

Heterometallic Sulphur systems containing Copper and Molybdenum

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Manuscript received online 17 February 2020, accepted on 30 March 2020

Abstract : Some complexes of tetrathiomolybdate with copper were synthesized and were characterized on the basis of chemical and spectral studies with a view to exploit the reactivity of these heterometallic sulphur systems for possible biological relevance to copper-molybdenum antagonism.

(Keywords : Heterometallic sulphur systems, tetrathiomolybdate and copper-molybdenum antagonism.)

Introduction

Thiometallates of molybdenum and tungsten are known since 1826 when Berzelius¹ synthesized the ions MoS_4^{2-} and WS_4^{2-} . The reactivity of these thiometallates and their application in complex chemistry has been explored systematically recently²⁻⁴. These thiometallates react with other transition metal salts like CoCl_2 , FeCl_2 , NiCl_2 and also with non-transition metal salts like SnCl_2 , PdCl_2 and ZnCl_2 to form series of heterometallic-metal sulphur assemblies. The ligation behaviour of thiometallates with coinage metal systems has not been studied in great detail until recently. This was partly due to the polymeric nature of the species formed where structural characterization has been difficult in view of their insoluble nature. In the light of the above fact, some complexes of tetrathiomolybdate with copper were synthesized. Purpose of this synthesis is to exploit the reactivity of prepared heterometallic sulphur systems for possible biological relevance to copper-molybdenum antagonism. The depletion in the availability of copper for metabolic purpose due to the copper-molybdenum interaction is

referred to as copper-molybdenum antagonism⁵. Synthesis of complexes of copper with tetrathiomolybdate, in fact, support the fact of copper-molybdenum antagonism as well as these complexes may serve as models to understand the phenomenon of copper-molybdenum antagonism.

Experimental

Materials and Methods: All the chemicals used were of AnalR grade.

Preparation of complexes: First of all, the starting materials like CuSCN , $(\text{NH}_4)_2\text{MoS}_4$, $(\text{PPh}_3)_2[\text{MoS}_4]$, $(\text{NH}_4)_2[\text{MoO}_2\text{S}_2]$ were prepared and then complexes, $\text{Et}_4\text{N}[(\text{bpy})\text{CuMoS}_4]$, $(\text{Et}_4\text{N})_2[\text{NCSCuMoS}_4]$, $[(\text{bpy})_2\text{Cu}_2\text{MoS}_4]$, $[\text{Cu}_2\text{P}_3(\text{C}_6\text{H}_5)_9\text{MoS}_4]$, $[(\text{bpy})_2\text{Cu}_2\text{MoO}_2\text{S}_2]$, $[\text{Cu}_3\text{P}_3(\text{C}_6\text{H}_5)_9\text{C}_1\text{MoS}_4]$, $[\text{Cu}_4\text{Py}_4(\text{SCN})_2\text{MoS}_4]$ and $[\text{Cu}_4\text{Py}_4\text{Cl}_2\text{MoS}_4]$ were synthesized and were characterized by chemical and spectroscopic studies. Analytical and spectroscopic data of the complexes are given in Table-1, Table-2 and Table-3 respectively.

Electronic spectra: Electronic spectra were obtained on a carry 17 D spectrophotometer using matched quartz cell. Solid state spectra were recorded using KBr pellet or the diffused reflectance spectra were recorded by rubbing the compound on white bond paper. The background absorption was minimised using a blank paper. The solvents used were of analytical grade. Electronic spectroscopy of thiometallate complexes particularly with metal containing open d-shell show the involvement of delocalized molecular orbitals characteristics of strong

