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Synthesis, properties and extended MS studies of a new heterometallic [Mn_4Ni_2]-core oxime-bridged complex

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ABSTRACT

Synthesis and properties of a new $[Mn_4Ni_2O_2(sao)_6(CH_3OH)_6]\cdot 1.3H_2O\cdot 4.4CH_3OH$ (**1**) compound are reported ($saoH_2$ = salicylaldoxime). The complex core displays two oxime-bridged $[Mn^{III}_2Ni^{II}\mu_3\text{–}O]$ triangular units. The presence of Mn/Ni sites is confirmed by EDX/elemental analyses, extended MS spectrometry studies and X-ray crystallography. MS/MS analyses are shown for the selected ions. Preliminary results for other properties of **1** (EPR, IR, preliminary studies of magnetic properties) are also presented.

1. Introduction

Mixed-transition metal heterometallic complexes are an established part of the chemistry of new magnetic materials with oximes acting as ligands linking metal ions [1]. In particular, Mn–Ni oxime-bridged compounds are known from studies on oligomeric units [2], such as trinuclear Mn^{III}–Ni^{II}–Mn^{III} Single Molecule Magnets [2a] or tetranuclear Ni^{II}–Mn^{II}_2–Ni^{II} complexes [2b]. The units can be assembled into polymeric chains being single chain magnets [3]. A family of higher-nuclearity Mn^{III}/Ni^{II} clusters, displaying SMM behavior, was reported by Chen et al. [4]. Oxime-bridged heterometallic complexes of Mn with other transition metals, e.g. Zn(II) [5] are also known.

In this paper we contribute a new example of an Mn^{III}–Ni^{II} metallacrown assembly (**1**) with complex $[Ni^{II}_2Mn^{III}_4]$ core related to a well-known class of oxime-bridged $[Mn_6O_2]$ compounds [6].

It is unreliable to distinguish between manganese and nickel sites solely based on X-ray diffraction analysis for a product crystallizing from a mixture of starting materials obtained *in situ*. However, in the case of crystalline **1** the presence of an $[Mn_4Ni_2]$ core is supported by other methods, in particular EDX and an extended MS analysis. These methods give the first unambiguous hint on the presence of Mn and Ni at 2:1 ratio, which is then used for the interpretation of the X-ray diffraction data.

The information on structure of the related metallacrown complexes in solution is of special importance [7]. An efficient strategy to describe such properties as stability/dynamics in solution is the application of mass spectrometry [8–12] and MS/MS methods [8]. In particular, extended MS studies carried out for **1** may be helpful in the analysis of the related compounds and are an important aim of this work.

2. Experimental

2.1. General

HPLC-purity methanol was used. Tetraethylammonium hydroxide (25% solution in methanol) was purchased from Aldrich and kept under Ar atmosphere. $MnCl_2\cdot 4H_2O$, salicylaldoxime and $Ni(NO_3)_2\cdot 6H_2O$ were purchased and used as received. These chemicals were used without further purification.

2.2. Synthesis

0.198 g (1 mmol) of $MnCl_2\cdot 4H_2O$ and 0.137 g (1 mmol) of salicylaldoxime were combined in 75 ml of methanol. Two milliliters of tetraethylammonium hydroxide solution in methanol was added, resulting in darkening of the resulting solution. After 30 min stirring

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0.582 g (2 mmol) of $Ni(NO_3)_2{\cdot}6H_2O$ was added. The resulting black mixture was stirred for 24 h, filtered and left for slow evaporation in a crystallization vessel covered with parafilm. After 5 days black crystals of $[Mn_4Ni_2O_2(sao)_6(CH_3OH)_6]$ (**1**) in form of blocks were obtained at 8% yield. Formation of a crystalline material was followed by precipitation of an amorphous part. As a result, the obtained yield is low (only crystalline material was taken for further analyses).

2.3. Characterization

IR spectra were recorded by means of a Bruker Alpha-P Infrared-spectrometer equipped with a Platinum-ATR with a diamond crystal.

IR bands [cm^{-1}] (relative intensity): 590.8 (m), 665.4 (m), 756.3 (s), 810.9 (w), 914.4 (s), 1020.5 (vs), 1124.4 (w), 1155.0 (w), 1197.3 (m), 1286.0 (vs), 1324.2 (vs), 1393.0 (m), 1439.8 (vs), 1474.6 (s), 1544.7 (m), 1596.4 (vs), 3332.2 (s).

EPR spectra were collected with the use of Bruker ESP300 device for powdered solid samples sealed in quartz tubes.

Energy dispersive X-ray spectroscopy (EDX) was performed on a CamScan 4DV + EDX Noran Instruments Voyager 4.0 with Pioneer Detector.

CHN elemental analyses were carried out on a Vario Micro-cube elemental analyser in CHNS Mode. *Anal.* Calc.: C, 37.9; H, 4.7; N, 8.4; Mn, 15.7. Found: C, 37.0; H, 4.1; N, 7.9; Mn, 15.0%. Elemental analysis is often problematic in the case of related compounds e.g. due to problems with interstitial solvent (e.g. [13]).

X-ray diffraction: X-ray diffraction data for a single-crystal of **1** were collected on a STOE IPDSII diffractometer [14] with Mo Kα radiation at 100(2) K. Selected X-ray data are collected in Table S1 (ESI). The crystals were handled in inert silicon oil in order to avoid interstitial solvent loss. The measured specimen was twinned (about 80% and 20% twin domains). Cutting of the crystals resulted in too weak X-ray diffraction, therefore a twinned crystal was taken for a full measurement. The twinning was handled during data integration [14] and refinement (see below for details). CCDC reference number for **1**: 890751.

