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Oxygen transfer from amidoximes to Mo(II) centers: synthesis and X-ray crystallographic characterization of $[CH_3C(NH_2)_2]_2[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]\cdot 2C_2H_5OH$

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Abstract

The deoxygenation of amidoximes has been observed with two molybdenum(II) complexes. $[CH_3C(NH_2)_2]_2[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]\cdot 2C_2H_5OH$ was obtained from $[Mo(NO)(acac)_2\{CH_3C(NH_2)NO\}]$ and $C_6H_5CONHNH_2$, and characterized by X-ray crystallography. It crystallizes in the orthorhombic space group *Pcab*, with $a = 13.385(5)$, $b = 12.172(3)$, $c = 18.358(5)$ Å. The structure was refined to $R = 0.031$ ($R_w = 0.039$) for 2140 reflections with $I > 3.0\sigma(I)$. The crystals contain centrosymmetrical cyclic organotetramolybdates which are connected to acetaminidium cations and solvent molecules through N–H···O and O–H···O intermolecular hydrogen bonds.

Introduction

We recently found that acetamidoxime can act as a nitrosylating reagent towards $[MoO_2(acac)_2]$, yielding the seven-coordinate complex $[Mo(NO)(acac)_2\{CH_3C(NH_2)NO\}]$ [1]. This reaction has now been extended to other systems and similar complexes have been obtained in the reactions of propanamidoxime and chloroacetamidoxime with $[MoO_2(acac)_2]$. The known $[Mo(NO)\{(C_2H_5)_2NCS_2\}_3]$ has also been identified among the products of the reactions of $CH_3C(NH_2)NOH$ with $[MoO_2\{(C_2H_5)_2NCS_2\}_2]$ and $[MoS_2\{(C_2H_5)_2NCS_2\}_2]$ [2]; reductive nitrosylation of $[VO_2(dipic)]^-$ [3] with acetamidoxime and benzamidoxime has also been observed [2]. Looking for the possibility to convert the $[Mo(NO)]^{3+}$ group into the $[Mo(N_2Ar)]^{3+}$ unit, we explored the reactivity of the nitrosyl complexes with substituted hydrazines. Evidence for such a reaction has not yet been obtained; instead we found that the cyclic tetramolybdate $[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]^{2-}$ is unexpectedly formed when $[Mo(NO)(acac)_2\{CH_3C(NH_2)NO\}_2]$ is refluxed in ethanol in the presence of $C_6H_5CONHNH_2$. Actually oxygen atom transfer from amidoximes to Mo(II) centers appears to be general. We report here preliminary results on these reactions.

Experimental

Preparation of $[CH_3C(NH_2)_2]_2[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]\cdot 2C_2H_5OH$

$[Mo(NO)(acac)_2\{CH_3C(NH_2)NO\}]$ [1] (0.56 g, 1.4 mmol) and $C_6H_5CONHNH_2$ (0.19 g, 1.4 mmol) were dissolved in C_2H_5OH (35 ml) and the mixture was refluxed for 4 h. The resulting red solution was cooled to room temperature. Transparent pale-yellow crystals grew from the solution within 3 days and the crystallization process was observed to continue for several weeks. A first crop of crystals was collected which were found to become quickly opaque when standing in air. The decomposition was assumed to arise from loss of solvent which was later confirmed.

Crystal structure determination

A crystal was sealed in a Lindeman tube containing a drop of ethanol. Data collection was carried out at ambient temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Unit cell parameters were obtained from 25 machine-centered reflections. Intensities of two checked reflections were monitored every hour; no

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significant decay was observed over the course of data collection. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based upon Ψ-scan was applied [4]. The data set was processed with the CRYSTALS program package [5]. The structure was solved by conventional heavy-atom techniques. The metal atoms were located by Patterson synthesis. Hydrogens of the NH_2 groups were located in a difference Fourier map. For methyl groups, two hydrogens were located on a difference Fourier map, their positions were idealized, and the remaining position was calculated. Hydrogens were included in the full-matrix least-squares refinement as fixed contributions; solvent hydrogens were omitted. Crystal data and information relating to data collection and structure refinement are listed in Table 1.

Results and discussion

The presence of strong Mo–O bonds in the 600–1000 cm^{-1} part of the IR spectrum of the product indicated that a polyoxomolybdate and been formed but the characteristic pattern of the cyclic Mo_4O_{12} core was not clearly seen due to perturbation by cation bands; an X-ray study was then undertaken.

The formulation of the complex based on the X-ray crystallographic analysis is $[CH_3C(NH_2)_2]_2$-$[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]\cdot 2C_2H_5OH$. The structure of the anion (Fig.1) is similar to those observed in other salts recently described [6]. This is the fourth determination of the $[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]^{2-}$ anion since the NBu_4^+ salt [6] contains two independent molecules. Some differences are observed in the bridging mode of the ligand which is more or less symmetrical. The location of the ligand relative to the Mo_4O_{12} core can be specified by quoting the angle between the normals to the ligand mean plane and to the Mo_4O_4 ring (90.9° in the present case) and the angle between the ligand plane and its normal Mo–Mo vector (89.4°). Significant variations in these values might be ascribed to packing effects.

