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N/P-ETHOXYPHENYL/DITHIOCARBAMATO COMPLEXES OF Au(III), As(III), Fe(III), Co(III) AND Mo(V)

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The complexes of Au(III), As(III), Fe(III), Co(III) and Mo(V) with N(*p*-ethoxyphenyl)-dithiocarbamate have been synthesized and characterized on the basis of elemental analyses, conductance measurements, infrared and electronic spectra, molecular weight determinations and magnetic moment data. The thermal behaviours of these complexes have been studied with the aid of TG and DTA techniques.

As a continuation of our previous work on metal dithiocarbamates [1–3] the present pater describes the synthesis, characterization and thermal investigation of Au(III), As(III), Fe(III), Co(III) and Mo(V) complexes with N/*p*-ethoxyphenyl/dithiocarbamate.

Experimental

Ammonium N/*p*-ethoxyphenyl/dithiocarbamate was synthesized by the general method described in the literature [4]. Tris N/*p*-ethoxyphenyl/dithiocarbamato complexes of gold(III), arsenic(III), iron(III) and cobalt(III) were prepared by mixing an aqueous solution of a salt of gold(III), arsenic(III), iron(III) or cobalt(III) with an aqueous solution of the ligand in a 1:3 metal-to-ligand ratio. The molybdenum(V) complex $Mo_2O_3[S_2CNH/p\text{-}OC_2H_5C_6H_4/]_4$ was prepared by adding an excess of sodium dithionate to an aqueous solution of $Na_2MoO_4 . 2H_2O$ (0.1 mole) and ligand (0.2 mole). The precipitated complex was filtered off, washed with distilled water and dried under vacuum over phosphorus pentoxide, yield: 68–76%.

The ligand was estimated by the method of Shankaranarayana and Patel [5]. The metal, nitrogen and sulphur contents were estimated by standard gravimetric methods [6].

Conductance measurements were made in nitrobenzene at 25 ± 0.1° with a Beckmann Conductivity Bridge Model No. RC–18A. Magnetic measurements were made by Gouy's method using mercury tetrathiocyanatocobaltate/II/ as calibrant ($\chi_g = 16.44 \times 10^6$ c.g.s. unit) at room temperature. Infrared spectra were recorded in KBr pellets in the region 4000–200 cm^{-1} with a Perkin-Elmer 621 gratig spectrophotometer. Electronic spectra of the complexes were run on a Perkin-Elmer 4000 Å instrument in the range 400–750 nm.

TG curves were recorded on a Stanton automatic thermorecording balance Model TR–I with a sample size of 100 mg and a heating rate of 4 deg.min^{-1}. The DTA was carried out with a Leed and Northrup DTA unit (U.S.A.) using 100 mg of sample with a heating rate of 10 deg.min^{-1}.

Results and discussion

Analytical data and other physical characteristics found for the complexes are listed in Table 1. The Au(III), As(III), Fe(III) and Co(III) complexes possess 1:3 metal-to-ligand stoichiometry, whereas the Mo(V) complex possesses a 1:2 metal-to-ligand ratio. Molecular weight determinations and conductance measurements revealed the non-electrolytic and monomeric nature of all these complexes (except the Mo(V) complex, which is dimeric).

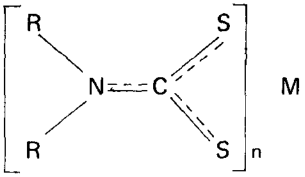
The IR spectra of these compounds exhibited one medium intensity band at ~ 1000 cm^{-1}. This indicates the presence of a four-membered ring system and also supports the bidentate nature of the dithiocarbamate ligand [7]. The thioureide C$\overset{...}{=}$N band at 1250–1350 cm^{-1} and that of the C=N band at 1640–1690 cm^{-1}, suggesting

