

*Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary*

SYNTHESIS AND CRYSTAL STRUCTURES OF TWO NEW CYANIDO-BRIDGED $[\text{Mn}^{\text{III}}_5\text{Mo}^{\text{IV}}]$ AND $[\text{Mn}^{\text{III}}_2\text{Au}^{\text{I}}]$ HETEROMETALLIC COMPLEXES

Silviu NASTASE,^a Catalin MAXIM,^a Carine DUHAYON,^{b,c} Jean-Pascal SUTTER^{b,c}
and Marius ANDRUH^{a,*}

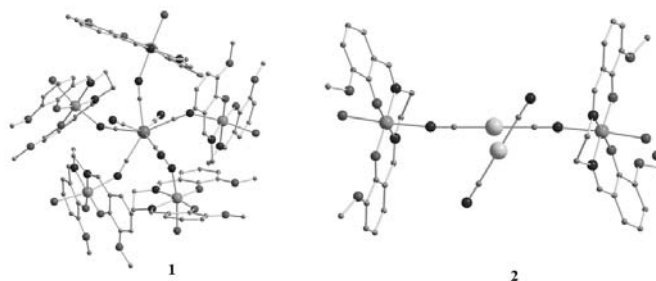
^aInorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, 23 Dumbrava Rosie Str.,
020464 Bucharest, Roumania

^bCNRS ; LCC (Laboratoire de Chimie de Coordination); 205, route de Narbonne, F-31077 Toulouse, France

^cUniversité de Toulouse; UPS, INPT; LCC; F-31077 Toulouse, France

Received February 27, 2013

Two new cyanido-bridged heterometallic complexes, $[\{\text{Mn}(\text{valen})(\text{H}_2\text{O})\}_5[\text{Mo}(\text{CN})_8]\}(\text{ClO}_4)\cdot 12\text{H}_2\text{O}$ **1**; $\{\text{Mn}(\text{valen})(\text{H}_2\text{O})[\text{Au}(\text{CN})_2]\}[\text{Au}(\text{CN})_2]\cdot \text{H}_2\text{O}$ **2**, (H_2valen is the bicompartamental Schiff-base proligand, resulting from the 2:1 condensation of 3-methoxysalicylaldehyde with ethylenediamine) were prepared by reacting the cationic $[\text{Mn}^{\text{III}}(\text{valen})(\text{solvent})_2]^+$ complex with $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{Au}(\text{CN})_2]^-$ building blocks, respectively. The crystallographic investigations revealed the occurrence of a cationic hexanuclear cluster $[\text{Mn}^{\text{III}}_5\text{Mo}^{\text{IV}}]$ in **1** and a trinuclear $[\text{Mn}^{\text{III}}_2\text{Au}^{\text{I}}]$ complex in **2**. The crystal packing of the two compounds is governed by the cooperation of the hydrogen bonds and the aromatic interactions. In the case of compound **2**, aurophilic interactions ($\text{Au}\cdots\text{Au} = 3.395 \text{ \AA}$) were also observed.



INTRODUCTION

Polycyanide complexes are frequently employed as tectons to construct heterometallic oligonuclear or coordination polymers. The huge interest in such systems arises from their magnetic properties given by the strong exchange coupling mediated by the short cyanido bridge.¹ Hence, in the rich family of the cyanide bridged assemblies,

most of the members are constructed from paramagnetic cyanido-complexes (either homo- or heteroleptic).² However, the diamagnetic analogues are also very valuable starting materials that can generate fascinating polynuclear compounds possessing interesting topologies. Among them, $[\text{M}(\text{CN})_8]^{4-}$ ($\text{M} = \text{Mo}^{\text{IV}}, \text{W}^{\text{IV}}$) and $[\text{M}(\text{CN})_2]^-$ ($\text{M} = \text{Ag}^{\text{I}}, \text{Au}^{\text{I}}$) linkers are particularly attractive as building-blocks in designing heterometallic

* Corresponding author: marius.andruh@dnt.ro

complexes.^{3,4} In the first case, the photo-redox properties of the octacyanometallate-type metalloligands along with their coordinative versatility make them ideal precursors for the synthesis of photomagnetic systems (materials that can modify their magnetic properties after light exposure).^{5,6}

Polycyanometallates act as metalloligands towards either naked metal ions (actually solvated) or cationic complexes (the “complex as ligand” strategy).^{3a,b,7} The co-ligands attached to the assembling cation play a crucial role by blocking several coordination sites, thus reducing the dimensionality of the coordination polymers, or inducing the formation of discrete complexes. Manganese(III)–salen-type Schiff base assembling units, denoted as $[\text{Mn}(\text{SB})(\text{solvent})_2]^+$, are among the most often used partners for polycyanido-type complexes, since an apical solvent molecule can be easily replaced by a cyanido ligand belonging to the metalloligand.⁸ In spite of these facilities, few assemblies built from the diamagnetic octacyano- and dicyanometallates and the above mentioned cationic complexes are known.^{9–12} In this paper, we report on two new oligonuclear compounds resulted by assembling $[\text{Mn}(\text{valen})(\text{H}_2\text{O})]^+$ cation with $[\text{Mo}(\text{CN})_8]^{4-}$ units and with $[\text{Au}(\text{CN})_2]^-$ units, respectively [valen²⁻ is a bicompartamental ligand, resulting from the condensation of 2 equivalents of 3-methoxysalicylaldehyde with one equivalent of ethylenediamine].

