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Polyoxometallate–Thiosemicarbazone Hybrid Compounds

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New polyoxometallate–thiosemicarbazone hybrid compounds derived from pyridine-2-carbaldehyde thiosemicarbazone (HL), pyridine-2-carbaldehyde N^4-methylthiosemicarbazone (HL′) and their copper(II) complexes have been synthesized. Their formulae are $(H_2L)_4(Mo_8O_{26})(H_2O)_4$ (**1**), $[\{(HL)_2H\}_2(Mo_6O_{19})]\cdot C_3H_6O\cdot 0.24H_2O$ (**2**), $[(H_2L')_4(HL')_2(Mo_8O_{26})(H_2O)_2]$ (**3**), $[\{Cu(L)\}_4(Mo_8O_{26})(H_2O)_4]$ (**4**), $[\{Cu(HL)(H_2O)\}_2(Mo_8O_{26})]$ (**5**), $[\{Cu(L')\}_4(Mo_8O_{26})(H_2O)_{14}]$ (**6**), $Na_6[\{Cu(HL')(H_2O)_2\}_4(\{Cu(L')\}_2\{Mo_{36}O_{116}(H_2O)_{12}\})]\cdot 20H_2O$ (**7**), $[\{Cu(HL)\}_2\{Cu(L)\}_4\{Mo_{36}O_{112}(H_2O)_{16}\}(H_2O)_{26}]$ (**8**), $[\{Cu(HL')\}_4\{Mo_{36}O_{112}(H_2O)_{16}\}(H_2O)_{30}]$ (**9**) and $[\{Cu(HL)(H_2O)\}_2\{Cu(L)S\}_2(H_4V_{10}O_{28})]_n\cdot 6nH_2O$ (**10**). Compounds **1–6** contain octamolybdate $[Mo_8O_{26}]^{4-}$ or hexamolybdate $[Mo_6O_{19}]^{2-}$ anions together with $(H_2L)^+$, $(H_2L')^+$, $[Cu(L)]^+$, $[Cu(HL)(H_2O)]^{2+}$ or $[Cu(L')]^+$ cations and neutral thiosemicarbazone molecules. The polyoxometallates (POMs) in **7–9** are $[Mo_{36}O_{116}(H_2O)_{12}]^{16-}$, $\{Mo_{36}\}$ (**7**), and $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$, $\{Mo_{36}'\}$ (**8**, **9**). $[Cu(HL')]^{2+}/[Cu(L')]^+$ and $[Cu(HL)]^{2+}/[Cu(L)]^+$ units complete the respective lattices. Compound **10** consists of decavanadate anions $(H_4V_{10}O_{28})^{2-}$ and thiosemicarbazone-copper(II) entities forming 1D $[\{Cu(HL)(H_2O)\}_2\{Cu(L)S\}_2(H_4V_{10}O_{28})]_n$ structures connected through the hydrogen bonds of chains of water molecules. Structures of **2**, **5**, **7** and **10** have been characterized by single-crystal X-ray diffraction and other instrumental techniques (infrared, thermal analysis, electron paramagnetic resonance, nuclear magnetic resonance, magnetic susceptibility and mass spectrometry) were used to analyse all the compounds presented herein. The structural parameters of more than 1000 published thiosemicarbazone-metal complexes have been used to determine some of the differences between metal complexes that contain anionic and neutral thiosemicarbazone ligands.

Introduction

In recent years, the chemistry of polyoxometallates (POMs) has generated considerable interest due to the interesting properties of these compounds and their applications in material science, catalysis and medicine.[1] According to their composition, POMs can be classified as isopolyoxometallates, $[M_mO_y]^{n-}$, composed of metal and oxygen, or heteropolyoxometallates, $[X_xM_mO_y]^{n-}$, if at least one heteroatom is present in the anion structure.[2] Organic cations can be used to obtain organic–inorganic hybrid compounds linking them to POMs through hydrogen bonds or functionalizing the polyanions by covalent grafting the organic molecules. Functionalization of POMs allows compounds to be obtained with new properties and applications, for example, in catalysis and material science.[3] In other cases, metal–organic frameworks are covalently bonded to an oxygen of the POM, originating metalorganic–inorganic hybrid materials.[4] Copper(II) cations, due to the wide range of geometries that they can adopt, are very good centres for coordinating organic molecules and POMs.[5]

On the other hand, thiosemicarbazone molecules can be coordinated to a wide range of metal cations through different binding modes.[6] Both, that is, the thiosemicarbazone and their metal derivatives, specifically copper complexes,[7] show interesting optical, analytical, magnetic and biological properties. Pyridine-2-carbaldehyde thiosemicarbazone and some N^4-alkyl derivatives joined to their metal complexes have been extensively investigated.[8]

Although POMs and thiosemicarbazones or their metal complexes have been thoroughly studied, as far as we are aware there is no structural evidences of any compound that combines both of them. Only one attempt to obtain a hybrid compound with the $[Mo_7O_{24}]^{6-}$ polyanion and pyridine-2-carbaldehyde thiosemicarbazone-copper(II) entities

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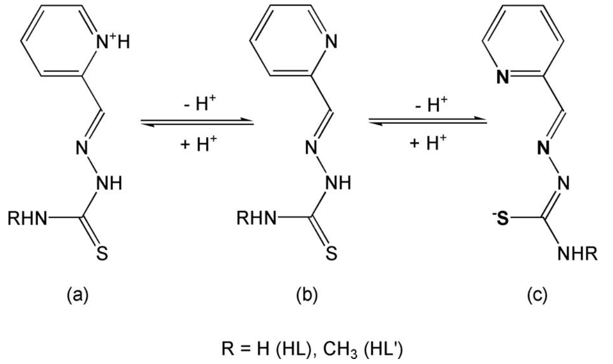
has been reported; the proposed product was the molybdate derivative $[(CuL)_2(MoO_4)]\cdot H_2O$.[8h] Recently, the structures of hybrid Lindqvist semicarbazone-molybdenum(VI) compounds have been published.[9]

This paper reports the synthesis and spectroscopic properties of 10 hybrid compounds with POMs and thiosemicarbazones or thiosemicarbazone-copper(II) fragments: $[(H_2L)_4(Mo_8O_{26})(H_2O)_4]$ (**1**), $[\{(HL)_2H\}_2(Mo_6O_{19})]\cdot C_3H_6O\cdot 0.24H_2O$ (**2**), $[(H_2L')_4(HL')_2(Mo_8O_{26})(H_2O)_2]$ (**3**), $[\{Cu(L)\}_4(Mo_8O_{26})(H_2O)_4]$ (**4**), $[\{Cu(HL)(H_2O)\}_2(Mo_8O_{26})]$ (**5**), $[\{Cu(L')\}_4(Mo_8O_{26})(H_2O)_{14}]$ (**6**), $Na_6[\{Cu(HL')(H_2O)_2\}_4(\{Cu(L')\}_2\{Mo_{36}O_{116}(H_2O)_{12}\})]\cdot 20H_2O$ (**7**), $[\{Cu(HL)\}_2\{Cu(L)\}_4\{Mo_{36}O_{112}(H_2O)_{16}\}(H_2O)_{26}]$ (**8**), $[\{Cu(HL')\}_4\{Mo_{36}O_{112}(H_2O)_{16}\}(H_2O)_{30}]$ (**9**) and $[\{Cu(HL)(H_2O)\}_2\{Cu(L)S\}_2(H_4V_{10}O_{28})]_n\cdot 6nH_2O$ (**10**). The crystal structures of compounds **2**, **5**, **7** and **10** have been resolved. The magnetic properties of **5** and **7** together with a discussion of the structural parameters useful for distinguishing between neutral and deprotonated thiosemicarbazone ligands (see Scheme 1) present in complex systems are also reported.



Scheme 1. (a) The cationic thiosemicarbazone, H_2L^+, (b) the neutral molecule, HL and (c) the thiolate form of the anionic ligand coordinated to copper(II) ions. Atoms represented in bold are the chelating centres of the ligand.

Results and Discussion

Synthesis

Octamolybdate and hexamolybdate derivatives were obtained when reactions were carried out in organic solvents. In these reactions, products containing the octamolybdate anion were always collected as a powder, independent of the stoichiometry of the starting compounds. Slow evaporation of the acetone mother liquors yielded single crystals of the hexamolybdate derivative once the octamolybdate-containing powder solid had been filtered off. We did not obtain any compound with the hexamolybdate anion by using water as solvent. Nevertheless, we obtained complexes with octamolybdate anions at pH = 2–4. The anion with 36 molybdenum atoms was the predominant POM at lower pH values.

During the experimental work, we used a great variety of preparative strategies. Some of them have not been described in this manuscript, like those carried out in inert dry atmospheres. However, we were not able to attain molybdenum complexes of NNS tridentate thiosemicarbazone ligands derived from pyridine.[10] We also tried to prepare thiosemicarbazone-copper(II)–vanadium(IV) heteronuclear magnetic systems, however, compound **10** was obtained. Unfortunately, we have not yet found a reproducible method of synthesizing this complex.

