Tri- and pentanuclear NCS-bridged [Mo^{III}–Cu^{II}] cluster compounds: Crystal structures and magnetic properties

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ABSTRACT

Two heteronuclear NCS-bridged compounds, namely [{Cu(3,3,3-tet)(CH$_3$CN)}$_2${Mo(NCS)$_6$}][Mo(NCS)$_6$][PPh$_4$]$_2$·6CH$_3$CN (**1**) and [{Cu(3,3,3-tet)(CH$_3$CN)}$_4${Mo(NCS)$_6$}][Mo(NCS)$_6$]$_3$[Cu(3,3,3-tet)(CH$_3$CN)]$_2$ (**2**) (with 3,3,3-tet = *N,N*-bis(3-aminopropyl)-1,3-propanediamine) have been synthesized and their crystal structures were characterized by single crystal X-ray diffraction studies. For the cationic trinuclear cluster of **1** one hexaisothiocynato Mo(III) unit, [Mo(NCS)$_6$]$^{3-}$, is linked to two Cu units through two NCS bridging ligands, and the anionic pentanuclear cluster of **2** results from the linkage of the Mo unit to four Cu moieties. In **1** and **2**, the coordination of a solvent molecule (i.e. acetonitrile) in one apical position of Cu prevents the extension of the system, while charge neutrality is achieved by co-crystallization of non-bonded Cu and/or Mo complexes. Magnetic studies of **1** and **2** reveal the weak antiferromagnetic interaction between the two spin carriers Cu^{II} and Mo^{III}, through the NSC ligand. For **1**, modeling the experimental data yields a value of $J_{MoCu} = -5.9$ cm^{-1} ($H = -J(\mathbf{S_1S_2 + S_2S_3})$) for the exchange interaction.

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1. Introduction

Paramagnetic transition metal ions of the second and third rows have been increasingly used as building units in the field of molecular magnetism over the past five years [1]. This interest is motivated by the stronger exchange coupling obtained between two paramagnetic centers when such an ion is involved [2]. The enlarged exchange interactions achieved result from the spatially more extended valence orbitals for 4d and 5d ions, as compared to 3d metal ions, that allow more spin density to be transferred to the ligands [3]. The temperature domain in which the collective properties of the magnetic system are expressed is closely related to the strength of the exchange interaction between the spin carriers; it is therefore not surprising that most of the molecule-based magnets with ordering temperature above 100 K involve 4d and 5d spin carriers [4]. Besides the metal ions, the bridging ligands also play a prominent role in the magnetic performances of magnets. So far and with very few exceptions, all these 4(5)d metal-based materials involve cyanides as linkers. Recently, we have shown that the thiocyanate ligand NCS$^-$, in association with Mo^{III} may also be a powerful ligand for the construction of magnetic systems [5]. This was illustrated by a series of compounds formed with the hexaisothiocynatate complex [Mo(NCS)$_6$]$^{3-}$ and Co^{II} or

Ni^{II} ions which exhibited substantial exchange interactions. These included a 2D magnet with T_c = 39 K. In an extension of this investigation we have considered magnetic systems involving the building unit [Mo(NCS)$_6$]$^{3-}$ in association with Cu^{II}, another 3d ion likely to accept sulfur atom as ligands. Herein we report on two compounds formed by reaction of the Mo^{III} metallo-ligand with [Cu(3,3,3-tet)]$^{2+}$ (3,3,3-tet stands for the tetradentate tripropylenetetramine ligand *N,N*-bis(3-aminopropyl)-1,3-propanediamine, Scheme 1), namely [{Cu(3,3,3-tet)(CH$_3$CN)}$_2$Mo(NCS)$_6$][Mo(NCS)$_6$][PPh$_4$]$_2$·6CH$_3$CN, **1**, and [{Cu(3,3,3-tet)(CH$_3$CN)}$_4$Mo(NCS)$_6$][Mo(NCS)$_6$]$_3$[Cu(3,3,3-tet)(CH$_3$CN)]$_2$, **2**. These mixed salts comprise discrete [Mo–Cu] entities originating from the association of one [Mo(NCS)$_6$]$^{3-}$ with, respectively, two and four Cu^{II} centers through NCS$^-$ bridging ligands. The formation of either compound is governed by the Mo salt used. Their crystal structures and magnetic behaviors are described.