RESULTS AND DISCUSSION

Description of the crystal structure of $\{[\text{Mn}(\text{valen})(\text{H}_2\text{O})]_5[\text{Mo}(\text{CN})_8]\}(\text{ClO}_4)\cdot 12\text{H}_2\text{O}(\mathbf{1})$

During the self-assembly process between the cationic $[\text{Mn}^{\text{III}}(\text{valen})]^+$ units and the anionic $[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ moieties, in a 1:4 molar ratio, the apical acetonitrile molecule belonging to the manganese(III) precursor is replaced by a nitrogen atom from a cyanido group, leading to a heterobimetallic complex Mn(III)–Mo(IV) (Fig. 1). Curiously, five of the cyanide ligands of the anionic building-block are coordinated to the peripheral $[\text{Mn}(\text{valen})]^+$ fragments, affording the cationic hexanuclear cluster $\{\text{MoMn}_5\}$ along with twelve crystallization water molecules. The charge of the cationic species is counterbalanced by an uncoordinated perchlorate anion. The presence of these ions was also indicated by the IR spectrum of **1** that illustrates vibrations modes characteristic for

both cyanide ($\nu(\text{CN})$: 2103 cm^{-1}) and perchlorate groups ($\nu(\text{ClO}_4)$: 1106 cm^{-1} , 1085 cm^{-1} , 625 cm^{-1}). All five manganese(III) nodes display an elongated octahedral geometry, as expected for Jahn-Teller ions. The valen²⁻ ligand defines the equatorial plane, while the two axial sites are occupied by a water molecule and a nitrogen atom originating from the cyanido bridge. In the $[\text{Mo}(\text{CN})_8]^{4-}$ fragment, molybdenum(IV) ion exhibits a distorted antiprism geometry. No significant differences regarding the bond length formed by the tetravalent metallic node with the two types of cyanido ligands, bridging and terminal, are observed. The bond distances are situated in the 2.155(5)–2.174(5) Å range. Selected bond distances and angles for the two compounds are presented in Table 1.

The packing of the compound **1** in the crystal can be easily predicted up to a certain level and is governed by the self-complementarity of the $[\text{Mn}(\text{valen})(\text{H}_2\text{O})]^+$ moieties, analogously to what was observed with related compounds.^{12–15} The aqua ligand belonging to a cationic entity is hosted through hydrogen bonds by the free compartment from an adjacent unit, generating supramolecular $(\text{valen})\text{Mn}(\text{OH}_2)\cdots(\text{H}_2\text{O})\text{Mn}(\text{valen})$ associations. Two phenolato- and two methoxy oxygen atoms play the role of hydrogen bond acceptors for the apical water molecule. The stability of such supercomplexes is reinforced by the π - π graphite-like stacking interactions occurring between the aromatic rings of the Schiff base. In the case of compound **1**, four of the five $[\text{Mn}(\text{valen})(\text{H}_2\text{O})]^+$ fragments, namely those constructed around the Mn(1), Mn(2), Mn(4), and Mn(5) metallic centres, participate in the formation of such dimeric motifs (Fig. 2). For example, in the supramolecular moiety constructed from the Mn(1)-type mononuclear unit, the O \cdots O distances vary between 2.949 and 3.001 Å and the π - π stacking contacts span from 3.56 Å to 3.95 Å. The intradimer Mn \cdots Mn distance is 5.003 Å. The reason the Mn(3)-Schiff base system does not develop a similar supramolecular aggregate resides in the presence of a crystallization water molecule (O11W) situated in the vicinity of the axial aqua ligand, forming hydrogen bonds (O1E \cdots O11W = 2.778 Å). The geometrical parameters associated to the hydrogen bonds are given in Table 2. The above-mentioned super-assemblies are further interconnected through hydrogen bonds, affording a supramolecular network. The non-covalent interactions are generated by the co-crystallized water molecules, the aqua ligands occupying the

apical positions of the manganese moieties, the perchlorate anions, the nitrogen atoms belonging to the terminal cyanido ligands, and the oxygen atoms

originating from the empty compartment (O_2O_2') of the valen²⁻ ligand. A sequence of this complicated topology is illustrated in Fig. 3.

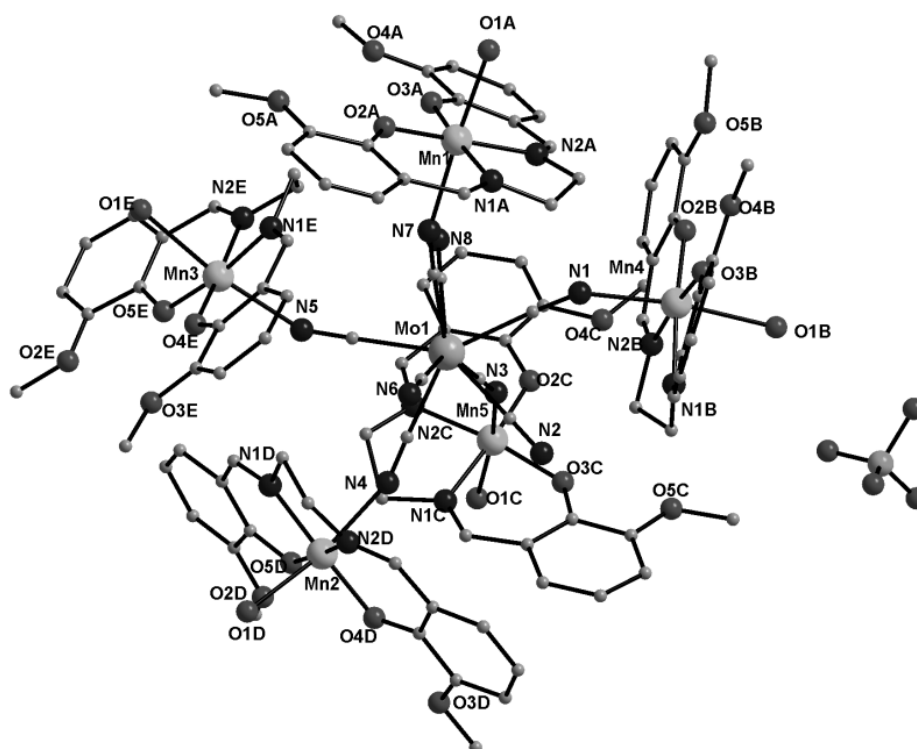


Fig. 1 – Perspective view of the hexanuclear complex **1**, along with the atom numbering scheme (the crystallization water molecules and the hydrogen atoms are omitted for clarity).