Crystal Structures of Compounds 2, 5, 7 and 10

The structure of compound **2** is composed of a hexamolybdate anion surrounded by four thiosemicarbazone molecules (Figure 1). The crystal structure is completed by different solvent molecules. The hexamolybdate anions exhibit a Lindqvist-type structure in which six MoO_6 subunits are linked through oxygen atoms to form the $[Mo_6O_{19}]^{2-}$ anion. Each MO_6 octahedron has a common vertex in the centre of the cluster (O_c), a terminal oxygen atom (O_t) and four bridging oxygen atoms (O_b). Thus, the M–O bond lengths can be classified in three groups: Mo–O_t 1.679(3)–1.683(3) Å, Mo–O_b 1.890(3)–1.980(3) and Mo–O_c 2.3157(4)–2.3332(4) Å. The values of the O_c–Mo–O_t and Mo–O_b–Mo angles are approximately 180 and 117°, respectively.

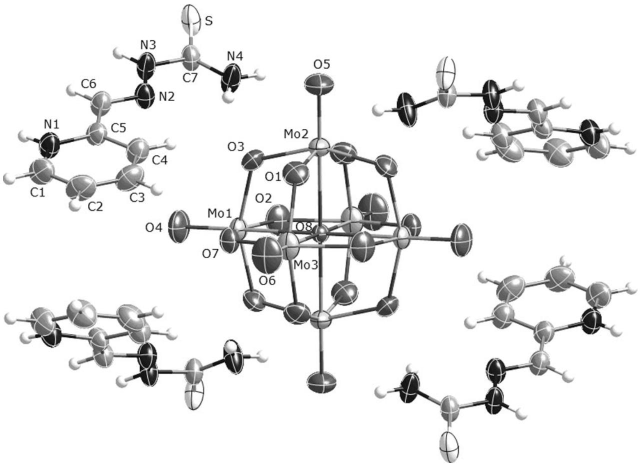


Figure 1. Crystal structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level.

Four thiosemicarbazone molecules surround each one of the hexamolybdate ions, as can be seen in Figure 1. To achieve a neutral balance of charges, two of these molecules must behave as H_2L^+ cations. However, the H1 atoms (pyridinic hydrogen atoms) were refined with an occupancy of 0.50, and there are no structural differences between the neutral and cationic forms of the thiosemicarbazones present in the crystal. Thus, we propose the formation of hydrogen-bridged $(HL)_2H^+$ pairs with the protons disordered around a two-fold axis. N1 and N2 are *anti* with respect to the C1–C2 bond. Such a conformation diverges from that observed for other compounds containing H_2L^+ cations.[11] However, structures containing neutral HL with different degrees of hydration ($HL\cdot nH_2O$, n = 1–2.25)[8o,12] present varied conformational behaviour with respect to the

$C_{pyridinic}$–$C_{azomethinic}$ moiety.[13] This suggests that the conformation of the thiosemicarbazone molecules is largely influenced by the steric constraints of the crystal lattice. On the other hand, N2 and S are *anti* with respect to the N3–C7 bond, which is in good agreement with the conformations of all the structures of HL or H_2L^+ free molecules known to date. The pyridinium planes of the thiosemicarbazones around the polyoxoanion form an angle of 76.7°. Selected hydrogen bonds and π–π stacking are discussed in the Supporting Information and Table S1.

The network comprises alternate channels along the [001] direction formed by hydrogen-bonded thiosemicarbazone molecules (see Figure 2). The largest of these channels (5.9 × 8.6 Å) are occupied by polyoxomolybdates. A molecule of acetone and 0.24 molecules of water per cluster complete the crystal structure. These solvent molecules are placed in the smallest channels (3.8 × 4.0 Å).

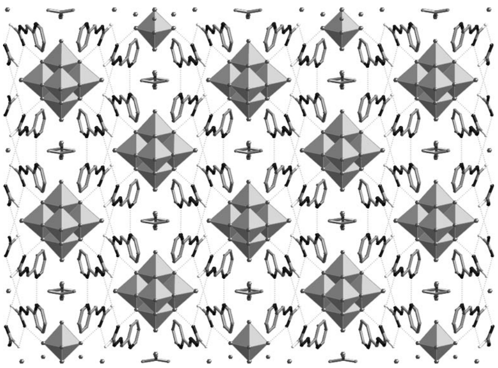


Figure 2. View of the lattice of **2** along the [001] direction. Hydrogen atoms have been omitted for clarity. Hydrogen bonds are drawn with dotted line.

The crystal structure of compound **5** contains motifs that incorporate two thiosemicarbazone-copper(II) entities linked to an β-octamolybdate anion (see Figure 3). The β-octamolybdate anions have eight MoO_6 octahedral subunits linked through some of their oxygen atoms to form the $[Mo_8O_{26}]^{4-}$ cluster. There are three different groups of molybdenum atoms in the POM: four molybdenum atoms have two *cis* terminal oxygen atoms, two molybdenum atoms only have one terminal oxygen and two molybdenum atoms have one terminal oxygen and another linked to a copper atom. There are five different classes of oxygen atoms: terminal oxygen atoms (O_t), oxygen atoms linked to copper atoms ($O_{\mu Cu}$) and oxygen atoms linked to two ($O_{\mu 2}$), three ($O_{\mu 3}$) or four ($O_{\mu 4}$) different molybdenum atoms. Thus, the corresponding groups of M–O bond lengths in **5** are Mo–O_t 1.686(4)–1.704(4) Å, Mo–$O_{\mu Cu}$ 1.747(4) Å, Mo–$O_{\mu 2}$ 1.753(4)–2.206(4) Å, Mo–$O_{\mu 3}$ 1.948(4)–2.360(4) Å and Mo–$O_{\mu 4}$ 2.152(4)–2.486(4) Å.

The coordination around the copper centre adopts a distorted square-pyramidal topology (τ = 0.01).[14] The pyridinic and azomethinic nitrogen atoms and the sulfur of pyridine-2-carbaldehyde thiosemicarbazone [Cu1–N1, Cu1–N2, Cu1–S1: 2.022(5), 1.941(5), 2.299(2) Å] and the POM oxygen [Cu1–O1: 1.942(4) Å] form the basal plane. The apical position is occupied by the oxygen of the water molecule [Cu1–O14: 2.289(6) Å]. Intermolecular hydrogen bonds form between the thiosemicarbazone ligand and the POM, as represented in Figure 4 The shortest distance between two copper atoms is 5.818 Å.

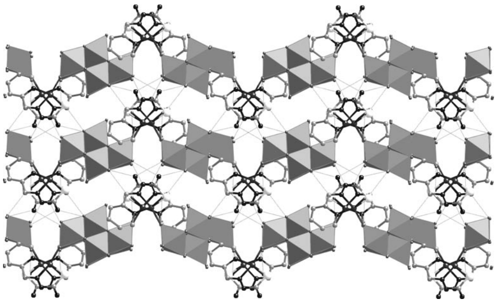


Figure 4. View of the crystal structure of **5** along the [001] direction. Hydrogen atoms have been omitted for clarity. Hydrogen bonds are drawn with a dotted line.

The structure of compound **7** is formed by two thiosemicarbazone-copper(II) entities, $[Cu(L')]^+$, linked to a large POM, $[Mo_{36}O_{116}(H_2O)_{12}]^{16-}$, $\{Mo_{36}\}$. Some views of it are given in Figure 5. Two sodium atoms act as a bridge between two $\{Mo_{36}\}$ units to generate a 1D chain, $[(Na_2\{Cu(L')\}_2\{Mo_{36}O_{116}(H_2O)_{12}\})^{12-}]_n$ (Figure 6). The crystal structure is completed by four thiosemicarbazone-copper(II) entities, $[Cu(HL')(H_2O)_2]^{2+}$, four sodium atoms and

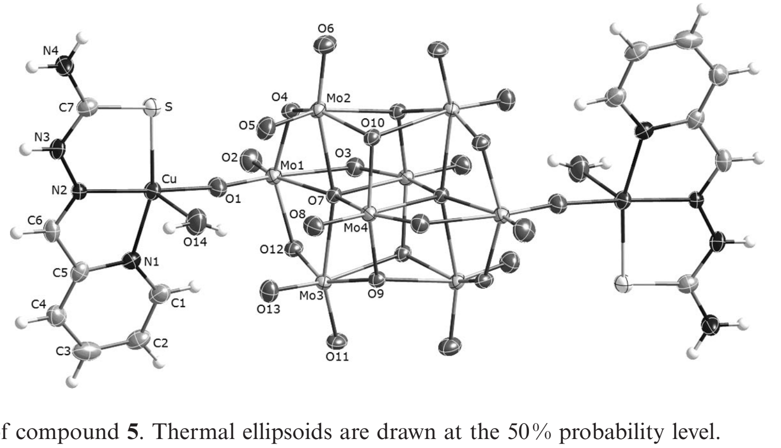
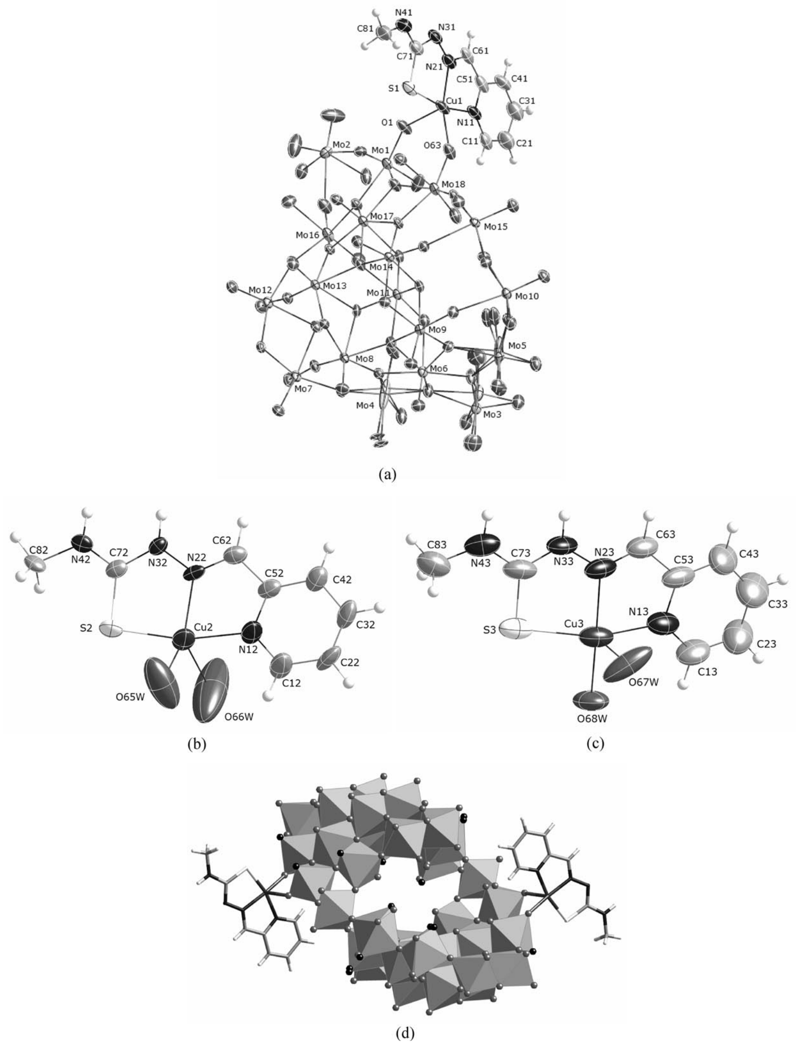