2. Experimental

2.1. Materials and physical measurements

All the syntheses were performed under a Nitrogen atmosphere using Schlenk technique. The chemicals were bought from commercial sources and used as received. Deoxygenated solvents were used for all the syntheses. Solvents were distilled under a Nitrogen atmosphere, and stored under N$_2$. The starting materials [(PPh$_4$)$_3$
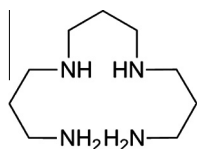
Scheme 1. Chemical structure of the ligand tripropylenetetramine (3,3,3-tet).

{Mo(NCS)$_6$}] [5a], [(NEt$_4$)$_3${Mo(NCS)$_6$}] [5b,6], and [{Cu(3,3,3-tet)}(ClO$_4$)$_2$] [7] were prepared as described in the literature.

Elemental C, H and N analyses were performed on a Perkin-Elmer 2400 II analyzer on freshly prepared and isolated samples. IR spectra were recorded in the 4000 to 650 cm^{-1} range with a Perkin-Elmer Spectrum 100 FTIR using the ATR mode. Magnetic measurements were carried out with a Quantum design MPMS 5S SQUID magnetometer in the temperature domain 2–300 K with an applied field of 1000 Oe. The molar susceptibility was corrected for sample holder and for the diamagnetic contribution of all the atoms by using Pascal's tables. The measurements were performed on crushed crystals from freshly isolated samples to avoid solvent loss. The powders were mixed to grease and put in gelatin capsules.

2.2. Crystallographic data collection and structure determination

X-ray diffraction data for the crystals were collected at 180 K on a Oxford Diffraction Xcalibur diffractometer using a graphite-monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å). The crystal was placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat with a nominal stability of 0.1 K. Multiscan absorption corrections were applied. The structures were solved by direct methods using SIR92 [8] for **1** and SUPERFLIP [9] for **2**, and refined by means of least-square procedures on *F* using the programs of the PC version of CRYSTALS [10]. Atomic scattering factors were taken from the International tables for

X-ray crystallography [11]. As far as possible, non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with riding constraints. For **2**, high thermal parameters have been noticed for the [Cu(3,3,3-tet)(CH$_3$CN)]$^{2+}$ cationic unit. Best results in the structure resolution have been obtained by refining isotropically this part and by restraining the C–C and the C–N bond distances in the 3,3,3-tet ligand and the acetonitrile molecule in the [Cu(3,3,3-tet)(CH$_3$CN)]$^{2+}$ unit. Crystallographic and refinement data are given in Table 1. Selected bond distances and bond angles for **1** and **2** are given in Table 2.

2.3. Synthesis

2.3.1. [{Cu(3,3,3-tet)(CH$_3$CN)}$_2$Mo(NCS)$_6$][Mo(NCS)$_6$][PPh$_4$]$_2$·6CH$_3$CN (**1**)

A solution of [{Cu(3,3,3-tet)}(ClO$_4$)$_2$] (45 mg; 0.1 mmol) in CH$_3$CN (10 mL) was syringed and carefully layered over a solution of [(PPh$_4$)$_3${Mo(NCS)$_6$}] (73 mg; 0.1 mmol) in CH$_3$CN (10 mL). The resulting two phases system was left undisturbed in the dark for several days until the complete inter-diffusion of the two layers. The resulting green crystals (suitable for X-ray diffraction) were collected under N$_2$. Yield: 95 mg (40% based on Cu). *Anal.* Calc. for C$_{82}$H$_{94}$N$_{22}$Cu$_2$Mo$_2$P$_2$S$_{12}$·6CH$_3$CN: C, 47.05; H, 4.70; N, 16.34. Found: C, 47.50; H, 4.60; N, 16.26%. IR (ATR): 3297 (w), 3234 (w) 2931 (w), 2888 (w), 2250 (w), 2052 (s), 1586 (m), 1483 (m), 1435 (s), 1369 (w), 1315 (w), 1287 (w), 1185 (w), 1155 (w), 1108 (s), 1025 (m), 995 (m), 964 (w), 890 (w), 823 (m), 755 (m), 722 (s), 689 (s), 641 (w).