Table 1

Selected bond distances (Å) and angles (°) for compounds **1** and **2**

Compound 1							
Mn1–N1A	1.959(7)	Mn3–O1E	2.381(4)	O1A–Mn1–O2A	88.75(14)	N1–Mn4–N2B	86.81(17)
Mn1–N2A	1.986(6)	Mn3–O4E	1.888(4)	O2A–Mn1–O3A	93.36(16)	N2B–Mn4–N1B	82.6(2)
Mn1–O2A	1.878(4)	Mn3–O5E	1.881(3)	O3A–Mn1–N2A	91.6(2)	N1B–Mn4–O1B	84.04(17)
Mn1–O3A	1.864(4)	Mn3–N1E	1.979(4)	N2A–Mn1–N1A	81.8(3)	O1B–Mn4–O3B	88.51(14)
Mn1–O1A	2.290(3)	Mn3–N2E	1.972(4)	N1A–Mn1–N7	86.6(2)	O3B–Mn4–O2B	93.05(16)
Mn1–N7	2.272(4)	Mn3–N5	2.288(4)	N7–Mn1–O3A	92.78(18)	O2B–Mn4–N1	96.09(17)
Mn2–N4	2.265(4)	Mn4–N1	2.242(4)	N4–Mn2–O4D	96.14(16)	N3–Mn5–O3C	92.75(17)
Mn2–O4D	1.881(4)	Mn4–N1B	1.981(5)	O4D–Mn2–O1D	93.93(14)	O3C–Mn5–O1C	89.49(15)
Mn2–O5D	1.876(3)	Mn4–N2B	1.978(4)	O1D–Mn2–O5D	91.24(14)	O1C–Mn5–N1C	85.22(15)
Mn2–O1D	2.319(3)	Mn4–O1B	2.374(4)	O5D–Mn2–N1D	92.57(17)	N1C–Mn5–N2C	82.3(2)
Mn2–N1D	1.981(4)	Mn4–O2B	1.882(4)	N1D–Mn2–N2D	83.46(19)	N2C–Mn5–N3	89.67(19)
Mn2–N2D	1.981(4)	Mn4–O3B	1.877(3)	N2D–Mn2–N4	88.31(17)	N3–Mn5–O2C	97.48(16)
Mn5–N1C	1.981(5)	Mo1–C045	2.155(5)	O1E–Mn3–O5E	86.73(16)	N7–C045–Mo1	176.4(5)
Mn5–N2C	1.990(5)	Mo1–C034	2.160(5)	O5E–Mn3–O4E	93.42(16)	N3–C034–Mo1	179.5(5)
Mn5–O1C	2.334(3)	Mo1–C022	2.163(5)	O4E–Mn3–N5	94.21(16)	N5–C015–Mo1	176.6(4)
Mn5–O2C	1.892(4)	Mo1–C085	2.166(6)	N5–Mn3–N1E	84.66(16)	N4–C022–Mo1	178.3(5)
Mn5–O3C	1.885(4)	Mo1–C066	2.170(6)	N1E–Mn3–N2E	82.12(18)	N8–C066–Mo1	179.0(5)

Table 1 (continued)

Mn5–N3	2.259(4)	Mo1–C070	2.171(7)	N2E–Mn3–O1E	87.91(17)	N2–C070–Mo1	176.5(6)
Mo1–C044	2.156(5)	Mo1–C015	2.174(5)	N1–C044–Mo1	176.6(5)	N6–C085–Mo1	178.1(6)
<i>Compound 2</i>							
Mn1–O2	1.887(5)			O5–Mn1–O2	88.7(2)		
Mn1–O3	1.870(5)			O5–Mn1–O3	89.3(2)		
Mn1–N1	1.977(6)			O3–Mn1–N2	91.9(2)		
Mn1–N2	1.991(6)			N2–Mn1–N3	90.3(3)		
Mn1–N3	2.273(7)			N1–Mn1–N3	88.7(3)		
Mn1–O5	2.337(5)			O2–Mn1–N1	90.9(2)		
C19–Au1	1.990(10)			C20–Au2–C20	180.0		
C20–Au2	1.994(10)			C19–Au1–C19	180.0		
Au1–Au2	3.395						

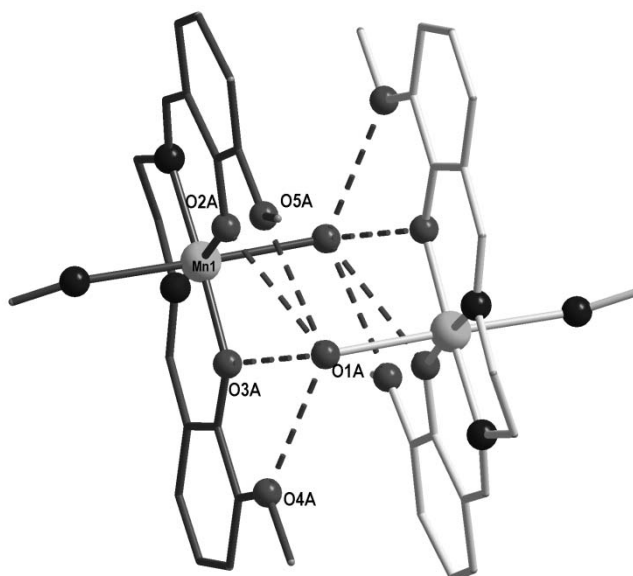


Fig. 2 – Formation of supramolecular dimers in compound 1.