Figure 3. Crystal structure of compound **5**. Thermal ellipsoids are drawn at the 50% probability level.



(a)

(b)

(c)

(d)

Figure 5. Crystal structures of the $\{Mo_{18}\}$ asymmetric unit (a) and thiosemicarbazone-copper(II) entities 2 (b) and 3 (c) of compound **7**. Thermal ellipsoids are drawn at the 50% probability level. The $[\{Cu(L')\}_2Mo_{36}O_{116}(H_2O)_{12}]^{14-}$ fragment in which the oxygen atoms of the water molecules in $\{Mo_{36}\}$ are represented in black (d).

20 water of crystallization molecules. The different chains are connected intermolecularly through π–π stacking between thiosemicarbazone ligands coordinated to Cu1 and hydrogen bonds between POM, thiosemicarbazone ligands and water molecules. The asymmetric unit of $\{Mo_{36}\}$, $[Mo_{18}O_{58}(H_2O)_6]^{8-}$, $\{Mo_{18}\}$, is constructed from 16 MoO_6 octahedra and two MoO_7 pentagonal bipyramids (see Table S2).

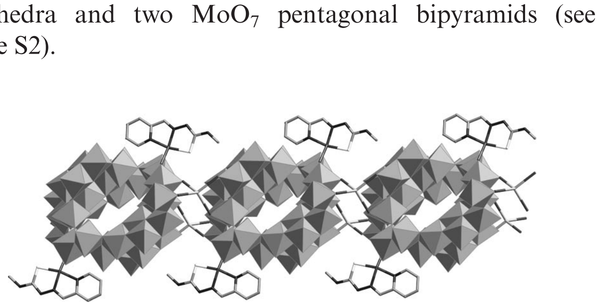


Figure 6. 1D $[(Na_2\{Cu(L')\}_2\{Mo_{36}O_{116}(H_2O)_{12}\})^{12-}]_n$ chain of compound **7**. Hydrogen atoms have been omitted for clarity.

The $\{Mo_{36}\}$ unit found in **7** has an internal channel of approximately 5.1 × 7.1 Å. It is very similar to other previously reported Mo_{36} POMs of formulae $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ and $[Mo_{36}O_{112}(H_2O)_{14}]^{8-}$, named here as $\{Mo_{36}'\}$ and $\{Mo_{36}''\}$, respectively.[15] In spite of the existence of structures formed by the coordination[16] or condensation[17] of organic frameworks with $\{Mo_{36}'\}$, this is the first structure with a metalorganic entity linked to this kind of Mo_{36} POM. On other occasions some of the oxo groups of $\{Mo_{36}'\}$ can be replaced by NO, originating a different POM, $[Mo_{36}O_{108}(NO)_4(H_2O)_{16}]^{12-}$, $\{Mo_{36}'''\}$.[18]

In $\{Mo_{18}\}$ there are six different types of oxygen atoms (Table 1): terminal oxygen atoms of oxo groups (O_t), terminal oxygen atoms of water molecules (OW_t), oxygen atoms linked to copper atoms ($O_{\mu Cu}$) and oxygen atoms linked to two ($O_{\mu 2}$), three ($O_{\mu 3}$) or four ($O_{\mu 4}$) different molybdenum atoms. Thus, the M–O bond lengths can be classified in six groups: Mo–O_t 1.61(8)–1.86(6) Å, Mo–OW_t

2.14(4)–2.52(8) Å, Mo–$O_{\mu Cu}$ 1.729(5)–1.743(5) Å, Mo–$O_{\mu 2}$ 1.722(10)–2.368(4) Å, Mo–$O_{\mu 3}$ 1.864(5)–2.275(5) Å and Mo–$O_{\mu 4}$ 2.063(5)–2.370(4) Å.

Table 1. Polyhedra types present in the $\{Mo_{18}\}$ asymmetric unit of **7**.[a]

Topology	Number of oxygen atoms O_t	$O_{\mu 2}$	$O_{\mu 3}$	$O_{\mu 4}$	Molybdenum atoms
PBP	1	1	4	1	Mo6, Mo17
Oh	3	1	3	0	Mo1, Mo3, Mo5, Mo18
Oh	2	4	0	0	Mo2, Mo7, Mo10, Mo12, Mo15
Oh	2	2	2	0	Mo4, Mo16
Oh	1	2	2	1	Mo8, Mo9, Mo13, Mo14
Oh	0	2	2	2	Mo11

[a] O_t: terminal oxygen, terminal water molecule or oxygen linked to a copper atom. $O_{\mu 2}$, $O_{\mu 3}$ and $O_{\mu 4}$: oxygen linked to two, three and four molybdenum atoms, respectively.

There are two kinds of thiosemicarbazone-copper(II) entities present in **7**. In one of them, $[Cu(L')]^+$, Cu1 is coordinated to a deprotonated ligand and two oxygen atoms of the POM. The coordination sphere around the copper centre is a distorted square pyramid ($\tau = 0.07$).[14] The pyridinic and azomethinic nitrogen atoms and the sulfur of pyridine-2-carbaldehyde N^4-methylthiosemicarbazone [Cu1–N11, Cu1–N21, Cu1–S11: 1.994(9), 1.962(6), 2.253(3) Å] and a POM oxygen [Cu1–O63: 1.954(4) Å] form the basal plane. The apical position is occupied by the other oxygen of the POM [Cu1–O1: 2.233(6) Å]. The other thiosemicarbazone-copper(II) entities, $[Cu(HL')(H_2O)_2]^{2+}$, contain a copper atom in a coordination polyhedra of square-pyramidal symmetry with τ[14] values of 0.38 and 0.10 for Cu2 and Cu3, respectively. The pyridinic and azomethinic nitrogen atoms and the sulfur of pyridine-2-carbaldehyde N^4-methylthiosemicarbazone [Cu2–N12, Cu2–N22, Cu2–S12: 2.023(8), 1.941(8), 2.275(3) Å]/[Cu3–N13, Cu3–N23, Cu3–S13: 2.009(10), 1.955(9), 2.301(4) Å] and the oxygen of a water molecule [Cu2–O65W: 2.087(14) Å]/[Cu3–O68W: 1.965(9) Å] form the basal planes, whereas the oxygen of other water molecules [Cu2–O66W: 2.21(3) Å]/[Cu3–O67W: 2.223(13) Å] assume the axial positions. The shortest distance found between two copper centres Cu1···Cu1# is 3.904(2) Å (#: $-x + 2, -y - 1, -z + 1$).

The structure of compound **10** is made up of chains (Table 2). These chains are formed by two thiosemicarbazone-copper(II) entities, $[Cu(HL)(H_2O)]^{2+}$, linked to a decavanadate ion $[H_4V_{10}O_{28}]^{2-}$ and a centrosymmetric $[\{Cu(L)(S)\}_2]^{2-}$ dimer (Figure 7). The decavanadate anion is composed of 10 VO_6 distorted octahedra linked through some of their oxygen atoms. The asymmetric unit of decavanadate, $[H_2V_5O_{14}]^-$, has different types of vanadium atoms, as can be seen in Table S3, and six different classes of oxygen atoms: terminal oxygen atoms of oxo groups (O_t), oxygen atoms linked to copper atoms ($O_{\mu Cu}$), oxygen atoms of hydroxo groups ($OH_{\mu 2}$) linked to two vanadium atoms and oxygen atoms linked to two ($O_{\mu 2}$), three ($O_{\mu 3}$) or six ($O_{\mu 6}$) different vanadium atoms. Thus, the M–O bond lengths can be classified in six groups: V–O_t 1.587(6)–1.606(7) Å, V–$O_{\mu Cu}$ 1.599(4) Å, V–$OH_{\mu 2}$ 1.817(6)–1.939(5) Å, V–$O_{\mu 2}$ 1.675(5)–2.069(5) Å, V–$O_{\mu 3}$ 1.922(6)–2.062(5) Å and V–$O_{\mu 6}$ 2.118(5)–2.248(4) Å.

