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THERMAL AND SPECTRAL STUDIES OF SOME METAL-4-AMINOPHENAZONE DITHIOCARBAMATES

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ABSTRACT

4-Aminophenazone dithiocarbamate (4-Apdtc) complexes of the type M-(4-Apdtc)$_n$, where M = Mo(V), Pb(II), Cd(II), Sb(III), Pt(II), UO_2(II) or Ag(I) and n is the oxidation number of the metal ion, have been prepared in aqueous alcoholic medium from stoichiometric amounts of the reactants and suitably characterized. Thermal studies of the complexes have been carried out to determine their mode of decomposition, apparent activation energy and the order of each thermal reaction. Infrared spectra suggest that 4-Apdtc acts as a bidentate ligand.

INTRODUCTION

Dithiocarbamates constitute a class of organo-sulphur compounds having strong binding properties, and are also known to have a profound effect on biological systems [1,2]. There has been growing interest in the study of metal dithiocarbamates, and several transition metal complexes of aliphatic and aromatic dithiocarbamates have already been studied [3–7]. In the present communication we report the preparation and detailed investigations of some metal 4-aminophenazone dithiocarbamates.

EXPERIMENTAL

A Beckman thermometer was used to determine the molecular weight by cryoscopic method. Thermal studies at 7°C min^{-1} heating rate were carried out in oxygen atmosphere at a flow rate of 10 ml min^{-1} on a Setaram G-70 thermobalance taking 20–30 mg sample size. Infrared spectra in the region 4000–200 cm^{-1} were recorded in the solid state (cesium iodide pellets) on a Perkin-Elmer 621 IR spectrophotometer. Conductance measurements were obtained on a Beckman model RC-17A conductivity bridge.

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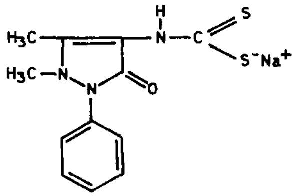
Synthesis of the ligand

The ligand, 4-aminophenazone dithiocarbamic acid [8], was prepared in situ by treating stoichiometric amounts of 4-aminophenazone (KL) dissolved in a minimum quantity of ethanol with purified carbon disulphide. The reaction mixture was set aside for about 5 min. 4-Aminophenazone dithiocarbamic acid, being unstable, could not be isolated. The sodium salt of this acid (I) was prepared by treating at 5°C with the appropriate amount of sodium hydroxide for about 2 h. The white crystalline product thus separated was recrystallized from acetone and dried in vacuo over P_4O_{10}, m.p. 122°C (Tables 1 and 2).



(I)

TABLE 1

Elemental analysis and physical characteristics of the complexes

Compound, colour, m.p. (°C)	% Found (Calcd.)					M. wt. found (calcd.)	Molar conductance (mho cm^2 mole^{-1})
	C	H	N	S	M		
Na-(4-Apdtc)[a],	40.1	3.2	13.6	21.0			
white, 122	(40.6)	(3.9)	(13.9)	(21.2)			
Pb-(4-Apdtc)$_2$,	35.2	3.1	10.9	16.4	26.5	750.24	0.3
yellowish brown, 120	(37.7)	(3.1)	(11.0)	(16.8)	(27.1)	(763.22)	
Cd-(4-Apdtc)$_2$,	43.0	3.4	12.0	18.9	15.9	660.50	0.5
yellow, 165	(43.1)	(3.6)	(12.5)	(19.2)	(16.8)	(668.40)	
Sb-(4-Apdtc)$_3$,	43.4	3.7	13.3	20.1	11.9	926.54	0.4
orange, 95	(45.5)	(3.8)	(13.3)	(20.2)	(12.8)	(949.80)	
Pt-(4-Apdtc)$_2$,	36.8	3.1	11.0	17.0	25.5	748.10	0.8
yellow, 135	(38.3)	(3.2)	(11.3)	(17.0)	(25.9)	(751.00)	
UO_2-(4-Apdtc)$_2$,	34.4	2.5	10.2	15.2	27.9	820.20	0.9
orange, 180	(34.8)	(2.9)	(10.2)	(15.5)	(28.8)	(826.08)	
Ag-(4-Apdtc),	37.0	3.1	10.4	16.2	27.4	296.95	0.2
grey, 185	(37.3)	(3.1)	(10.9)	(16.6)	(27.9)	(308.90)	
Mo_2O_3-(4-Apdtc)$_4$,	42.4	3.2	11.9	18.2	14.0	1335.25	0.2
deep purple, 205	(42.6)	(3.5)	(12.4)	(18.9)	(14.19)	(1351.90)	

[a] 4-Apdtc = 4 aminophenazone dithiocarbamate.