2.3.2. [{Cu(3,3,3-tet)(CH$_3$CN)}$_4$Mo(NCS)$_6$][Mo(NCS)$_6$]$_3$[Cu(3,3,3-tet)(CH$_3$CN)]$_2$ (**2**)

[(NEt$_4$)$_3${Mo(NCS)$_6$}] (200 mg; 0.24 mmol) was dissolved in CH$_3$CN (10 mL), syringed and carefully layered over the solution of [{Cu(3,3,3-tet)}(ClO$_4$)$_2$] (108 mg; 0.24 mmol) in H$_2$O (10 mL). The resulting two phases system was left undisturbed in the dark for several days until the complete inter-diffusion of the two layers. Blue crystals suitable for X-ray diffraction were formed and collected under N$_2$. Yield: 38 mg (28% based on Cu). *Anal.* Calc. for C$_{90}$H$_{162}$N$_{54}$Cu$_6$Mo$_4$S$_{24}$: C, 30.58; H, 4.62; N, 21.39. Found: C, 30.15, H, 4.12, N, 21.14%. IR (ATR): 3192 (m), 2929 (m), 2876 (m), 2993 (w), 2042 (s), 1578 (m), 1467 (m), 1418 (m), 1365 (w), 1314 (w), 1286 (w), 1052 (m), 1083 (m), 1022 (s), 988 (w), 887 (m), 821 (m).

3. Results and discussion

3.1. Synthesis

In the precursor {Cu(3,3,3-tet)}$^{2+}$, four coordination positions around the metal centre are occupied by the strongly coordinated tetraamine macrocyclic 3,3,3-tet ligand which lies in the equatorial positions of the Cu polyhedron. This arrangement leaves the possibility to the Cu atom to complete its coordination sphere with additional axial ligands in trans position. Compounds **1**, [{Cu(3,3,3-tet)(CH$_3$CN)}$_2$Mo(NCS)$_6$][Mo(NCS)$_6$][PPh$_4$]$_2$·6CH$_3$CN, and **2**, [{Cu(3,3,3-tet)(CH$_3$CN)}$_4$Mo(NCS)$_6$][Mo(NCS)$_6$]$_3$[Cu(3,3,3-tet)(CH$_3$CN)], were both prepared by reacting the two building blocks [Mo(NCS)$_6$]$^{3-}$ and {Cu(3,3,3-tet)}$^{2+}$ in stoichiometric proportions, either in acetonitrile or mixed water/acetonitrile medium. The Mo precursors, i.e. PPh$_4^+$ salt for **1** and NEt$_4^+$ salt for **2**, were dissolved in acetonitrile. The solution of the Cu complex (ClO$_4^-$ salt) was prepared in acetonitrile for **1** and in water for **2**. The reproducible syntheses of **1** and **2** as crystals were achieved similarly by the inter-diffusion process between the miscible solutions of the two building units. Modulation of the synthetic conditions for **1** by changing the cation associated to the metallo-ligand

Table 1
Crystallographic data and structure refinement details for compounds **1** and **2**.

	1	**2**
Formula	C$_{94}$H$_{112}$Cu$_2$Mo$_2$N$_{28}$P$_2$S$_{12}$	C$_{90}$H$_{162}$Cu$_6$Mo$_4$N$_{54}$S$_{24}$
FW	2399.82	3535.26
Crystal system	triclinic	triclinic
Crystal color	green	blue
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.9701(2)	10.3887(2)
b (Å)	16.6263(3)	18.5595(5)
c (Å)	18.1357(4)	21.6388(5)
α (°)	76.966(2)	64.632(3)
β (°)	86.023(3)	86.660(2)
γ (°)	77.714(2)	78.978(2)
V (Å^3)	2861.0(1)	3699.0(2)
Z	1	1
T (K)	180	180
ρ_{calc} (g cm^{-1})	1.39	1.59
μ (Mo Kα) (mm^{-1})	0.883	1.569
$F(000)$	1236	1806
Absorption correction	multi-scan	multi-scan
T_{min}; T_{max}	0.82; 0.88	0.69; 0.73
Index ranges	$-13 \leqslant h \leqslant 13$	$-14 \leqslant h \leqslant 11$
	$-22 \leqslant k \leqslant 22$	$-25 \leqslant k \leqslant 25$
	$-22 \leqslant l \leqslant 24$	$-28 \leqslant l \leqslant 29$
Reflections collected	27413	35546
Independent reflections (R_{int})	15172 (0.027)	19643 (0.024)
R_1/wR_2	0.0300/0.0301 ($I > 3\sigma(I)$)	0.0854/0.0878 ($I > 3\sigma(I)$)
R_1/wR_2 (all data)	0.0452/0.0378	0.1168/0.1085