Table 2. Polyhedra types present in the $[H_2V_5O_{14}]^-$ asymmetric unit of **10**.[a]

Topology	Number of oxygen atoms O_t	$O_{\mu 2}$	$O_{\mu 3}$	$O_{\mu 6}$	Vanadium atoms
Oh	1	2	2	1	V1, V2
Oh	1	4	0	1	V3, V5
Oh	0	2	2	2	V4

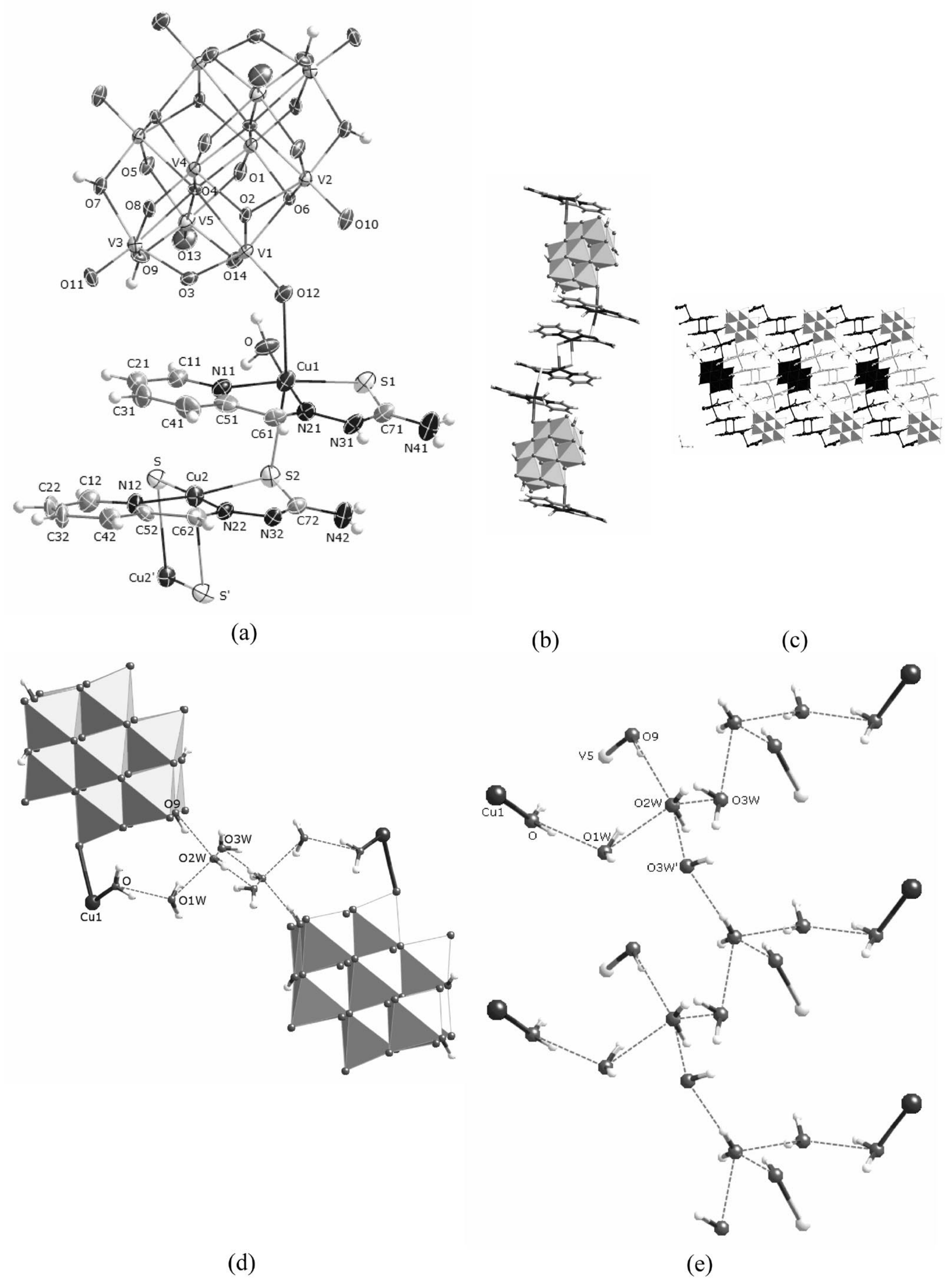
[a] O_t: terminal oxygen or oxygen linked to copper atom. $O_{\mu 2}$: O or OH linked to two vanadium atoms. $O_{\mu 3}$ and $O_{\mu 6}$: oxygen linked to three and six vanadium atoms, respectively.

There are two different types of thiosemicarbazone-copper(II) entities in **10**: the $[Cu(HL)(H_2O)]^{2+}$ entity 1, wich contains a thiosemicarbazone neutral ligand, and the $[Cu(L)(S)]^-$ entity 2, with a deprotonated ligand. The geometry of the copper coordination sphere in entity 1, Cu1, is an elongated distorted octahedron. The equatorial plane is formed by the pyridinic and azomethinic nitrogen atoms and the sulfur of the thiosemicarbazone ligand and an oxygen of a water molecule [Cu1–N11, Cu1–N21, Cu1–S1, Cu1–O: 2.021(7), 1.952(7), 2.254(3), 1.963(6) Å] and the axial positions are occupied by an oxygen of the POM and the sulfur of the thiosemicarbazone ligand of entity 2 [Cu1–O12, Cu1–S2: 2.617(5), 3.179(3) Å]. The donor atom set around Cu2 acquires a distorted square pyramidal topology with $\tau = 0.28$.[14] The basal plane is formed by pyridinic and azomethinic nitrogen atoms and the sulfur of pyridine-2-carbaldehyde thiosemicarbazone and the sulfur of S^{2-} [Cu2–N12, Cu2–N22, Cu2–S2, Cu2–S^{xi}: 2.020(7), 1.962(7), 2.266(3), 2.229(3) Å (xi: $-x + 2, -y + 1, -z$)]. The apical position is occupied by the sulfur of the other S^{2-} group [Cu2–S: 2.783(2) Å].

The spatial arrangement of the chains is stabilized by many hydrogen bonds between the thiosemicarbazone ligands, decavanadate ions and water molecules (Figure 7). In fact, the water molecules form chains perpendicular to the decavanadate–thiosemicarbazone-copper(II) chains and act as linkers between them.

Comparative Study of the Structural Features of Complexes with Neutral or Anionic Thiosemicarbazone Ligands

A decade ago, a comparative structural study of 17 metal complexes coordinated to pyridine-2-carbaldehyde thiosemicarbazone containing either a neutral or anionic ligand was published.[19] The results obtained in this study showed that some structural parameters (C7–S bonding distance, M···N3 and N2···C7 non-bonding distances and M–N2–N3, N2–N3–C7, S–C7–N3 and S–C7–N4 angles) are useful for distinguishing between anionic and neutral coordinated ligands. We have now enlarged this study to all complexes with a metal centre coordinated to any thiosemicarbazone or bis-thiosemicarbazone ligand compiled by the Cam-



(a) (b) (c)

(d) (e)

Figure 7. (a) Asymmetric [{Cu(HL)(H_2O)}{Cu(L)S}($H_4V_{10}O_{28}$)] unit of compound **10**. Thermal ellipsoids are drawn at the 50% probability level. (b) View of the [{Cu(HL)(H_2O)}$_2${Cu(L)S}$_2${$H_4V_{10}O_{28}$}]$_n$ chain. (c) The crystal structure of **10** along the [010] direction in which the [{Cu(HL)(H_2O)}$_2${Cu(L)S}$_2$($H_4V_{10}O_{28}$)]$_n$ chains (black and light gray) are connected by several hydrogen bonds to water molecules (gray). (d) and (e) show in detail the chain of water molecules and hydrogen bonds. Hydrogen bonds are drawn with a dotted line.

bridge Crystallographic Data Centre (CCDC) upto 2009 (more than 1000 complexes with around 1300 metal–thiosemicarbazone structural fragments). For a better understanding of the influence of the thiosemicarbazone ligand and the metal centre, we have divided this study into four different groups, establishing new ranges for the previously mentioned parameters (Table 3).

From the results shown in Table 3 and Figure S2, it is clear that the M···N3 distance and M–N2–N3 angle are unsuitable parameters for distinguishing between anionic and neutral coordinated thiosemicarbazone ligands because both ranges overlap in all cases. The S–C7–N3 and S–C7–N4 angles are clearly different for copper complexes with tridentate thiosemicarbazones, CuL_3 versus $CuHL_3$. How-

Table 3. Ranges of the structural parameters considered (L: deprotonated ligand; HL: neutral ligand).