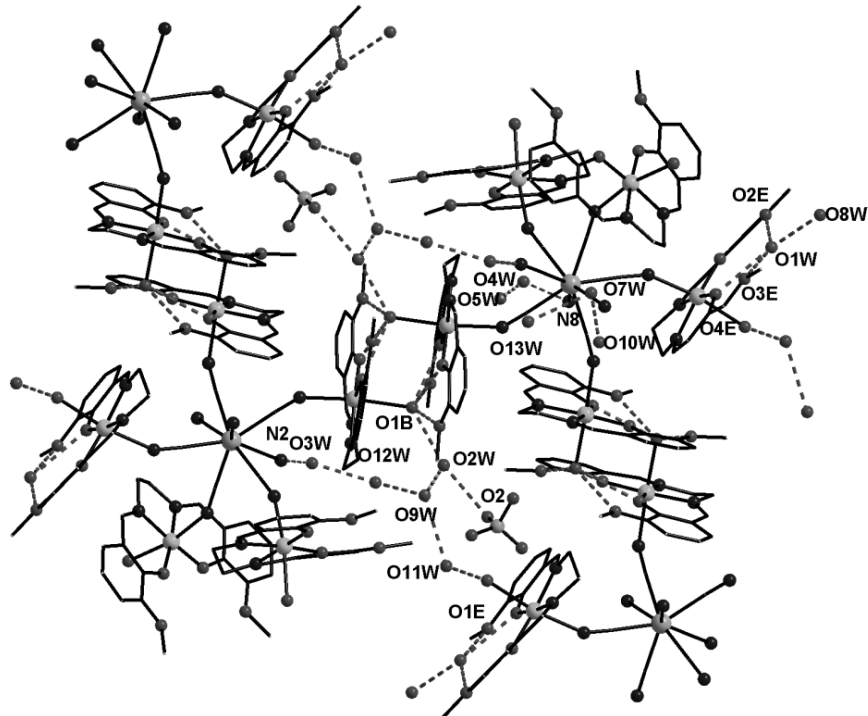


Fig. 3 – Hydrogen bonds in the supramolecular network of compound 1.

Table 2

Geometrical parameters of strong hydrogen bonds in complexes **1** and **2**

D...A	D...A (Å)	D...A	D...A (Å)
<i>Compound 1</i>			
O1D...O3D ⁱ	2.930	O1E...O11W	2.778
O1D...O4D ⁱ	2.892	O9W...O11W ^v	3.015
O1D...O5D ⁱ	2.891	O9W...O2W	2.833
O1D...O2D ⁱ	2.861	O2W...O1B	2.833
O1C...O4C ⁱⁱ	2.999	O2W...O2	3.006
O1C...O2C ⁱⁱ	2.951	O9W...O12W	2.764
O1C...O3C ⁱⁱ	2.868	O3W...O12W	2.705
O1C...O5C ⁱⁱ	2.974	O3W...N2	2.851
O1B...O5B ⁱⁱⁱ	2.982	O4W...N8	2.901
O1B...O2B ⁱⁱⁱ	2.890	O4W...O5W	2.833
O1B...O3B ⁱⁱⁱ	2.832	O13W...O7W	2.887
O1B...O4B ⁱⁱⁱ	2.920	O7W...O10W	2.725
O1A...O4A ^{iv}	2.949	O8W...O1W	2.803
O1A...O4A ^{iv}	2.999	O7W...O2E	2.846
O1A...O2A ^{iv}	3.001	O1W...O3E	2.853
O1A...O5A ^{iv}	2.950	O1W...O4E	2.986
<i>Compound 2</i>			
O5...O6	2.764		
O5...O6 ^{vi}	2.898		
O6...O4 ^{vii}	2.842		
O6...O3 ^{vii}	2.971		
O6...O1 ^{vii}	2.830		
Symmetry operations for complexes 1 ^{i-v} and 2 ^{vi,vii} : ⁱ 1-x, 1-y, -z. ⁱⁱ 1-x, 1-y, -z. ⁱⁱⁱ 1-x, 1-y, 1-z. ^{iv} -x, 2-y, 1-z. ^v -1+x, 1+y, z. ^{vi} 2-x, -0,5 +y, 0,5 -z. ^{vii} x, 1+y, z.			

Description of the crystal structure of $\{[\text{Mn}(\text{valen})(\text{H}_2\text{O})][\text{Au}(\text{CN})_2]\}\{[\text{Au}(\text{CN})_2]\}\cdot\text{H}_2\text{O}(\mathbf{2})$