Table 1 Analytical data and physical characteristics

Compound	Colour	M.p., K	Found (Calc.), % N	S	M	Mol. Wt. Found (Calc.)
AL*	White	380	12.20 (12.17)	27.80 (27.83)	–	222 (230.0)
AuL_3	Dark yellow	397	5.10 (5.04)	23.10 (23.05)	23.75 (23.65)	824 (832.97)
AsL_3	Light yellow	448	5.85 (5.91)	26.90 (27.00)	10.58 (10.54)	698 (710.90)
FeL_3	Brownish black	489	6.02 (6.07)	27.60 (27.65)	8.23 (8.07)	684 (691.85)
CoL_3	Dark green	424	6.16 (6.04)	27.40 (27.63)	8.40 (8.48)	682 (694.93)
$Mo_2O_3L_4$	Purple	403	5.10 (5.15)	23.60 (23.53)	17.56 (17.64)	1072 (1087.9)

AL = $NH_4[S_2CNH(p\text{-}OC_2H_5C_6H_4)]$

more double bond character. The following general formula may therefore be assigned to the compounds:



where $n = 3$ when M is Au(III), As(III), Fe(III) and Co/III), and $n = 4$ when $M = Mo_2O_3$.

The metal dithiocarbamates showed new bands in the region 400–350 cm^{-1}, viz. ν/Au–S/372 cm^{-1}, ν/As–S/ 360 cm^{-1}, ν/Fe–S/ 370 cm^{-1}, ν/Co–S/ 360 cm^{-1} and ν/Mo–S/365 cm^{-1}. In addition, the molybdenum complex shows new bands at 930 cm^{-1} and 760 cm^{-1}, which may be assigned to ν/Mo=O/ and antisymmetrical Mo-O-Mo vibration, respectively.

Room temperature magnetic moment studies of the complexes show that the Fe/III/ complex is paramagnetic, having a magnetic moment of 3.40 B.M., corresponding to three unpaired electrons in the central metal atom of the complex. The electronic spectrum of the Fe(III) complex is rich in bands. Throughout the visible region the absorption is so intense that it must be attributed to charge transfer band. In the near infrared region, there are in addition further broad and weak bands at 12400 and 6200 cm^{-1}, which may be assigned to the superimposed transitions $^6A_1 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_1$ [8]. The Au(III), As(III), Co(III) and Mo(V) complexes are diamagnetic as expected.

Thermal analysis

The TG and DTA curves of the ligand and the complexes are presented in Figs 1 and 2.

Ammonium N(*p*-ethoxyphenyl)dithiocarbamate is thermally stable up to 368 K. Beyond this temperature it starts decomposing, and the crucible was completely empty at 823 K. The DTA profile of the ligand shows one endotherm and one exotherm, corresponding to the melting and burning of the ligand, respectively.

The TG curves of the Au(III), As(III) and Mo(V) complexes show two-step decomposition. The first stage in the decomposition, which is common to all the three complexes, is due to the formation of sulphide. The second step in the weight loss corresponds to the formation of metal, volatilization of sulphide and oxidation of sulphide to oxide for the Au(III),As(III) and Mo(V) complexes, respectively. The first endothermic peak in the DTA curves of these complexes corresponds to the melting of the complexes, while the first stage in the decomposition of sulphide is represented by the last two exotherms in the case of the Au(III) complex, while only one exothermic peak is obtained for this step in the case of the Mo(V) complex. The DTA curve exhibits one exotherm and one endotherm for the second step in the decomposition of