	CuL$_3$[a]	CuHL$_3$[a]	CuL$_x$[b]	CuHL$_x$[b]	ML$_{py3}$[c]	MHL$_{py3}$[c]	ML$_x$[d]	MHL$_x$[d]
C7–S	1.71–1.77	1.69–1.72	1.71–1.79	1.68–1.72	1.71–1.79	1.67–1.72	1.70–1.80	1.67–1.72
M···N3	2.88–2.99	2.86–2.93	2.86–3.00	2.86–3.00	2.85–3.05	2.87–3.36	2.84–3.29	2.86–3.10
N2···C7	2.20–2.28	2.31–2.36	2.20–2.28	2.31–2.39	2.20–2.29	2.31–2.37	2.19–2.31	2.31–2.39
M–N2–N3	118–126	115–122	115–127	111–122	120–127	118–122	115–127	111–123
N2–N3–C7	110–115	116–121	110–115	116–122	109–117	116–122	108–118	116–123
S–C7–N3	123–128	120–123	122–129	120–124	122–130	120–125	120–132	119–126
S–C7–N4	113–121	120–124	113–122	120–124	113–121	119–125	112–121	119–124

[a] Copper coordinated to any tridentate thiosemicarbazone (CuL$_3$: 111 fragments; CuHL$_3$: 36 fragments). [b] Copper coordinated to any thiosemicarbazone or bis-thiosemicarbazone (CuL$_x$: 192 fragments; CuHL$_x$: 57 fragments). [c] Any metal coordinated to any tridentate pyridine-2-carbaldehyde thiosemicarbazone (ML$_{py3}$: 317 fragments; MHL$_{py3}$: 86 fragments). [d] Any metal coordinated to any thiosemicarbazone or bis-thiosemicarbazone (ML$_x$: 1067 fragments; MHL$_x$: 232 fragments).

Table 4. Thiosemicarbazone-copper structural parameters in compounds **5**, **7** and **10** compared with the same parameters for CuL$_3$ versus CuHL$_3$ entities.

Compound Fragment	**5** Cu(HL)	**7** Cu1(L′)	**7** Cu2(HL′)	**7** Cu3(HL′)	**10** Cu1(HL)	**10** Cu2(L)	CuL$_3$	CuHL$_3$
C7–S	1.70	1.73	1.70	1.72	1.71	1.75	1.71–1.77	1.69–1.72
N2···C7	2.31	2.25	2.31	2.31	2.32	2.24	2.20–2.28	2.31–2.36
N2–N3–C7	117.9	112.8	117.5	117.5	115.8	113.9	110–115	116–121
S–C7–N3	121.3	124.4	120.0	121.4	121.2	123.2	123–128	120–123
S–C7–N4	122.1	119.0	122.3	122.8	120.0	118.9	113–121	120–124

ever, this distinction is less clear for different metal ions or numbers of chelating centres in the ligand. Nevertheless, note that S–C7–N3 is bigger than S–C7–N4 for compounds with anionic ligands. The most outstanding parameters are the C7–S bond length, the N2···C7 distance and the N2–N3–C7 angle. The lone-pair electron on N3 in complexes with an anionic ligand induces a decrease in the N2–N3–C7 angle and the N2···C7 distance. Compounds with neutral thiosemicarbazones present a double-bond thione character for the C7–S thioamide group, which diminishes in the thiolate form of the anionic deprotonated ligands and thus the C7–S distance is longer in the latter.

Table 4 allows the C7–S bonding distances, N2···C7 nonbonding distances and N2–N3–C7, S–C7–N3 and S–C7–N4 angles to be verified for all thiosemicarbazone-copper fragments present in compounds **5**, **7** and **10** and a comparison with the corresponding data given in Table 3 for the CuL$_3$ and CuHL$_3$ systems. In all cases the values in Table 4 agree well with the expected values.

Thermogravimetric Analyses

The thermal stability of compounds **1**–**9** between 20 and 700 °C was analysed by thermogravimetric analysis (TGA), as can be seen in Figures S3–S11. The thermal decomposition curves of compounds **1**–**3** show two different steps. The first step corresponds to the loss of solvent molecules: the weight loss upto 110 °C in **1** (exp. 3.5%; calcd. 3.6%) and **3** (exp. 4.6%; calcd. 1.5%) is due to the evaporation of water molecules. In the case of **2**, the loss of water and acetone molecules ends at 190 °C and is concomitant with the beginning of ligand pyrolysis (exp. 5.3%; calcd. 3.7%). The second stage corresponds to the pyrolysis of thiosemicarbazone molecules: the weight loss of compounds **1** (exp. 48%; calcd. 40%) and **2** (exp. 41%; calcd. 43%), both of them with H_2L^+, begins at 110 and 190 °C and ends at 580 and 550 °C, respectively. Compound **3**, with N^4-methyl-substituted thiosemicarbazones, suffers this mass loss between 135 and 480 °C (exp. 35%; calcd. 48%).

The TG curves of **4** and **6** exhibit two stages of weight loss, however, the thermogram of **5** presents three steps, two of them practically overlapping. The first step is attributed to the loss of water molecules: this step begins at 20 °C and continues until 225 °C for compound **4** (exp. 3.0%; calcd. 3.2%; in fact, two steps can be differentiated at 30–110 °C and 110–230 °C), 95 °C for **5** (exp. 2.6; calcd. 2.1) and 110 °C for **6** (exp. 4.9%; calcd. 10.2%). The second stage is associated with thiosemicarbazone thermolysis: experimental weight loss of 28% for **4** (230–400 °C), 22% for **5** (95–355 °C) and 28% for **6** (216–470 °C).

The thermal decomposition of **7**–**9** can be divided into two steps. The first stage for each of them is associated with the dehydration of crystallization and coordinated water molecules: mass loss from 20 to 137 °C for **7** (exp. 8.9%; calcd. 9.3%), to 315 °C for **8** (exp. 10.0%; calcd. 10.2%) and to 105 °C for **9** (exp. 11.0%; calcd. 11.7%). Above these temperatures, compound **7** has a mass loss between 137 and 375 °C (exp. 17.0%; calcd. 16.7%), which can be attributed to the pyrolysis of the organic ligands together with the reorganization of POM $[Mo_{36}O_{116}]^{16-}$ to $[Mo_{36}O_{108}]$ or the partial formation of MoO_3 and Cu. A mass increase is observed from 360 to 400 °C (exp. 3.1%), which could be due, at least in part, to the formation of CuO. The TG curve of **8** also shows the same processes from 315 to 455 °C (exp. 16%) and, after that, CuO formation (exp. 6.4%). In the case of **9** it is only possible to appreciate one step from 200 to 400 °C, associated with organic ligand loss and POM reorganization, originating CuO and [$Mo_{36}O_{108}$] (exp. 13.4%).

In the case of compounds **1**, **3**, **5** and **7**–**9**, the amount of inorganic residue at the end of the thermal treatment was enough to perform X-ray diffraction measurements. Two different patterns were obtained. The maxima appearing in the diffraction of the residues of **1** and **3** agree with the reflections of MoO_3 (JCPDS No. 76-1003). In the case of samples of copper compounds, in addition to the MoO_3 phase, maxima are observed that have been assigned to the triclinic form of $CuMoO_4$ (JCPDS No. 85–1530, see Figure S12). Note that decomposition of the metalorganic hybrids yields this mixed oxide as a result of the short diffusion distance between the cations whereas with the ceramic method longer times and temperatures are needed to obtain the mixed oxide.[20] However, a detailed discussion of the last stage is difficult due to the coexistence of pyrolysis, oxidative and combination processes. As a general comment valid for all the studied compounds, oxidation to CuO follows the initial formation of metallic Cu (see the increase in weight in the TGs of compounds **4**, **5**, **7** and **8** in the 300–400 °C range). Finally, CuO combines with MoO_3 to give $CuMoO_4$. There is no evidence of the presence of Cu, CuO, CuS, $CuCO_3$, Cu_2O or Cu_2S in the final residues.

DSC measurements showed that all the chemical processes above 250 °C are exothermic.

Infrared Data

The IR spectra of compounds **1**–**10** exhibit the typical bands of thiosemicarbazone and thiosemicarbazone-copper(II) complexes. Absorptions between 3500 and 3200 cm^{-1} correspond to the stretching modes of the NH and NH_2 groups. Compounds with the HL′ ligand show bands at around 2950 cm^{-1} due to the vibration of CH_3 terminal groups. Intense bands above 1620 cm^{-1} present in the spectra of compounds **1**–**3**, with non-coordinated ligands, appear displaced to approximately 1600 cm^{-1} in compounds **4**–**10**, which contain thiosemicarbazone ligands complexed to copper ions. These bands can be attributed to $\nu(C=N)_{azomethinic}$, $\nu(C=N)_{pyridinic}$ and $\delta(NH_2)$ modes.[8i] Signals present between 1600 and 1000 cm^{-1} can be assigned to thioamide I–III bands and δ(C–C) and δ(C–H) modes of the pyridine ring. IR bands of thiosemicarbazone ligands present in the 1000–550 cm^{-1} range are sometimes hidden behind the intense bands of the POM, which will be described later. In the region of 700–400 cm^{-1} there are bands that can be attributed to δ(C–H), δ(N–H), γ(C–C–C/N) and $\nu(Cu–N_{azomethine})$ vibrations.

Some absorptions that appear between 1000 and 550 cm^{-1} in the spectra of compounds **1**–**10** correspond to polyoxometallate ions, as can be seen in Table S4. Each compound shows one or two bands in the region of 1000–880 cm^{-1} due to $\upsilon(M–O_t)$ and, at lower wavenumbers, υ(M–O–M) modes.

Compound **2**, in addition to thiosemicarbazone and hexamolybdate IR bands, exhibits absorptions due to acetone crystallization molecules: $\nu(CH_3)$ at 2961 and ν(C=O) at 1715 cm^{-1}.