The crystal structure of compound **2** (Fig. 4) consists of heterotrimeric Mn(III)–Au(I)–Mn(III) species, in which an anionic $[\text{Au}(\text{CN})_2]^-$ spacer connects two mononuclear $[\text{Mn}(\text{valen})(\text{H}_2\text{O})]^+$ units through cyanido bridges. The cationic trimeric assembly co-crystallizes together with an uncoordinated dicyanoaurate(I) complex and a water molecule. The presence of the two coordination modes (bridge and terminal) of the cyanide ligands was confirmed by the IR spectrum of compound **2**. Thus, the $\nu(\text{CN})$ bands specific to the two types of $[\text{Au}(\text{CN})_2]^-$ units occur at 2173 cm^{-1} and 2152 cm^{-1} , and are assigned to the bridging and to the terminal coordination modes of the cyanide anions, respectively.¹⁶ Moreover, the absence of perchlorate ions vibrations also supports the stoichiometry revealed by the crystallographic investigations. Each manganese(III) ion is hexacoordinated, having an axially distorted octahedral geometry. Therefore, the equatorial

positions are occupied by two phenoxo oxygen atoms ($\text{Mn1-O2} = 1.887(5)\text{ \AA}$; $\text{Mn1-O3} = 1.870(5)\text{ \AA}$) and two imine-type nitrogen atoms ($\text{Mn1-N1} = 1.977(6)\text{ \AA}$; $\text{Mn1-N2} = 1.991(6)\text{ \AA}$), respectively. One aqua ligand ($\text{Mn1-O5} = 2.337(5)\text{ \AA}$) and one nitrogen atom from the cyanido bridge ($\text{Mn1-N3} = 2.273(7)\text{ \AA}$) are coordinated into the apical positions. These distances are close to those already reported in our previous papers.¹²⁻¹⁵ The coordination geometry around the gold(I) centres is linear with the NC–Au–CN angles very close to 180° . No significant differences in NC–Au bond distances are observed for the two dicyanoaurate(I) entities ($\text{C19-Au1} = 1.990(10)\text{ \AA}$; $\text{C20-Au2} = 1.994(10)\text{ \AA}$). The $[\text{Au}(\text{CN})_2]^-$ moieties are interconnected through Au...Au contacts ($\text{Au}\cdots\text{Au} = 3.395\text{ \AA}$) (Fig. 5), presenting higher values than those reported in the case of a helical chain constructed from this metalloligand and the cationic $[\text{Mn}(\text{salen})]^+$ building-block ($\text{Au}\cdots\text{Au} = 3.096\text{ \AA}$).¹¹

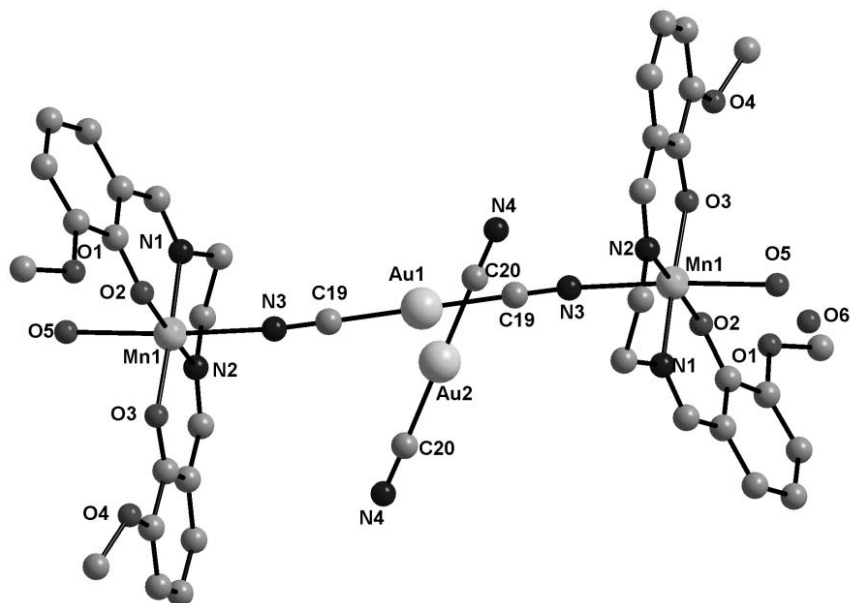


Fig. 4 – Perspective view of the compound **2**, along with the atom numbering scheme (the hydrogen atoms are omitted for clarity).

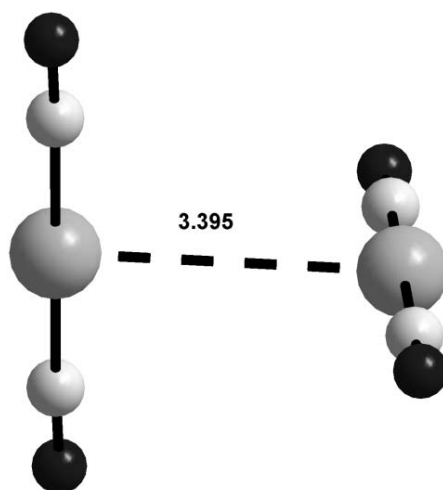


Fig. 5 – Aurophilic interactions in compound **2**.

The crystal packing of compound **2** is governed by three non-covalent forces: hydrogen bonds, π - π stacking interactions, and the above mentioned metallophilic contacts. Thus, the trinuclear $\text{H}_2\text{O}-\text{Mn}(\text{valen})-\text{NC}-\text{Au}-\text{CN}-\text{Mn}(\text{valen})-\text{OH}_2$ assemblies communicate through hydrogen bonds established with the co-crystallized water molecules, as follows: (a) the aqua ligands (O5) from the apical positions of manganese(III) ions are hydrogen bonded to the uncoordinated water molecules (O6 and O6^{vi} ($^{\text{vi}} = 2-x, -0.5 + y, 0.5-z$)); (b) the crystallization O6 molecules are hosted in the $(\text{O}_2\text{O}_2')$ compartment of the $\{\text{Mn}(\text{valen})\}$ entities, with an average $\text{O6}\cdots\text{O}^{\text{vii}}$ distance of 2.881 Å. The propagation of the hydrogen bonds leads to

a ladder-like architecture (Fig. 6). These supramolecular arrangements are parallelly aligned, being interconnected by the linear $[\text{Au}(\text{CN})_2]$ spacer through $\text{Au}\cdots\text{Au}$ contacts, generating a 3-D extended network. The stability of this topology is, once again, reinforced by the π - π graphite-like stacking interactions between the aromatic rings of the Schiff base ligands originating from adjacent $\text{Mn}-\text{Au}-\text{Mn}$ units. The existence of O6 crystallization water molecule in the proximity of apical O5 aqua ligand forming hydrogen bonds explains the absence of supramolecular dimeric motifs present in the case of compound **1**.