interaction between the central metal and thiometallate ligand. The simplified molecular orbital scheme for MS_4^{n-} ion with T_d symmetry suggests the involvement of π bonds which is also demonstrated by various other physical measurements. The known complexes of the type $[M'(MS_4)_2]^{2-}$ show characteristic absorption bands whose proportions are only roughly comparable to those in free thiometallates. The $S \rightarrow M$ transition in these complexes is split due to the lowering of local symmetry about the central atom of the MS_4^{2-} unit. Because to the strong $M \rightarrow L$ interaction, the spectra in the region of ligand internal transitions depends markedly on the nature of the central atom. Thus, there is a characteristic splitting of the ν_1 band of MS_4^{2-} in the nickel complex. In contrast, the longest wavelength band in the corresponding thiomolybdate analogue is strongly shifted in the direction of longer wavelength. The electronic spectra of the $M'-M-S$ complexes show characteristic absorption bands whose positions are roughly comparable to those in the thiometallates. The ν_1 absorption in the thiometallate ions generally splitted on complexation due to the lowering in symmetry. Whenever, the central metal (M') contains open d-shell configuration, the spectra in this region of ligand internal transition markedly change due to strong metal ligand interactions. Furthermore, the coordination geometry of the central metal, for example in the trimetallic system, causes a considerable perturbation of the electronic structure of the ligand. Most of the weak d-d transitions may lie under envelop of the strong ligand to metal and metal to ligand charge transfer. Complexes containing d_{10} central atom should give less complex electronic spectra which mainly correspond to ligand internal transitions of the free ligand ions.

IR spectra:

IR spectra of the complexes were recorded in the range of 4000 to 400 cm^{-1} and 4000 to 200 cm^{-1} on Perkin Elmer model spectrometer. Samples were prepared as KBr

pellets. The pertinent IR spectroscopic data of the complexes are tabulated in Table-3. The structure of the thiometallate complexes of the type $[M'(MS_4)_2]^{2-}$ have been determined by IR spectroscopic investigations⁶⁻¹¹. Outcome of these studies have now made it possible to characterize especially the bidentate nature of these ligands. In practice the terminal M-S groups are characterize by one or two vibrational frequencies between 480 and 520 cm^{-1} and the bridging M-S group by frequencies in the range 430 to 460 cm^{-1} . In dinuclear species like $[Cl_2FeMoS_4]^{2-}$, the $\nu(M-S)_{br}$ and $\nu(M-S)_{term}$ vibrations are relatively characteristics. However, ν_s term is the most and ν_s br the least characteristic vibrations^{12,13}. The preferential sulphur coordination over oxygen in ligands of the type $MO_2S_2^{2-}$ could be easily seen by comparing the spectra of complexes using $MO_2S_2^{2-}$ and MS_4^{2-} ligands. The terminal $\nu(M-O)$ and $\nu(M-S)$ could be easily identified along with $\nu(M-S)_{br}$ in these complexes.

General properties of the complexes:

The synthesized complexes as described contain the stoichiometry between tetrathiomolybdate and copper in the ratio 1:1, 1:2, 1:3 and 1:4 respectively as obvious from its formula assigned to these complexes. Among these only the complex having 1:1 stoichiometry are anionic and the rest are neutral in nature. The involvement of coligands invariably rests with copper-ligand attachment keeping the tetrathiomolybdate moiety intact which coordinates through sulphur to copper. All these complexes are red in colour, however, there is a trend of the darkening of colour when the ratio of copper is increased. Complexes synthesized with oxothiomolybdate are generally orange red to red in colour. The anionic complexes in this series are generally soluble in polar solvents like DMF and DMSO. The neutral complexes are exceptionally stable in the solid state and they are slightly soluble in DMF and DMSO. Thermally, these complexes are generally stable up to 250°C.