Nuclear Magnetic Resonance

The ^1H NMR spectroscopic data for compounds **1**–**3** can be seen in the Exp. Sect. These spectra have the same signals as those of their corresponding free neutral molecules, HL[21] and HL′.[22] The spectra only exhibit signals corresponding to the HL and HL′ neutral forms although organic fragments in compounds **1**–**3** are neutral and/or cationic in the solid state. This could be due to the fact that the pyridinium hydrogen present in the solid state of H_2L^+ and $H_2L'^+$ is very acidic and so, in DMSO solution, is lost to give HL (**1** and **2**) and HL′ (**3**).

Moreover, the ^1H NMR spectrum of **2** shows signals typical of the methyl groups of the acetone molecules present in the crystal network, just as we mentioned in the structural section.

Electron Paramagnetic Resonance

Compounds **4**–**9** were characterized by X- and Q-band EPR spectroscopy. The spectra of **4** and **6** seem to be inverted axial spectra with large signal widths that are greater for the apparent perpendicular contributions. They fit well to axial tensors with *g* values of $g_\parallel = 2.035$, $g_\perp = 2.118$ (**4**) and $g_\parallel = 2.039$, $g_\perp = 2.120$ (**6**). Both the widths and the shapes of the signals are characteristic of magnetic coupled systems of close copper(II) ions without good exchange pathways. If the angle formed by the magnetically nonequivalent chromophores is close to 90°, as the spectra suggest, the approximate values for the components of the molecular *g* tensor corresponding to a system with a $d_{x^2-y^2}$ ground state would be $g_\parallel = 2.20$ and $g_\perp = 2.04$. The spectra of **5** and **8** are also very similar. They have been fitted assuming orthorhombic signals with the following *g* values: $g_1 = 2.217$, $g_2 = 2.077$, $g_3 = 2.057$ (**5**) and $g_1 = 2.217$, $g_2 = 2.076$, $g_3 = 2.057$ (**8**). The signals are thin enough to evidence a reasonably good magnetic exchange between the chromophores. The spectrum of **9** is broad and complex. It shows the presence of hyperfine coupling, the origin of which is not clear, and the presence of impurities cannot be discarded. However, a good fit was not attained for this spectrum. The *g* values for compound 7 are $g_\parallel = 2.170$ and $g_\perp = 2.056$. None of the spectra reported herein exhibit remarkable changes on lowering the temperature from 298 to 4 K, in good agreement with the presence of weak magnetic interactions. The *g* values of all these compounds are similar to those described for other hybrid metalorganic POM systems containing copper(II) ions.[23,24]

Magnetic Properties

Plots of molar susceptibility (χ_m) and $\chi_m T$ versus T for compounds **5** and **7** are presented in Figure 8. The magnetic measurements obey the Curie–Weiss law at temperatures higher than 20 K for **5** and 60 K for **7**. The Weiss temperatures are +0.2 K (**5**) and –0.1 K (**7**). The experimental C_m values are 0.83 and 1.909 $\mathrm{cm^3\,K\,mol^{-1}}$ for **5** and **7**, respectively. The measurements on compound **5** gave curves typical of ferromagnetic behaviour, whereas those for 7 are characteristic of antiferromagnetic coupling.

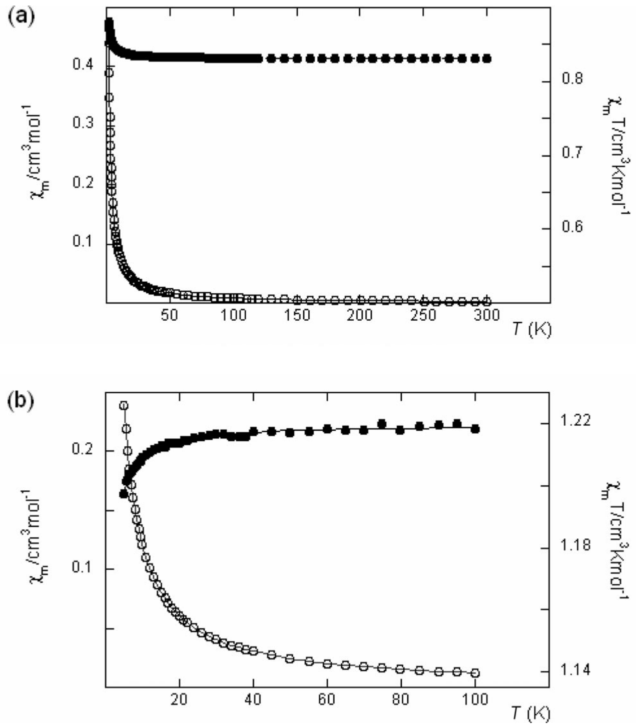


Figure 8. Thermal variation of molar susceptibility (○○○) and $\chi_m T$ (●●●) for (a) **5** and (b) **7**. Solid lines represent the best fit.

Taking into account the structures of these complexes (Figure 3 for **5** and see the π–π stacking for **7** in Figure S1b), we fitted the susceptibility data of both compounds by the expression given by Bleaney and Bowers for copper(II) dinuclear compounds[25] derived from $H = -2JS_1S_2$, see Eq. (1). The best least-squares fitting was obtained from the parameters J/k = +0.26 K (**5**) and –0.17 K (**7**) and the g values calculated for **5** and **7** are 2.104 and 2.08, respectively.

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3+\exp\left(\frac{-2J}{kT}\right)}\right] \qquad (1)$$

Conclusions

The first hybrid compounds containing POMs and thiosemicarbazone molecules or their copper(II) complexes have different structural arrangements. The type of POM depends on the reaction conditions (solvent, pH, etc.). The organic or metalorganic fragments of the hybrid compounds can be covalently bonded to POMs (complexes **5**, **7** and **10**) or not (complex **2**). Nevertheless, in all cases, intermolecular forces, hydrogen bonds or π–π stacking, are very important for stabilizing the crystal networks. As proof, compound **10** has a chain of water molecules that links two different $[\{Cu(HL)(H_2O)\}_2\{Cu(L)S\}_2(H_4V_{10}O_{28})]_n$ chains.

Attempts to obtain NNS thiosemicarbazone-molybdenum(VI) complexes were unsuccessful.

The ranges of some structural parameters that allow neutral and anionic forms of thiosemicarbazone ligands to be distinguished were determined. These structural parameters are the C7–S and N2···C7 distances and N2–N3–C7, S–C7–N3 and S–C7–N4 angles. These parameters could be useful for verifying the interactions of thiosemicarbazones with macromolecules or structurally complex systems like those reported herein.

Experimental Section

Materials: Sodium molybdate dihydrate, copper(II) perchlorate hexahydrate, oxidovanadium(IV) sulfate, hydrochloric acid, perchloric acid, sodium hydroxide, acetone and ethanol were purchased from commercial sources and used as received. HL, $(H_2L)Cl\cdot H_2O$, HL′, $[MoO_2(acac)_2]$ and $[Cu(HL)(ox)(H_2O)]$ were synthesized according to previously reported methods.[8m,11a,26]

CAUTION: *Perchlorate salts are potentially explosive. Although we have not experienced any accident following the methods described below, it is strongly recommended to handle only small amounts.*

Physical Measurements: Measurements of pH were made using a CRISON micropH 2002 instrument. Microanalyses were performed with a LECO CHNS-932 analyser. FAB$^+$ mass spectrometry data were obtained with a Micromass AutoSpec spectrometer. Thermogravimetric measurements were performed with a Netzsch STA 449C instrument. Crucibles containing 20 mg of sample were heated at 10 °C min^{-1} in a dry air atmosphere. IR spectra were recorded on samples prepared as KBr pellets in the 4000–400 cm^{-1} region with a Nicolet Impact 410 FTIR spectrophotometer. ^{1}H NMR studies were performed with [D$_6$]DMSO solutions of the compounds at room temperature with a Varian UNITY INOVA 400 MHz spectrometer. The proton assignment is based on the labelling presented in Figure 1. X-band EPR spectra were recorded with a Bruker EMX spectrometer equipped with a standard Oxford continuous-flow cryostat. Q-band measurements were taken with a Bruker ESP300 spectrometer equipped with a Bruker BNM 200 gaussmeter and a Hewlett–Packard 5352B microwave frequency counter to fit the magnetic field and the frequency inside the cavity. The simulation of the EPR spectra was carried out by using the SimFonia program (WINEPR SimFonia v1.25, Bruker Analytische Messtecnik GmßH, 1996). Magnetic measurements of powdered samples were carried out in the temperature range 5–300 K using a Quantum Design MPMS-7 SQUID magnetometer operating at a magnetic field of 0.1 T. Diamagnetic corrections were estimated from Pascal tables.

Preparation of Compounds 1–10

Compounds 1 and 2: A solution of $[MoO_2(acac)_2]$ (0.163 g, 0.5 mmol) in acetone was added to an acetone solution of HL (0.090 g, 0.5 mmol). The reaction mixture was stirred and 2 h later the yellow precipitate of **1** was filtered off, washed with acetone and dried under vacuum (0.0293 g, 21 %). The mother liquors of the reaction were placed in a beaker covered with holed parafilm. After a few days, dark-green crystals of **2** suitable for X-ray analysis were obtained. Compound **1** can be also synthesized following a general procedure for the attainment of octamolybdate derivatives.[27] An aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.194 g, 0.8 mmol) was acidified with four drops of HCl (37%) and small solid portions of $(H_2L)Cl·H_2O$ (0.094 g, 0.4 mmol) were added to the mixture with vigorous stirring. After 2 h, the yellow precipitate of **1** was filtered off, washed with water, ethanol and acetone and dried under vacuum; yield of **1**: 0.1845 g, 93%.