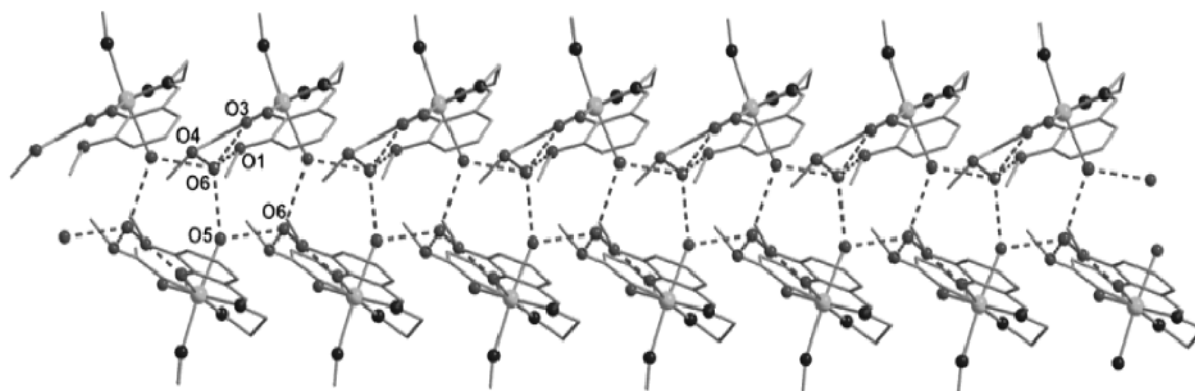


Fig. 6 – Ladder-like architecture in the supramolecular network of compound **2** (see text).

EXPERIMENTAL

Materials and methods

All solvents and chemicals were purchased from commercial sources and used without further purification. The manganese precursor, $[\text{Mn}(\text{valen})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)\cdot\text{CH}_3\text{CN}$, and the molybdenum starting material, $\text{K}_4[\text{Mo}(\text{CN})_8]$, were prepared as described in previous papers.^{12,17}

Synthesis of $\{[\text{Mn}(\text{valen})(\text{H}_2\text{O})]_5[\text{Mo}(\text{CN})_8]\}(\text{ClO}_4)\cdot 12\text{H}_2\text{O}$ **1**

To a solution containing 25 mg (0.048 mmol) of $[\text{Mn}(\text{valen})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)\cdot\text{CH}_3\text{CN}$ dissolved in 20 mL ethanol/water (1:1, v/v) were slowly added 20 mL solution containing 6 mg of $\text{K}_4[\text{Mo}(\text{CN})_8]$ (0.012 mmol) dissolved in the same mixture of solvents. The slow evaporation of the resulted brown solution was performed at room temperature and in the absence of light. The brown-reddish crystals of **1**, suitable for single-crystal X-ray diffraction, were formed within several days, and were isolated by filtration.

Selected IR data (KBr, cm^{-1}): 3415, 2938, 2836, 2103, 1553, 1625, 1251, 1443, 1296, 1106, 1085, 739, 645.

Synthesis

of $\{[\text{Mn}(\text{valen})(\text{H}_2\text{O})][\text{Au}(\text{CN})_2]\}[\text{Au}(\text{CN})_2]\cdot\text{H}_2\text{O}$ **(2)**

A solution containing 29 mg of $[\text{Mn}(\text{valen})(\text{H}_2\text{O})(\text{CH}_3\text{CN})](\text{ClO}_4)\cdot\text{CH}_3\text{CN}$ (0.05 mmol) dissolved in 20 mL acetonitrile/water (1:1, v/v) was mixed with 10 mL solution of potassium dicyanoaurate(I) (0.05 mmol dissolved in the same mixture of solvents). The resulted brown mixture was allowed to stand unperturbed at room temperature and yielded after one week of slow evaporation brown crystals. Selected IR data (KBr, cm^{-1}): 3441, 2928, 2838, 2173, 2152, 1621, 1552, 1441, 1300, 1253, 735.

Physical measurements and X-ray crystallography

The IR spectra (KBr pellets) were recorded on a Bruker Tensor 37 spectrophotometer in the 4000 – 400 cm^{-1} region. The X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with a Mo-K α ($\lambda = 0.71073 \text{ \AA}$) X-ray tube with a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least squares techniques. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELX-97¹⁸ or CRYSTALS¹⁹ crystallographic software packages. The relevant crystallographic data are collected in Table 3.