Table-1 Analytical data of the synthesized complexes

Compound	Colour	m.p./ decomp/ trans. temp. °C	% analysis, found/(calcd)								
			C	H	N	P	O	S	Cl	Cu	Mo
Et ₄ N[(bpy)CuMoS ₄]	Red	> 250°C	37.80 (37.50)	4.98 (5.20)	7.35 (7.30)	-	-	22.32 (22.20)	-	11.12 (11.03)	16.40 (16.60)
(Et ₄ N) ₂ [NCSCuMoS ₄]	Red	> 250°C	32.20 (33.60)	6.53 (6.60)	6.85 (6.93)	-	-	26.52 (26.40)	-	10.52 (10.48)	15.92 (15.84)
[(bpy) ₂ Cu ₂ MoS ₄]	Red	> 250°C	35.84 (35.67)	3.16 (3.00)	8.34 (8.49)	-	-	19.89 (19.27)	-	19.40 (19.00)	14.80 (14.40)
[Cu ₂ P ₃ (C ₆ H ₅) ₉ MoS ₄]	Red	> 250°C	56.92 (52.49)	34.08 (33.95)	-	8.40 (8.12)	-	11.40 (11.26)	-	11.25 (11.17)	8.56 (8.44)
[(bpy) ₂ Cu ₂ MoO ₂ S ₂]	Red	> 250°C	37.20 (37.80)	3.40 (3.15)	8.96 (8.82)	-	-	10.88 (10.08)	-	1.98 (2.00)	15.12 (15.12)
[Cu ₃ P ₃ (C ₆ H ₅) ₉ ClMoS ₄]	Red	> 250°C	52.68 (52.42)	4.60 (4.36)	-	7.60 (7.52)	-	10.84 (10.35)	2.96 (2.87)	14.86 (15.40)	7.94 (7.76)
[Cu ₄ Py ₄ (SCN) ₂ MoS ₄]	Red	> 250°C	30.00 (29.00)	1.98 (2.20)	9.56 (9.23)	-	-	21.56 (21.10)	-	27.56 (27.91)	10.82 (10.55)
[Cu ₄ Py ₄ Cl ₂ MoS ₄]	Red	> 250°C	27.52 (27.75)	2.52 (2.31)	6.55 (6.47)	-	-	15.02 (14.80)	8.20 (8.20)	30.00 (29.36)	10.98 (11.10)

Conclusion:

The recent investigation on the interaction of Cu-Mo-S systems reveals that the interaction, in principle, is between copper and thiomolybdate¹⁴. In vitro generation of thiomolybdate by rumen contents when combined with molybdate and sulphur sources under anaerobic conditions further supports this thiomolybdate hypothesis¹⁵. Thus, it may be assumed at this stage that copper interacts with

tetrathiomolybdate to form stable Cu-Mo-S complex which seems to be stable enough to prevent copper to be available for physiological activity. From chemical point of view it would be of prime importance to know about the exactness of the species. The synthesized complexes support the phenomenon of copper-molybdenum antagonism and may serve as models for further studies.

Table-2 Electronic spectral data of the synthesized complexes (in nm)

Compound	Electronic		Transitions	
	ν_1	ν_2	ν_3	
(NH ₂) ₂ MoS ₄	467	318	242	207
(Et ₄ N) ₂ [(bpy)CuMoS ₄]	495	338	260	242
(Et ₄ N) ₂ [NCSCuMoS ₄]	295	338	258	242
[(bpy) ₂ Cu ₂ MoS ₄]	495	375	258	242
[Cu ₄ Py ₄ (SCN) ₂ MoS ₄]	490	370	245	210

Table-3 Pertinent IR spectroscopic data of the complexes

Compound	$\nu(\text{Mo-S})_{\text{br}}$	$\nu(\text{Mo-S})_{\text{term}}$	$\nu(\text{Mo-S})_{\text{term}}$	reference
(NH ₂) ₂ MoS ₄	--	472	--	
Et ₄ N[(bpy)CuMoS ₄]	425, 448	488, 499	--	
(Et ₄ N) ₂ [NCSCuMoS ₄]	440, 450	485, 495	--	
[(bpy) ₂ Cu ₂ MoS ₄]	460	--	--	
[(bpy) ₂ Cu ₂ MoO ₂ S ₂]	445	--	920, 910	
[Cu ₄ Py ₄ (SCN) ₂ MoS ₄]	450	--	--	
[Cu ₄ Py ₄ Cl ₂ MoS ₄]	450	--	--	

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Abstracted / Indexed in : Chemical Abstract U.S.A.

JC-1356/2K20 (ISSN:0973-239X), INDIA

Journal Chemtracks Vol. 22 (1&2), 115-118, January to December 2020