1: IR (KBr): $\tilde{\nu}$ = 3379 (br m), 3172 (m), 1624 (s), 1588 (m), 1524 (s), 1456 (m), 1381 (w), 1357 (m), 1291 (m), 1246 (m), 1128 (m), 1097 (w), 947 (s), 909 (w, sh), 901 (s), 883 (w), 848 (m), 706 (br m), 668 (br m), 549 (w), 528 (m), 473 (w), 452 (w) and 429 (w) cm^{-1}. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 11.61 (br. s, 1 H, N3-H), 8.56 (d, ^3J = 4.4 Hz, 1 H, 1-H), 8.32 (br. s, 1 H, N4-H), 8.27 (d, ^3J = 8.0 Hz, 1 H, 4-H), 8.14 (br. s, 1 H, N4-H), 8.09 (s, 1 H, 6-H), 7.82 (m, 1 H, 3-H), 7.37 (m, 1 H, 2-H) ppm. $C_{28}H_{44}Mo_8N_{16}O_{30}S_4$ (1980.51): calcd. C 17.0, H 2.2, N 11.3, S 6.5; found C 17.2, H 2.7, N 10.9, S 6.4.

2: IR (KBr): $\tilde{\nu}$ = 3444 (w), 3323 (m), 3252 (m), 3169 (m), 3088 (m), 2961 (m), 1715 (w), 1618 (s), 1587 (m), 1533 (s), 1469 (m), 1419 (m), 1358 (m), 1279 (m), 1249 (m), 1121 (m), 1090 (m), 1068 (m), 959 (vs), 881 (m), 798 (s), 631 (m), 554 (w), 455 (w) and 426 (w) cm^{-1}. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 11.65 (br. s, 1 H, N3-H), 8.56 (d, ^3J = 4.9 Hz, 1 H, 1-H), 8.37 (br. s, 1 H, N4-H), 8.28 (d, ^3J = 8.0 Hz, 1 H, 4-H), 8.18 (br. s, 1 H, N4-H), 8.08 (s, 1 H, 6-H), 7.82 (m, 1 H, 3-H), 7.37 (m, 1 H, 2-H), 2.08 (s, 1.5 H $CH_{3,acetone}$) ppm. $C_{28}H_{40.48}Mo_6N_{16}O_{20.24}S_4$ (1664.95): calcd. C 22.4, H 2.5, N 13.5, S 7.7; found C 22.5, H 2.8, N 13.4, S 7.6.

Compound 3: An aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.194 g, 0.8 mmol) was acidified with four drops of HCl (37%) and small solid portions of $(H_2L')Cl$[28] (0.099 g, 0.4 mmol) were added to the mixture with vigorous stirring. After 2 h, the yellow precipitate of **3** was filtered off, washed with water, ethanol and acetone and dried under vacuum; yield: 0.1561 g, 98%. IR (KBr): $\tilde{\nu}$ = 3425 (br m), 3259 (br m), 3093 (vw), 2998 (vw), 1617 (m), 1586 (m), 1556 (m), 1509 (s), 1469 (m), 1435 (w), 1326 (w), 1298 (m), 1264 (m), 1225 (s), 1152 (w), 1128 (m), 1093 (w), 1050 (m), 998 (w), 943 (vs), 915 (vs), 887 (w), 848 (m), 779 (w), 711 (br m), 679 (m), 625 (w), 587 (w), 558 (w), 515 (w), 474 (w), 414 (w) cm^{-1}. ^1H NMR (400 MHz, $[D_6]DMSO$, 25 °C): δ = 11.69 (br. s, 1 H, N3-H), 8.67 (br. d, ^3J = 4.4 Hz, 1 H, N4-H), 8.56 (d, ^3J = 4.9 Hz, 1 H, 1-H), 8.25 (d, ^3J = 7.6 Hz, 1 H, 4-H), 8.08 (s, 1 H, 6-H), 7.85 (m, 1 H, 3-H), 7.38 (m, 1 H, 2-H), 3.03 (d, ^3J = 4.4 Hz, 3 H, CH_3) ppm. $C_{48}H_{68}Mo_8N_{24}O_{28}S_6$ (2389.10): calcd. C 24.1, H 2.9, N 14.1, S 8.1; found C 24.4, H 3.2, N 14.1, S 7.7.

Compounds 4 and 5: HL (0.090 g, 0.5 mmol) was added as a solid to an aqueous solution of $[Cu(ClO_4)_2]·6H_2O$ (0.185 g, 0.5 mmol). After 30 min, this solution was filtered off and the solution added to an aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.241 g, 1 mmol) acidified to pH = 3 with $HClO_4$ (60%). After 2 h, the green precipitate of **4** was filtered off, washed with acidified water and dried under vacuum; yield of **4**: 0.2510 g, 90%. After 20 days, dark-green crystals of **5** suitable for X-ray analysis were obtained. Compound **5** can be also synthesized as a powder using the same procedure employed for compound **4**, but, in this case we used only 0.25 mmol of HL and $[Cu(ClO_4)_2]·6H_2O$ per mmol of $[Na_2MoO_4]·2H_2O$ adjusting the final solution to pH = 2; yield of **5**: 0.2076 g, 97%.

4: IR (KBr): $\tilde{\nu}$ = 3405 (m), 3323 (m), 3185 (w), 3020 (w), 1634 (s), 1606 (s), 1561 (w), 1485 (m), 1451 (vs), 1379 (w), 1325 (m), 1300 (w), 1269 (w), 1225 (m), 1165 (s), 1154 (m), 1122 (w), 1108 (w), 1020 (w), 947 (vs), 926 (vw), 916 (w), 897 (vs), 841 (m), 823 (w), 770 (w), 734 (w, sh), 713 (br s), 673 (w), 624 (w), 554 (w), 519 (w), 457 (w), 413 (w) cm^{-1}. MS (FAB$^+$): m/z = 241.97 $[CuL]^+$, 483.94 $[Cu_2L_2]^+$. $C_{28}H_{44}Cu_4Mo_8N_{16}O_{30}S_4$ (2226.63): calcd. C 15.1, H 1.6, N 10.1, S 5.8; found C 14.8, H 1.6, N 9.4, S 5.3.

5: IR (KBr): $\tilde{\nu}$ = 3411 (m), 3274 (m), 3172 (m), 3045 (w), 2939 (vw), 1611 (vs), 1567 (m), 1476 (w), 1448 (w), 1406 (w), 1336 (w), 1304 (w), 1288 (w), 1236 (w), 1195 (w), 1157 (vw), 1107 (vw), 1021 (vw), 970 (w), 955 (vw, sh), 947 (vs), 919 (vs), 835 (s), 769 (w), 708 (br s), 681 (br s), 629 (vw), 611 (vw), 551 (w), 519 (w), 448 (w), 410 (w) cm^{-1}. MS (FAB$^+$): m/z = 242.41 $[CuL]^+$, 243.39 $[CuHL]^+$. $C_{14}H_{20}Cu_2Mo_8N_8O_{28}S_2$ (1707.08): calcd. C 9.9, H 1.2, N 6.6, S 3.8; found C 9.6, H 1.4, N 6.1, S 3.1.

Compounds 6 and 7: HL′ (0.097 g, 0.5 mmol) was added as a solid to an aqueous solution of $[Cu(ClO_4)_2]·6H_2O$ (0.185 g, 0.5 mmol). After 30 min, this solution was filtered off and the solution added to an aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.241 g, 1 mmol) acidified to pH = 3 with $HClO_4$ (60%). After 2 h, the green precipitate of **6** was filtered off, washed with acidified water and dried under vacuum; yield of **6**: 0.2427 g, 79%. The mother liquors were heated to reduce the volume and the resulting solution was kept at room temperature. After several days, dark-green crystals of **7** suitable for X-ray analysis were obtained. Compound **7** can also be synthesized as a powder solid by adding HL′ (0.049 g, 0.25 mmol) as a solid to an aqueous solution of $[Cu(ClO_4)_2]·6H_2O$ (0.093 g, 0.25 mmol). After 30 min, this solution was filtered off and the solution was added slowly to an aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.241 g, 1 mmol) acidified to pH = 1.4 with $HClO_4$ (60%). After 30 min, the green precipitate of **7** was filtered off, washed with acidified water and dried under vacuum; yield of **7**: 0.1276 g, 60%.

6: IR (KBr): $\tilde{\nu}$ = 3427 (br m), 3279 (s), 3079 (vw), 2937 (vw), 1592 (m), 1574 (w), 1538 (s), 1495 (w), 1464 (m), 1442 (w), 1399 (s), 1364 (m), 1306 (m), 1280 (m), 1243 (w), 1228 (m), 1179 (m), 1122 (m), 1102 (m), 1041 (w), 950 (vs), 910 (vs), 852 (s), 771 (m), 721 (br s), 667 (br m), 628 (vw), 555 (w), 525 (w), 515 (w), 475 (w), 444 (w), 411 (w) cm^{-1}. MS (FAB$^+$): m/z = 256.01 $[CuL']^+$, 512.03 $[Cu_2L'_2]^+$. $C_{32}H_{64}Cu_4Mo_8N_{16}O_{40}S_4$ (2462.90): calcd. C 15.6, H 2.6, N 9.1, S 5.2; found C 15.5, H 2.2, N 8.7, S 4.9.