Table 3

Crystallographic data, details of data collection and structure refinement parameters for compounds **1** and **2**

Compound	1	2
Chemical formula	$\text{C}_{98} \text{H}_{90} \text{Cl Mn}_5 \text{ Mo N}_{18} \text{ O}_{41}$	$\text{C}_{40} \text{H}_{44} \text{Au}_2 \text{ Mn}_2 \text{ N}_8 \text{ O}_{12}$
M (g mol^{-1})	2581.97	1332.62
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Temperature (K)	293(2)	180
Wavelength (\AA)	0.71073	0.71073
Cell parameters		
a (\AA)	18.8282(8)	12.836(3)
b (\AA)	18.9296(8)	6.7892(14)
c (\AA)	19.3635(8)	24.972(5)
α ($^\circ$)	82.831(3)	90.00
β ($^\circ$)	84.271(3)	91.66(3)
γ ($^\circ$)	61.878(3)	90.00
V (\AA^3)	6032.4(4)	2175.2(8)
Z	2	2
D_c (g cm^{-3})	1.421	2.034
μ (mm^{-1})	0.718	7.362

Table 3 (continued)

$F(000)$	2632	1280
Goodness of fit	0.839 (on F^2)	0.998 (on F)
Final R1, wR^2 [$I > n\sigma(I)$]	0.0670; 0.1196 (n=2)	0.0474; 0.0544 (n=2.5)
R1, wR^2 (all data)	0.1794; 0.1514	0.0614; 0.0644
Largest difference peak and hole ($e \text{ \AA}^{-3}$)	0.740; -0.480	3.89; -2.84

CONCLUSIONS

The two new heterobimetallic compounds described in this paper illustrate the ability of the polycyanido complexes to act as metalloligands towards a cationic complex. $[\text{Mn}^{\text{III}}(\text{valen})(\text{solvent})_2]^+$ was chosen as assembling cation. In the “complex as ligand” strategy approached in this study, the easily accessible solvent molecule coordinated into the apical position of the manganese(III) ion was replaced by a cyanide bridge belonging to diamagnetic $[\text{Mo}(\text{CN})_4]^{4-}$ and $[\text{Au}(\text{CN})_2]^-$ units. The self-assembly process with the octacyanometallate-type precursor led to a hexanuclear $[\text{Mn}^{\text{III}}_3\text{Mo}^{\text{IV}}]$ cluster (**1**), whereas the reaction with the dicyanoaurate(I) complex afforded a trimeric $[\text{Mn}^{\text{III}}_2\text{Au}^{\text{I}}]$ entity together with a co-crystallized $[\text{Au}(\text{CN})_2]^-$ moiety (**2**). The crystal packing of the two compounds is governed by the cooperation of the hydrogen bonds and the aromatic interactions. In the case of compound **2**, aurophilic interactions were also observed.

Appendix A. Supplementary data

CCDC 926695 and 926696 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

REFERENCES

- (a) V. Gadet, T. Mallah, I. Castro, M. Verdaguer, *J. Am. Chem. Soc.*, **1992**, *114*, 9213; (b) M. Verdaguer, *Polyhedron*, **2001**, *20*, 1115, and references therein; (c) J.-N. Rebilly, T. Mallah, *Struct. Bonding*, **2006**, *122*, 103; (d) D. Visinescu, C. Desplanches, I. Imaz, V. Bahers, R. Pradhan, F. Villamena, P. Guionneau, J.-P. Sutter, *J. Am. Chem. Soc.*, **2006**, *128*, 10202.
- See, for example: M. Ohba, N. Fukita, H. Ōkawa, *J. Chem. Soc., Dalton Trans.*, **1997**, 1733. (b) V. Marvaud, C. Decroix, A. Scuilier, C. Guyard-Duhayon, J. Vaissermann, F. Gonnet, M. Verdaguer, *Chem. –Eur. J.*, **2003**, *9*, 1677; (c) V. Marvaud, C. Decroix, A. Scuilier, F. Tuyères, C. Guyard-Duhayon, J. Vaissermann, J. Marrot, F. Gonnet, M. Verdaguer, *Chem. –Eur. J.*, **2003**, *9*, 1692; (d) R. J. Parker, L. Spiccia, S.R. Batten, J.D. Cashion, G.D. Fallon, *Inorg. Chem.*, **2001**, *40*, 4696; (e) R.J. Parker, L. Spiccia, B. Moubaraki, K.S. Murray, D.C.R. Hockless, A.D. Rae, A.C. Willis, *Inorg. Chem.*, **2002**, *41*, 2489; (f) C. Paraschiv, M. Andruh, Y. Journaux, Z. Žak, N. Kyritsakas, L. Ricard, *J. Mater. Chem.*, **2006**, *16*, 2660; (g) M. Hernandez-Molina, J. Long, L.-M. Chamoreau, J.-L. Cantin, J. von Bardeleben, V. Marvaud, *New J. Chem.*, **2009**, *33*, 1301; (h) S. Tanase, M. Andruh, N. Stanica, C. Mathonière, G. Rombaut, S. Golhen, L. Ouahab, *Polyhedron*, **2003**, *22*, 1315; (i) C. Maxim, L. Sorace, P. Khuntia, A.M. Madalan, V. Kravtsov, A. Lascialfari, A. Caneschi, Y. Journaux, M. Andruh, *Dalton Trans.*, **2010**, *39*, 4838; (j) D. Visinescu, A.M. Madalan, M. Andruh, C. Duhayon, J.-P. Sutter, W. Van den Heuvel, L.F. Chibotaru, *Chem. –Eur. J.*, **2009**, *15*, 11808; (k) S. Tanase, F. Tuna, P. Guionneau, T. Maris, G. Rombaut, C. Mathonière, M. Andruh, O. Kahn, J.-P. Sutter, *Inorg. Chem.*, **2003**, *42*, 1625.
- See, for example: (a) P. Przychodzeń, T. Korzeniak, R. Podgajny, B. Sieklucka, *Coord. Chem. Rev.*, **2006**, *250*, 2234; (b) B. Sieklucka, R. Podgajny, P. Przychodzeń, T. Korzeniak, *Coord. Chem. Rev.*, **2005**, *249*, 2203; (c) H. Zhao, M. Shatruk, A.V. Prosvirin, K.R. Dunbar, *Chem. –Eur. J.*, **2007**, *13*, 6573; (d) J.M. Herrera, A. Bleuzen, Y. Dromzée, M. Julve, F. Lloret, M. Verdaguer, *Inorg. Chem.*, **2003**, *42*, 7052; (e) F.-T. Chen, D.-F. Li, S. Gao, X.-Y. Wang, Y.-Z. Li, L.-M. Zheng, W.-X. Tang, *Dalton Trans.*, **2003**, 3283; (f) H.H. Ko, J.H. Lim, H.S. Yoo, J.S. Kang, H.C. Kim, E.K. Koh, C.S. Hong, *Dalton Trans.*, **2007**, 2070; (g) D. Visinescu, J.-P. Sutter, C. Duhayon, A.M. Madalan, B. Jurca, M. Andruh, *J. Coord. Chem.*, **2011**, *64*, 93.
- See, for example: (a) C. Paraschiv, M. Andruh, S. Ferlay, M.W. Hosseini, N. Kyritsakas, J.M. Planeix, N. Stanica, *Dalton Trans.*, **2005**, 1195; (b) C.J. Shorrocks, B.Y. Xue, P.B. Kim, R.J. Batchelor, B.O. Patrick, D.B. Leznoff, *Inorg. Chem.*, **2002**, *41*, 6743; (c) D.B. Leznoff, B.Y. Xue, R.J. Batchelor, F.W.B. Einstein, B.O. Patrick, *Inorg. Chem.*, **2001**, *40*, 6026; (d) D.B. Leznoff, B.Y. Xue, C.L. Stevens, A. Storr, R.C. Thompson, B.O. Patrick, *Polyhedron*, **2001**, *20*, 1247; W. Dong, L.N. Zhu, Y.Q. Sun, M. Liang, Z.Q. Liu, D.Z. Liao, Z.H. Jiang, S.P. Yan, P. Cheng, *Chem. Commun.*, **2003**, 2544; (e) E. Colacio, F. Lloret, R. Kivekas, J. Ruiz, J. Suarez-Varela, M.R. Sundberg, R. Uggla, *Inorg. Chem.*, **2003**, *42*, 560; (f) C. Maxim, F. Tuna, A.M. Madalan, N. Avarvari, M. Andruh, *Cryst. Growth & Des.*, **2012**, *12*, 1654.
- A. Bleuzen, V. Marvaud, C. Mathonière, B. Sieklucka, M. Verdaguer, *Inorg. Chem.*, **2009**, *48*, 3453.
- C. Maxim, C. Mathonière, M. Andruh, *Dalton Trans.*, **2009**, 7805.
- Several excellent reviews on heterometal cyano-bridged complexes have been published: (a) K.R. Dunbar, R.A. Heintz, *Progr. Inorg. Chem.*, **1997**, *45*, 283; (b) M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuilier, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier,