Mass spectrometry: MS experiments were preformed on micrO-TOF-Q (BRUKER) instrument with an ESI source. Spectra were recorded in the positive and negative ion mode (electrospray voltage 4.5 kV, capillary temperature 180–200 °C) at the flow rate of 3 μL/min. The collision energies of MS/MS experiments were 10 and 20 eV. The spectra were analyzed with Bruker Daltonik GmbH DataAnalysis software [15]. Before each run the instrument was calibrated externally with the Tunemix^{TM} mixture in quadratic regression mode. The mass accuracy for the calibration was better than 5 ppm, enabling together with the true isotopic pattern (using SigmaFit) an unambiguous confirmation of the elemental composition of the obtained complex. Solutions in methanol and acetonitrile were investigated with addition of one equivalent of NaCl in order to increase the possibility to observe non-charged species in both positive and negative ionization modes.

Magnetic properties (preliminary): Magnetic measurements were recorded with the magnetic property measurement system (MPMS) made by Quantum Design for a 9.9 mg sample of **1**. The magnetic data were obtained in the temperature range from 2 to 300 K at the field of 500 and 1000 Gs (Figs. S6 and S7, respectively). The sample was prepared in a gelatine capsule (37.8 mg). Field-dependent measurement was carried out at 5 K (Fig. S8). The data were corrected with respect to the gelatine sample holder as well as diamagnetic corrections were introduced using Pascal constants [16].

2.4. Details of the structure refinement

The structure was solved with direct methods in SHELXS [17] using the HKLF4-format file generated for the main twin domain. The essentially complete structure model was refined against HKLF5-format file, introducing one BASF parameter (the final refined value of 0.21(1)). Four sites with methanol molecules of solvation were found. For one molecule (with O1 M) the site is fully occupied. For the remaining three molecules the occupancies were initially refined as free variables and subsequently fixed at refined values (0.5, 0.25 and 0.45, respectively). For all disordered methanol molecules DFIX restraints were used to keep C–O bond lengths within 1.50(1) Å. Anti-bumping DFIX restraints had to be applied to H3···H7 at $-x+1$, $-y+1$, $-z+1$ and H2···H2M3 distances. One difference Fourier maximum was interpreted as one water molecule of solvation with occupancy refined and fixed at 0.65. No water H atoms were found on difference Fourier map. Where possible, H atoms were placed in calculated positions and a riding model was applied with U_{eq} at 1.2/1.5 U_{eq}(parent atom). On the final difference Fourier map the highest maximum of 0.70 e/Å^3 is situated at 1.00 Å from Ni1.

3. Results and discussion

3.1. Syntheses

1 can be isolated from a system where pre-formed manganese(III) oxime-bridged complexes obtained *in situ* in methanol under basic conditions probably undergo metal ion exchange ($saoH_2$ = salicylaldoxime):

$$\begin{tikzcd}
MnCl_2 + saoH_2 + CH_3OH \arrow[d, "\begin{array}{l}\text{1. [NEt}_4\text{]OH, 30 min. stirring}\\ \text{2. Ni(NO}_3)_2\text{, stirring 24 h, filtration}\end{array}"] \\
{[Mn_4Ni_2O_2(sao)_6(CH_3OH)_6]\ (\mathbf{1})\quad 8\%}
\end{tikzcd}$$

The following overall equation may be proposed to describe the formation of **1**:

$$\begin{aligned}&4MnCl_2 + 6saoH_2 + 2Ni(NO_3)_2 + 12[NEt_4]OH + O_2 + 6CH_3OH\\ &\rightarrow [Mn_4Ni_2O_2(sao)_6(CH_3OH)_6] + 4[NEt_4]NO_3 + 8[NEt_4]Cl\\ &\quad + 12H_2O\end{aligned}$$

Extensive previous studies of researchers working in this field show that under basic conditions in a reaction of a manganese(II) salt and salicylaldoxime-derivatives ligands $[Mn^{III}{}_3O]$- and $[Mn^{III}{}_6O_2]$-core complexes are formed [18]. **1** is a product isolated on addition of nickel(II) nitrate to such mixture. On the other hand, it is interesting to note that a reaction of nickel(II) salts with salicylaldoxime yields a mononuclear $[Ni(saoH)_2]$ complex, which is used in analytical chemistry for nickel(II) determination [19a]. Other examples of Mn/Ni metallacrown complexes include e.g. the mixed metal metallacrown compounds reported by Psomas et al. [19b].

Similar procedure carried out with other transition metals salts, such as Co(II) or Cu(II), did not yield crystalline products. This result is also true when other Ni(II) starting salts, such as chloride, are used.

3.2. Crystal structures

The centrosymmetric core in **1** (Fig. 1) comprises two $[Mn_2Ni\mu_3{-}O]$ units bridged by three salicylaldoxime oxime groups. Within each $[Mn_2Ni\mu_3{-}O]$ unit the $Mn{-}O_{phenoxido}$ bond lengths are at 1.884(3)–1.885(2) Å, $Mn{-}O_{\mu\text{-oxido}}$ is of 1.845(2) Å, $Mn{-}O_{oxime}$ are at 1.904(3)–1.924(2) Å, $Mn{-}N_{oxime}$ are at 2.004(3)–2.027(3) Å range (Table S3). All these parameters are within the range reported for $[Mn^{III}{}_6O_2]$ complexes [18]. In each triangular $[Mn_2Ni\mu_3{-}O]$