



Triangular Clusters of Molybdenum Coordinated with Diethylthiocarbamate: Synthesis, Structure and Solution Behavior

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Abstract

Two novel clusters $[\text{Mo}_3\text{S}_4(\text{dtc})_3(\mu\text{-dtc})(\text{L})]$ (where $\text{L} = (\text{CD}_3)_2\text{SO}$ and tetrahydrothiophene, tht) were prepared and structurally characterized. The tht complex and its previously reported congener with $\text{L} = \text{py}$ were studied by means of temperature-dependent ^1H NMR spectroscopy, indicating order of lability $\text{tht} \gg \text{py}$.

Keywords Molybdenum · Sulphur · Clusters · NMR

Introduction

Chalcogenide clusters play crucial role in the chemistry of Mo and W in middle oxidation states, with numerous examples of the triangular clusters with M_3Q_4 and M_3Q_7 cores (where $\text{M} = \text{Mo}$, W and $\text{Q} = \text{S}$, Se) being no exception (Scheme 1) [1]. Since their discovery in 1960s, the clusters of this type found several applications after being put into the proper ligand environment. The complexes of Mo_3Q_7 core coordinated with dithio- or diselenolates serve as the precursors for the single-source conducting materials [2–7] or HER catalysts [8]. The derivatives of the Mo_3S_4 core with additional diphosphane or diamine ligands catalyze reduction of nitroarenes [9, 10] (or reduction coupled with further transformations [11, 12]) and hydrodefluorination of pentafluoropyridine [13]. Heterometallic derivatives of molybdenum clusters, $[\text{Mo}_3\text{M}'(\mu_3\text{-Q})_4]^{n+}$, also show catalytic properties in a variety of

organic reactions [14–20]. In addition, the tris-chelated cluster core M_3S_4 possesses an intrinsic chirality, and the use of the optically pure ligands (or counterions [21]) makes it possible to isolate the cluster as pure enantiomer. However, the phosphanes as the source of the chirality of the triangular clusters (or their heterometallic derivatives) have some pronounced disadvantages, such as complicated synthesis of chiral phosphanes, their toxicity, instability towards oxygen and ensuing high cost. It is therefore natural to look for other sources of the cluster chirality, and here naturally occurred chiral carboxylic acids seem cheap and attractive alternative. Recently, a series of clusters of general formula $[\text{M}_3\text{S}_4(\text{dtp})_3(\mu\text{-RCOO})(\text{py})]$ was reported [22, 23], where RCOO is the optically active carboxylate (lactate, mandelate, or phenyllactate), and dtp is $(\text{EtO})_2\text{PS}_2^-$. Study of the solution behavior of these clusters in non-polar solvents (CDCl_3 , CD_2Cl_2) by means of ^1H and ^{31}P NMR spectroscopy revealed complicated dynamic behavior which three processes which may influence their performance as chiral agents: (1) diastereomer interconversion, which is inhibited at low temperatures, (2) pyridine rotation around the Mo–py bond (180° -flip), and (3) pyridine exchange in the presence of added pyridine. The aim of the present work was the synthesis, structural and solution study of analogues of these clusters with dtc (= diethyldithiocarbamate) ligands instead of dtp.

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