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Synthesis and Characterization of Di-μ-oxobis[oxo(thiosemicarbazido)molybdenum(V)]

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Abstract

An oxomolybdenum complex with thiosemicarbazide (HTSC) of composition $Mo_2O_4(TSC)_2$ has been prepared. The magnetic moment (0.51 BM) and the electronic spectral data indicate a dimeric structure with a 'Mo_2O_4' core. The negative shifts in ν(NH) and ν(CS) indicate the involvement of nitrogen and sulphur atoms in coordination. The IR bands at 970, 740 and 480 cm^{-1} indicate the presence of terminal (Mo=O) and bridging (MoO_2Mo) oxygen atoms. XPS studies indicate the pentavalent state of molybdenum and the coordination of thiosemicarbazide through nitrogen and sulphur. The complex exhibits an irreversible cathodic wave at -1.05 V *versus* SCE characteristic of a $Mo_2O_4^{2+}$ core. The thermal decomposition behaviour of the complex in air, nitrogen and hydrogen atmospheres is discussed. A di-μ-oxo bridged oxomolybdenum(V) structure with thiosemicarbazide completing five coordination around each molybdenum atom is proposed.

Introduction

Molybdoenzymes such as xanthine, oxidase, xanthine dehydrogenase, aldehyde oxidase and sulfite oxidase contain molybdenum in the +5 oxidation state [1]. The presence of terminal oxygen with other coordination sites being nitrogen and or sulphur is inferred from biological studies [2]. Both dimeric and monomeric molybdenum(V) complexes have been recognized as acting as models for molybdoenzymes. In the present study, the preparation and characterization of a dimeric di-μ-oxomolybdenum(V) complex with thiosemicarbazide is described.

Experimental

The chemicals employed for the synthesis were of laboratory grade. Thiosemicarbazide was recrystallized twice from water before use.

Synthesis

MoO_3 (1.4 g) was dissolved in conc. HCl (1 cm^3) and DMF (20 cm^3). To the resultant solution, thiosemicarbazide (0.9 g) in water (10 cm^3) was added and warmed over water bath. The complex which precipitated on cooling was filtered, washed with water, methanol and dried.

Anal. Calc. for $C_2H_{10}N_6O_4S_2Mo_2$: C, 5.50; H, 2.31; N, 19.26; S, 14.61; Mo, 44.52. Found: C, 5.54; H, 2.30; N, 19.30; S, 14.58; Mo, 44.56%.

UV–Vis (nm) (M^{-1} cm^{-1}): 460, 3000; 310, 23 000.

IR (cm^{-1}) HTSC: 3360s, 3248s, 3170s, 3100sh, 2970m, 1648s, 1626s, 1532s, 1508sh, 1486m, 1315m, 1284m, 1220w, 1160m, 1000s, 805s. $Mo_2O_4(TSC)_2$: 3380s, 3250s, 3140s, 3080w, 1640s, 1610s, 1530w, 1420m, 1320m, 1250m, 1150w, 1110m, 1010w, 970s, 750m, 700m.

Physical Measurements

Carbon, hydrogen and nitrogen were analysed using a Hewlett-Packard CHN analyser. Thermal decomposition studies were carried out in air, nitrogen and hydrogen on a Stanton-Red Croft STA-780 thermal analyser. Magnetic susceptibility was measured for the powdered sample at room temperature using a Gouy balance and the magnetic moment was calculated after applying diamagnetic corrections [3]. X-ray photoelectron spectra were recorded on an ESCA LAB MK II spectrometer using Al $K\alpha_{1,2}$ radiation (1485.6 eV). Samples were deposited as thin films on to a silver plate so as to minimize charging effects. The C1s line (b.e. = 285.0 eV) from residual pump-oil contamination was used as an internal standard for spectral calibration.

The electrochemical measurements for the complex were conducted in DMSO using tetraethylammoniumperchlorate (TEAP) as the supporting electrolyte. The measurements were carried out by a three electrode system on a McKee Pedersen potentiostatic circuit constructed from operational amplifiers. The working electrode was a Pt wire and a Pt foil served as auxiliary electrode with a saturated calomel electrode as reference. The solution under investigation and the reference electrode were separated by a non-aqueous salt bridge. Sweep rates varied

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TABLE I. Electron Core Binding Energies (eV)

	N(1s)	S(2p)	Mo($3d_{5/2}$)	O(1s)
TSC	400.5(4.0)^a	162.0(1.4)		
TSC^b	400.1, 401.9			
$Mo_2O_4(TSC)_2$	399.8(4.2)	162.9(1.2)	231.4(1.4)	531.8(3.3)
$Mo_2O_4(TSC)_2{}^b$	399.8, 401.8			531.4, 533.6

^{a}FWHH values. ^{b}On deconvulsion.

between 0.01–0.2 V s^{-1}. Deaeration of the solution was performed before commencing the experiment by a stream of purified nitrogen.