TABLE 1. Crystal data

Formula	$C_{12}H_{36}Mo_4N_8O_{16}$
Formula weight	932.2
Space group	*Pcab*
a (Å)	13.385(5)
b (Å)	12.172(3)
c (Å)	18.358(5)
V (Å^3)	2291
Z	4
μ(Mo Kα) (cm^{-1})	16.76
D_{calc} (g cm^{-3})	2.07
Scan method	θ–2θ
2θ range (°)	$3 < 2\theta < 50$
Scan width (°)	$1.0 + 0.345 tg\theta$
Scan speed (° min^{-1})	$1.8 < sp. < 5.5$
No. unique reflections	2620
No. reflections with $I > 3\sigma(I)$	2140
No. variables	182
R^a	0.031
R_w (unit weights)^b	0.039

$^aR = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

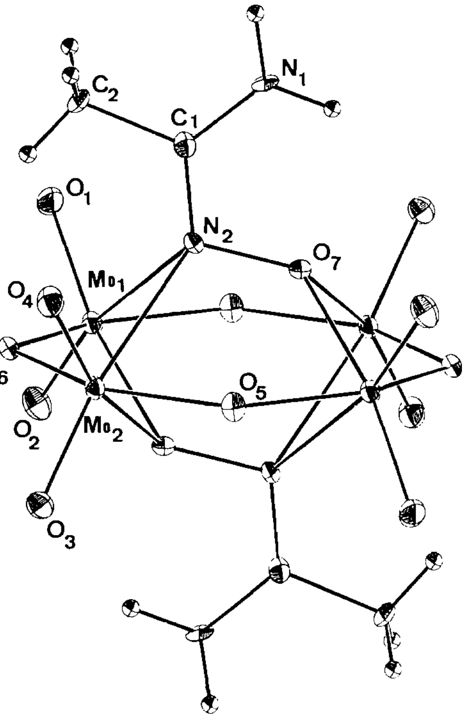

Fig. 1. ORTEP drawing of $[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]^{2-}$.

The geometry of the acetamidinium cation is in agreement with that found in previous studies [7]. Although the hydrogen atoms were included in calculated positions in the last cycles of refinement, most of them were located on difference Fourier maps, allowing a discussion of possible hydrogen bonds. Inspection of intermolecular contacts and of angles at the hydrogen atoms of the NH_2 groups suggests that one hydrogen atom of the NH_2 group of the ligand is involved in an intramolecular N–H···O bond and that each cation links two anions through N–H···O intermolecular hydrogen bonds with terminal oxygen atoms. In addition, each solvent molecule interacts with one cation and one anion through O···H–O and O–H···O hydrogen bonds. N···O and O···O intermolecular contacts range from 2.811(6) to 2.896(6) Å. This indicates that hydrogen bonding is rather weak, in agreement with the ease of desolvation of the crystals.

Although the mechanism of formation of $[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]^{2-}$ from $[Mo(NO)(acac)_2\{CH_3C(NH_2)NO\}]$ is not straightforward, nor is the fate of the nitrosyl ligand and the role of benzoylhydrazine, the identification of acetamidine supports oxygen transfer from acetamidoxime to Mo(II). Deoxygenation of amidoximes has been previously demonstrated with $[Fe(CO)_5]$ [8] but does not seem to have been reported with low-valent molybdenum compounds despite the fact that oxygen transfer plays a key role in the chemistry and biochemistry of molybdenum [9, 10]. Deoxygenation of amidoximes has also been recently observed with oxovanadium(V) complexes [2].

Deoxygenation of amidoximes with Mo(II) compounds is not restricted to nitrosyl complexes. In CH_3CN, the reaction of acetamidoxime with $[Mo_2(CH_3CO_2)_4]$ gives $[Mo_4O_{12}\{CH_3C(NH_2)NO\}_2]^{2-}$ and $CH_3C(NH_2)_2{}^+$. $ArC(NH_2)NOH$ ($Ar = C_6H_5$ or p-MeC_6H_4) also reacts with $[Mo_2(CH_3CO_2)_4]$ in CH_3CN yielding $[Mo_2O_5\{ArC(NH)NHO\}_2]$ [11] and $[ArC(NH_2)_2][CH_3CO_2]$. These reactions may be compared to the deoxygenation of oximes by $[Cr_2(CH_3CO_2)_4]$ [12].

These results open a new route to organonitrogen derivatives of polyoxomolybdates. This synthetic methodology is being explored for the preparation of derivatives of other polyoxometallates.

Supplementary material

Final atomic positional parameters, anisotropic thermal parameters, interatomic bond distances and angles and observed and calculated structure factors are available from the authors on request.

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