 1634 (s), 1617 (vs), 1595 (s), 1568 (s), 1490 (s), 1464 (vs), 1439 (m), 1384(s), 1364 (vs), 1315 (w), 1224 (w), 1153 (m), 1067 (m), 1012 (m), 929 (w), 853 (w), 764 (w), 708 (m), 635 (m), 538 (w), 433 (w). UV-Vis spectrum in CH_3OH [λ_{max}, (ε, M^{-1} cm^{-1}), c = 2.5 × 10^{-5}]: 216 (51 360), 238^{sh} (37 900), 381 (28 400), 367 nm (54 400).

Table 2 Crystal data and structure refinement for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{42}H_{34}Ag_2Cl_2Mn_3N_{12}O_4$	$C_{34}H_{38}Ag_2C_{l2}Mn_3N_{12}O_6$
M/g mol^{-1}	1222.27	1162.22
Crystal size/mm^3	0.15 × 0.15 × 0.10	0.21 × 0.15 × 0.12
Temperature/K	296(2)	96(2)
θ range/° (completeness)	4.22–64.73 (95.90%)	2.44–63.50 (95.90%)
h; k; l range	±12; −14, 13; −18, 19	±8; ±9; ±20
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	10.7323(8)	7.6594(5)
b/Å	12.8099(10)	8.3378(5)
c/Å	17.3311(13)	18.1442(12)
α/°	90	90.522(3)
β/°	102.411(5)	91.722(3)
γ/°	90	107.291(3)
V/$Å^3$	2327.0(3)	1105.67(12)
Z	2	1
D_{calc}/g cm^{-3}	1.744	1.745
μ/mm^{-1}	14.591	15.345
F(000)	1210	577
Max./min. transm.	0.323/0.218	0.260/0.141
Refl. collected	16 348	10 300
Indep. refl. (R_{int})	3788 (0.0568)	3466 (0.0379)
Data/restraints/parameters	3788/0/347	3466/0/344
Max./min. $\Delta\rho$/e $Å^{-3}$ [a]	0.896/−0.656	0.436/−0.854
R_1/wR_2 [$I > 2\sigma(I)$][b]	0.0485/0.0863	0.0230/0.0590
R_1/wR_2 (all data)[b]	0.0730/0.0941	0.0240/0.0596
Goodness-of-fit on F^2 [c]	1.028	1.021

[a] Largest difference peak and hole. [b] $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]$; w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.

X-ray crystallography

Suitable single crystals were carefully selected under a polarizing microscope and mounted on a loop. *Data collection*: Bruker APEX2 CCD diffractometer (with microfocus tube), Cu-Kα radiation (λ = 1.54178 Å), multilayer mirror monochromator, ω- and ϕ-scan at 296 ± 2 K and 95 ± 2 K, respectively; data collection with Apex2,[44] cell refinement and data reduction with SAINT,[44] experimental absorption correction with SADABS.[45] *Structure analysis and refinement*: The structures of **1** and **2** were solved by direct methods and finally refined by full-matrix least squares on F^2 using the SHELXL-97 program suite.[46] All non-hydrogen positions were refined with anisotropic displacement parameters. All hydrogen atoms in **2** and most of the hydrogen atoms of **1** were found during the refinement. Remaining hydrogen atoms were positioned geometrically (C–H = 0.95 Å for aromatic CH, C–H = 0.98 Å for CH_3) and refined using a riding model (AFIX 43 for aromatic CH, AFIX 33 for CH_3), with $U_{iso}(H) = 1.2U_{eq}(CH)$ and $U_{iso}(H) = 1.5U_{eq}(CH_3)$.

Crystal data and details on the structure refinement are given in Table 2. Graphics were drawn with DIAMOND,[47] and analyses on the intermolecular O–H···Cl-interactions were performed with PLATON for Windows.[48]

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