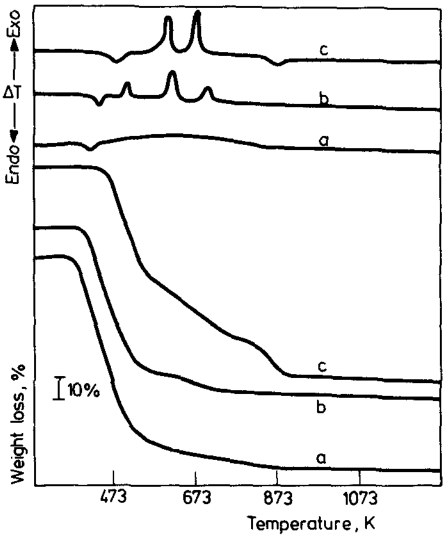


Figure 1 TG and DTA curves of (a) PED, (b) $Au(PED)_3$, (c) $As(PED)_3$

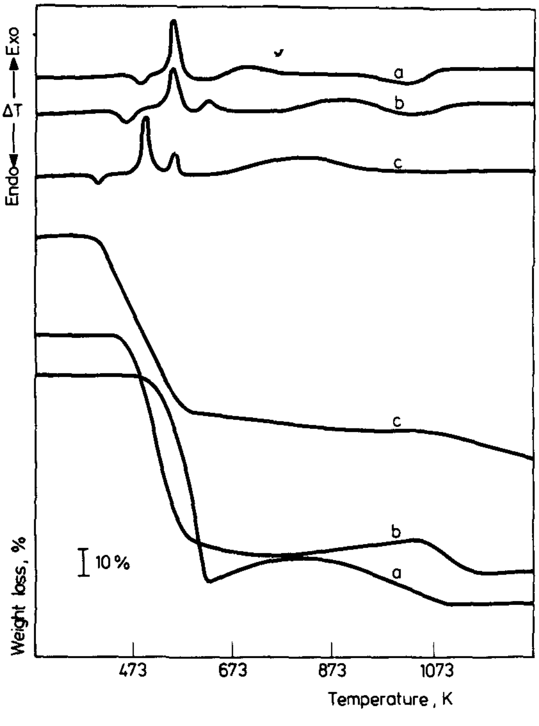


Figure 2 TG and DTA curves of (a) $Fe(PED)_3$, (b) $Co(PED)_3$ (c) $Mo_2O_3(PED)_4$

Table 2 Temperature range, weight loss and heat of reaction for different decomposition steps of the complexes

	TG			DTA		
	Decomposition range, K	% Weight loss Obs.	Calc.	Oxidation range, K	Peak temp., K	ΔH, kJ mol^{-1}
1.	$NH_4[S_2CNH(p\text{-}OC_2H_5C_6H_4)]$					
I	368-878	99.82	100	368-398	388	5.14
				458-823	b	–
2.	$Au[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_3$					
I	393-553	70.52	70.60	388-418	400	10.7
				448-488	478	28.3
II	588-723	5.92	5.75	568-598	578	251.3
				633-693	678	131.3
3.	$As[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_3$					
	443-588	84.08	84.12	433-473	460	34.1
				543-588	573	128.4
II	598-873	15.96	15.88	618-708	643	247.2
				813-873	b	–
4.	$Fe[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_3$					
I	473-623	84.68	84.99	463-513	b	–
				523-583	558	244.9
II	623-773	–	–	658-773	b	–
III	873-1093	–	–	918-1073	b	–
5.	$Co[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_3$					
I	413-573	66.32	66.48	410-473	460	14.6
				498-588	528	179.1
II	573-748	17.98	18.14	573-613	600	65.2
III	748-1048	–	–	823-1038	b	–
IV	1048-1148	3.53	3.83	1048-1123	b	–
6.	$Mo_2O_3[S_2CNH(p\text{-}OC_2H_5C_6H_4)]_4$					
I	398-583	67.42	67.65	393-423	405	14.9
				448-538	423	229.1
				538-578	555	77.7
II	588-918	5.99	5.89	648-923	b	–

the As(III) complex. The exotherm corresponds to the conversion of sulphide to oxide, while the endotherm is due to the volatilization of the oxide.

The TG curve of the Fe(III) complex shows three major changes, corresponding to the formation of sulphide, the oxidation of sulphide to sulphate, and the decomposition of sulphate to oxide, respectively. The DTA profile of the complex exhibits two endotherms and two exotherms. The first endotherm corresponds to the melting of the compound. The second endotherm is due to the decomposition of iron sulphate to iron oxide. The first broad exotherm corresponds to the decomposition of dithiocarbamate to sulphide, while the next sharp exotherm might be due to the oxidation of iron sulphide to iron sulphate. The thermal behaviour of the Co(III) complex is almost comparable to that of the Fe(III) complex, except that the decomposition of the sulphide proceeds through intermediate thiocyanate, which is represented by an additional exothermic peak in the DTA curve.

The thermal stability data, decomposition ranges, percentage weight losses and heats of reaction for various decomposition reactions are given in Table 2. Since the samples were run in air atmosphere, decomposition of the compounds takes place along with oxidation. Hence exothermic peaks are observed in the DTA curves.

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