Results and Discussion

The very low magnetic moment value of 0.51 BM indicated a spin-pair interaction of the unpaired electrons over the adjacent molybdenum atoms [4]. The UV–Vis maxima at 460 and 310 nm in DMSO are assigned to d → d transition and ligand to Mo charge transfer respectively. The electronic spectra of $Mo_2O_4{}^{2+}$ species do not in general display the low energy d → d transitions which are characteristic of both MoO^{3+} monomers and $Mo_2O_3{}^{4+}$ dimers [5]. The shift in the absorption bands of $\nu(NH_2)$ (~20–30 cm^{-1}) observed in the region 3360–2970 cm^{-1} indicate the coordination of amine nitrogen to molybdenum [6]. The ν(CS) band observed at 805 cm^{-1} in the ligand is shifted to 700 cm^{-1} in the complex indicating coordination through the sulphur atom. The coordination through nitrogen and sulphur are inferred from the IR spectral studies. The band at 970 cm^{-1} is due to ν(Mo=O, terminal) and the bands at 750 and 480 cm^{-1} are assigned [7] to the asymmetric and symmetric stretching bridge vibrations of the MoO_2Mo group. The bands at 430 and 360 cm^{-1} are attributed [8] to ν(Mo–N) and ν(Mo–S) respectively.

Electron core binding energies (eV) derived from the X-ray photoelectron spectra of HTSC and $Mo_2O_4(TSC)_2$ are listed in Table I. The value of 231.4 eV (Mo, $3d_{5/2}$) for the complex offers evidence [9, 10] on the pentavalent state of molybdenum. The significant binding energy decrease for one of the N(1s) bands in the complex after band deconvulsion indicates its coordination to molybdenum in the complex. The observed shift in the binding energy value of the sulphur atom is attributed to the deprotonation and coordination of sulphur to molybdenum. The single O(1s) band in the complex after deconvulsion splits into 530.4 and 532.1 eV which are attributed to the terminal (Mo=O) and bridging (MoO_2Mo) oxygen atoms respectively.

A cyclic voltammogram (Fig. 1) of the complex in DMSO exhibits a cathodic wave at −1.05 V *versus* SCE involving a two electron transfer assigned to the Mo(V)/(IV) couple. The *n* value at −1.05 V found from coulometry experiment varies from 1.8–2.0. $Mo_2O_4(TSC)_2$ is reduced directly by an irreversible two electron transfer. Thus the electrochemical behaviour of the complex is similar to the hitherto reported [11] $Mo_2O_4{}^{2+}$ complexes.

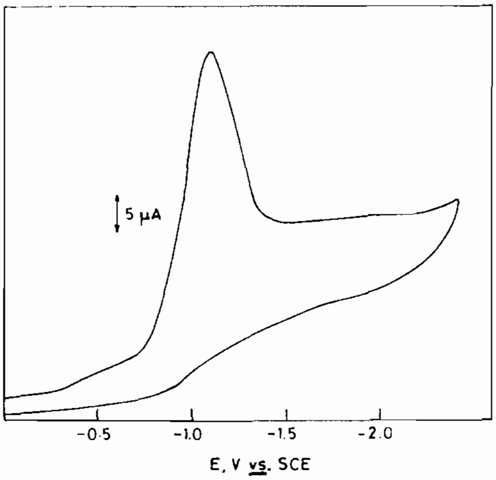

Fig. 1. Cyclic voltammogram of $Mo_2O_4(TSC)_2$ (1 mM) in 0.1 M TEAP/DMSO. Sweep rate = 0.1 V s^{-1}.

The end residues obtained on thermal decomposition of $Mo_2O_4(TSC)_2$ in air, nitrogen and hydrogen atmospheres are MoO_3, MoS_2 and Mo respectively. In air the complex melts with an endothermic peak at 145 °C. The release of hydrazine, hydrogen sulphide and carbon disulphide occurs [12] with exothermic peaks at 240, 280 and 390 °C respectively. An endothermic peak at 200 °C is due to the fusion of thiosemicarbazide. In nitrogen, the pattern is similar to that in air. In hydrogen an exothermic peak at 380 °C due to the decomposition of the complex is observed. The end residues formed during the temperature ranges 150–400 °C in air (calc. for MoO_3:66.05, found: 64.91%), 160–420 °C in nitrogen (calc. for MoS_2:73.39, found: 71.11%) and 150–450 °C in hydrogen (calc. for Mo 44.03, found: 43.91%) are identified by chemical analyses and X-ray diffraction data. In DTA, the peaks observed at 420 (exo), 450 (exo) and 490 (endo) °C in air, nitrogen and hydrogen are assigned to the formation of MoO_3, MoS_2 and Mo respectively. The kinetic parameters for the thermal decomposition of the complex in air were calculated using the Coats and Redfern equation [13]. The order of the reaction has been bound to be 1 and the E_a is 210.5 cal. A structure with di-μ-oxomolybdenum(V) coordinated by the nitrogen and sulphur of thiosemicarbazide is proposed.

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