- F. Villain, *Coord. Chem. Rev.*, **1999**, 190-192, 1023; (c) M. Ohba, H. Ōkawa, *Coord. Chem. Rev.*, **2000**, 198, 313; (d) J. Černák, M. Orendáč, I. Potočníák, J. Chomič, A. Orendáčová, J. Skoršepa, A. Feher, *Coord. Chem. Rev.*, **2002**, 224, 51; (e) O. Kahn, J. Larionova, L. Ouahab, *Chem. Commun.*, **1999**, 945; (f) M. Shatruk, C. Avendano, K.R. Dunbar, *Progr. Inorg. Chem.*, **2009**, 56, 155.
8. H. Miyasaka, A. Saitoh, S. Abe, *Coord. Chem. Rev.*, **2007**, 251, 2622, and references therein.
 9. H.H. Ko, J.H. Lim, H.S. Yoo, J.S. Kang, H.C. Kim, E.K. Koh, C.S. Hong, *Dalton Trans.*, **2007**, 2070.
 10. P. Przychodzen, K. Lewinski, M. Bałanda, R. Pełka, M. Rams, T. Wasiutynski, C. Guyard-Duhayon, B. Sieklucka, *Inorg. Chem.*, **2004**, 43, 2967.
 11. Y. Feng, Y. Guo, Y.O. Yang, Z. Liu, D. Liao, P. Cheng, S. Yan, Z. Jiang, *Chem. Commun.*, **2007**, 3643
 12. S. Nastase, F. Tuna, C. Maxim, C.A. Muryń, N. Avarvari, R.E.P. Winpenny, M. Andruh, *Cryst. Growth & Des.*, **2007**, 7, 1825.
 13. S. Nastase, C. Maxim, F. Tuna, C. Duhayon, J.-P. Sutter, M. Andruh, *Polyhedron*, **2009**, 28, 1688.
 14. S. Nastase, C. Maxim, M. Andruh, J. Cano, C. Ruiz-Pérez, J. Faus, F. Lloret, M. Julve, *Dalton Trans.*, **2011**, 40, 4898.
 15. C.D. Ene, S. Nastase, C. Maxim, A.M. Madalan, F. Tuna, M. Andruh, *Inorg. Chim. Acta*, **2010**, 363, 4247.
 16. G. Socrates, "Infrared and Raman Characteristic Group Frequencies", John Wiley and Sons Ltd., Chichester, 2001.
 17. J.G. Leipoldt, L.C.D. Bok, P.J. Cilliers, *Z. Anorg. Allg. Chem.*, **1974**, 409, 343.
 18. G.M. Sheldrick, *SHELX-97: Programs for Crystal Structure Analysis*, Release 97-2, Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1998.
 19. P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *J. Appl. Crystallogr.*, **2003**, 36, 1487.