7: IR (KBr): $\tilde{\nu}$ = 3430 (br vs), 2925 (w), 1600 (vs), 1477 (vw), 1455 (vw), 1395 (w), 1309 (w), 1282 (w), 1232 (w), 950 (m), 880 (vs), 851 (w, sh), 790 (br s), 701 (m), 649 (w, sh), 626 (m), 578 (s) cm^{-1}. MS (FAB$^+$): m/z = 256.03 $[CuL']^+$. $C_{48}H_{138}Cu_6Mo_{36}N_{24}Na_6O_{156}S_6$ (7713.20): calcd. C 7.5, H 1.8, N 4.4, S 2.5; found C 7.5, H 2.2, N 4.0, S 2.2.

Compounds 8 and 9: Compounds **8** and **9** were synthesized following the same procedure but with a different ligand, HL for compound **8** and HL′ for compound **9**. HL (0.036 g, 0.2 mmol)/HL′ (0.039 g, 0.2 mmol) was added as a solid to an aqueous solution of $[Cu(ClO_4)_2]·6H_2O$ (0.074 g, 0.2 mmol). After 30 min, this solution was filtered off and the solution added to an aqueous solution of $[Na_2MoO_4]·2H_2O$ (0.290 g, 1.2 mmol) acidified to pH = 1.1 with $HClO_4$ (60%). After 2 h, the green precipitate of **8**/**9** was filtered off, washed with acidified water and dried under vacuum; yields: 0.1866 g, 75% for **8**; 0.081 g, 34% for **9**.

8: IR: $\tilde{\nu}$ = 3544 (m), 3411 (m), 3270 (w), 3170 (w), 1611 (vs), 1567 (m), 1477 (w), 1448 (w), 1405 (w), 1335 (w), 1305 (w), 1288 (w), 1236 (w), 1195 (w), 1122 (w), 1107 (w), 1021 (w), 957 (w, sh), 947 (vs), 918 (vs), 879 (s), 834 (m), 770 (w), 704 (br m), 662 (w), 648 (w), 628 (w), 575 (m), 540 (w), 520 (w), 473 (w), 447 (w), 426 (w), 419 (w), 407 (s) cm^{-1}. MS (FAB$^+$): m/z = 242.96 $[CuHL]^+$, 485.92 $[Cu_2(HL)_2]^+$. $C_{42}H_{128}Cu_6Mo_{36}N_{24}O_{154}S_6$ (7460.93): calcd. C 6.8, H 1.7, N 4.5, S 2.6; found C 6.9, H 2.0, N 4.4, S 2.5. IR

Table 5. Crystallographic data for compounds **2**, **5**, **7** and **10**.

	2	**5**	**7**	**10**
Formula	$C_{31}H_{34}Mo_6N_{16}O_{20.24}S_4$	$C_{14}H_{20}Cu_2Mo_8N_8O_{28}S_2$	$C_{24}H_{69}Cu_3Mo_{18}N_{12}Na_3O_{78}S_3$	$C_{14}H_{14}Cu_2N_8O_{18}S_3V_5$
M	1654.59	1707.08	3856.60	1060.29
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$C2/m$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a [Å]	16.6205(18)	8.3883(14)	16.777(2)	16.618(5)
b [Å]	18.637(2)	19.896(4)	16.968(2)	9.013(5)
c [Å]	10.4422(12)	11.502(3)	18.675(2)	22.215(5)
α [°]	90	90	87.4710(10)	90
β [°]	122.332(2)	97.23(2)	66.9190(10)	105.201(5)
γ [°]	90	90	77.347(2)	90
V [Å^3]	2733.0(5)	1904.4(8)	4766.5(10)	3211(2)
Z	2	2	2	4
D_c [g cm^{-3}]	2.011	2.977	2.687	2.193
μ [mm^{-1}]	1.5711	3.8504	3.129	2.973
F(000)	1616.0	1620.0	3690	2076
2θ range [°]	2–25	3–25	2–29	2–26
Measured reflections	13571	18177	38282	2416
Independent reflections	2618	3337	21747	2416
GOF	1.084	1.127	1.037	0.808
R_1	0.0280	0.0424	0.0671	0.0695
R_1 [$I > 2\sigma(I)$]	0.0251	0.0314	0.0483	0.0303
wR_2	0.0645	0.0983	0.1307	0.0618
wR_2 [$I > 2\sigma(I)$]	0.0633	0.0789	0.1192	0.0567

9: IR (KBr): $\tilde{\nu}$ = 3445 (br vs), 2923 (w), 1598 (s), 1529 (w), 1479 (w), 1455 (w), 1392 (w), 1280 (w), 1231 (w), 1106 (w), 977 (s), 952 (m), 914 (w, sh), 879 (vs), 853 (w), 792 (br s), 699 (m), 650 (m), 623 (m), 576 (s), 544 (w), 531 (w), 483 (m), 420 (s), 407 (vs) cm^{-1}. MS (FAB$^+$): m/z = 256.99 [CuHL′]$^+$, 512.34 [Cu$_2$L′$_2$]$^+$. $C_{32}H_{132}Cu_4Mo_{36}N_{16}O_{158}S_4$ (7105.59): calcd. C 5.4, H 1.9, N 3.2, S 1.8; found C 5.5, H 2.2, N 3.1, S 1.9.

Compound 10: An aqueous solution of [Cu(HL)(ox)(H$_2$O)] (0.088 g, 0.25 mmol) was stirred for 1 h with light heating and some drops of concentrated HNO$_3$ were added until pH = 0.8. Meanwhile, another different aqueous solution was prepared with VOSO$_4$ (0.408 g, 2.5 mmol). The copper solution was poured into the oxidovanadium(IV) solution and the final mixture was basified with NaOH (5 M) until pH = 3.7. After 30 min of vigorous stirring, the solution was placed in a beaker. After 24 h, an unidentified green compound was filtered off. After a few days, dark-green crystals of **10** suitable for X-ray analysis were obtained in the reaction mother liquors. Unfortunately, we were not able to reproduce or improve the synthesis and hence the limited characterization data for this compound; $C_{28}H_{50}Cu_4N_{16}O_{36}S_6V_{10}$ (2142.60). IR (KBr): $\tilde{\nu}$ = 3456 (m), 3319 (m), 3129 (w), 2923 (vw), 1631 (w, sh), 1620 (s), 1557 (w), 1476 (w), 1455 (m), 1435 (m), 1385 (vs), 1329 (w), 1300 (w), 1275 (w), 1231 (m), 1173 (m), 1155 (w, sh), 1106 (w), 1020 (w), 987 (w, sh), 968 (s), 948 (w, sh), 880 (w), 833 (br m), 776 (w), 735 (br m), 649 (vw), 594 (br m), 519 (w), 449 (br w), 421 (w) cm^{-1}.

X-ray Crystallographic Studies: Crystal data collection was carried out using a Bruker Smart single-crystal diffractometer equipped with a CCD area detector. Absorption corrections were made using the SADABS program.[29] Direct methods (SHELXS-97)[30] were employed to solve the structures, which were then refined by full-matrix least-squares methods using the SHELXL-97 computer program[31] within WINGX.[32] All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atom H1A in **2** was refined with an occupancy of 0.50. The acetone molecule in **2** was refined as a disordered molecule with atoms C8, C9 and O9 placed at two different positions with an occupancy of 0.50. Atom O10 of a water molecule was refined with an occupancy of 0.12 and solvent molecules in **2** were refined without consideration of the hydrogen atoms. All hydrogen atoms in **5** were refined with fixed isotropic displacement parameters. Solvent molecules in **7** were refined without consideration of the hydrogen atoms. Groups of atoms O9W–Mo3–O10, O4W–Mo4–O13 and O5W–Mo5–O20 present in **7** were refined delocalized between two different positions, A and B, with an occupancy of 0.50. The scattering factors and anomalous dispersion coefficients were taken from the International Tables of X-ray Crystallography.[33] Refinements were made on F^2 for all reflections. Crystallographic data for the four crystal structures are shown in Table 5.

CCDC-773095 (for **2**), -773096 (for **5**), -773097 (for **7**) and -773098 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Tables and figures of π–π stacking parameters, graphics for the structural parameters to compare the deprotonated and neutral forms of the thiosemicarbazone ligands, TG curves, powder diffractograms of the inorganic residues after thermal treatment, IR spectra, ^{1}H NMR measurements and the corresponding numbering scheme and EPR spectra.

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[21] ^{1}H NMR of HL (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.61 (br. s, 1 H, N3-H), 8.53 (dd, ^3J = 4.9, ^4J = 1.0 Hz, 1 H, 1-H), 8.33 (br. s, 1 H, N4-H), 8.24 (d, ^3J = 8.0 Hz, 1 H, 4-H), 8.16 (br. s, 1 H, N4-H), 8.05 (s, 1 H, 6-H), 7.79 (m, 1 H, 3-H), 7.34 (m, 1 H, 2-H) ppm.

[22] ^{1}H NMR of HL′ (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.68 (br. s, 1 H, N3-H), 8.65 (br. d, ^3J = 4.5 Hz, 1 H, N4-H), 8.53 (d, ^3J = 4.9 Hz, 1 H, 1-H), 8.22 (dd, ^3J = 8.0, ^4J = 0.9 Hz, 1 H, 4-H), 8.05 (s, 1 H, 6-H), 7.81 (m, 1 H, 3-H), 7.34 (m, 1 H, 2-H), 3.00 (d, ^3J = 4.6 Hz, 3 H, CH$_3$) ppm.

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