TABLE 2

IR spectral data, thermal decomposition ranges and activation energies

Compound	ν(C–N) (cm^{-1})	ν(C–S) (cm^{-1})	ν(M–S) (cm^{-1})	ν(M–O) (cm^{-1})	Decompn. temp. range (°C)	Mass loss %		Activation energy (kcal mole^{-1})
						Calcd.	Found	
Na-(4-Apdtc)	1485s	1050s						
Sb-(4-Apdtc)$_3$	1490s	1120s	360w		220–380	44.03	42.00	54.18
					400–550	46.73	45.50	13.82
Pb-(4-Apdtc)$_2$	1487s	1000s	385w		220–340	60.27	60.20	20.47
					450–720	29.68	28.65	15.13
Cd-(4-Apdtc)$_2$	1488s	1010s	345w		225–330	68.22	67.20	21.46
					420–530	39.54	38.25	9.67
Pt-(4-Apdtc)$_2$	1480s	1008s	390w		220–400	61.25	59.20	24.89
					430–690	27.49	25.45	7.79
Ag-(4-Apdtc)	1485s	1010s	380w		160–430	40.03	40.00	69.09
UO$_2$-(4-Apdtc)$_2$	1490	1010s	378w	832 sy	220–420	55.69	50.50	17.76
				915 asy	420–600	21.85	19.55	5.63
Mo$_2$O$_3$-(4-Apdtc)$_4$	1489s	990s	380w	930 sy	190–420	68.09	67.10	16.58
				760 asy	420–560	66.67	65.19	5.90

Preparation of the complexes

The stoichiometric amount of an aqueous solution of the metal salt $Pb(ac)_2$, $Cd(ac)_2$, $SbCl_3/HCl$, $AgClO_4$, $UO_2(NO_3)_2$, K_2PtCl_4 or $Na_2MoO_4 \cdot 2\ H_2O$ was added, with constant stirring, to an ethanolic solution of 4-aminophenazone dithiocarbamic acid prepared in situ. Sodium dithionite was used to reduce Mo(VI) to Mo(V). In each case, except UO_2(II), a solid complex separated out immediately on mixing. The uranyl complex could be prepared after refluxing for about half an hour. Complexes thus synthesized were first washed with distilled water followed by cold ethanol, and finally dried over P_4O_{10}.

RESULTS AND DISCUSSION

The analytical data and physical constants of the 4-Apdtc complexes are listed in Table 1. Elemental analysis was carried out by Pregl's method [9]. Metal ions, nitrogen and sulphur were estimated by standard procedures [10]. No anions were detected in any complex. All the complexes are soluble in common organic solvents. The complexes are diamagnetic and their molecular weights suggest a monomeric nature. Low conductance in nitrobenzene solution at room temperature indicates that the complexes are non-electrolytes.

Infrared and electronic spectra

The dithiocarbamates can behave either as bidentate [11,12] or monodentate [13] ligands. The dentacity of a ligand in any case can be decided on the basis of IR studies. According to Bonati and Ugo [14] a bidentate dithiocarbamate ligand shows a single band at 1000 cm^{-1} due to two equivalent $C{\overset{\dots}{=}}S$ stretching vibrations, whereas in the case of a monodentate, a doublet at ~ 1005 cm^{-1} and ~ 983 cm^{-1} due to two non-equivalent $C{\overset{\dots}{=}}S$ stretching modes is observed.

The IR spectra of various metal dithiocarbamates are almost identical to that of the parent ligand except for the presence of bands due to M–S and M–O, the latter appearing in the case of uranyl and oxomolybdenum groups only. Three main regions of the spectra are of particular interest. The absorption in the region 1500–1450 cm^{-1} is associated primarily with the 'thiouriede' group due to $\nu(C{\overset{\dots}{=}}N)$ vibration of the $C{\overset{\dots}{=}}N$ bond of the ligand. The second region between 1050–950 cm^{-1} is due to ν(C–S) vibrations, whereas the third region from 400–200 cm^{-1} is assigned to ν(M–S) [15]. Two bands at ~ 830 and ~ 915 cm^{-1} may be assigned, respectively to ν_{sy} and ν_{asy} of the linear O–U–O group [16,17] and bands at ~ 930 cm^{-1} and ~ 760 cm^{-1} to ν(Mo=O) and antisymmetrical Mo–O–Mo vibration, respectively [18]. The unsplit band at 1050–950 cm^{-1} [Table 2] indicates that the ligand is acting in the bidentate mode.

The electronic spectrum of the molybdenum(V) dithiocarbamate complex exhibits two bands, a shoulder at 26250 cm^{-1} and another band at 19600 cm^{-1}. The band at 26250 cm^{-1} is apparently a true sulphur to molybdenum charge transfer band as observed in the case of MoS_4^{2-} [19] due to an internal ligand transition [20]. The band at 19600 cm^{-1} may be assigned to $^2B_2 \rightarrow {}^2B_1$ transition. The visible spectrum of the Pt(II) complex exhibits three bands at 16800, 20200 and 24300 cm^{-1} which correspond to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$, respectively. These observations suggest a planar geometry around the central metal ion with a D_{2h} point group.

Thermal studies

Thermogravimetric studies were carried out in an atmosphere of oxygen, and the kinetic parameters were calculated using the method of Coats and Redfern [21].

The observed activation energy of thermal decomposition can be explained in terms of the probability that a molecule will possess energy in excess of an amount E per mole at temperature T, and is related to the Boltzman factor $e^{-E/RT}$, where R is the molar gas constant. The reaction rate will clearly be dependent on the product of A and $e^{-E/RT}$, where A is the frequency factor representing the total frequency encounters between two reactant molecules, irrespective of whether they possess sufficient energy or not. Thus the decomposition equation for a reaction of the type $A_{(S)} \rightarrow B_{(S)} + C_{(G)}$ is

$$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = A\ e^{-E/RT}$$

for a first order reaction, i.e., when $n = 1$ and

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = A\ e^{-E/RT}$$

when the order of reaction $n \neq 1$.

The DTG/TG curves of Pb(II), Cd(II), Pt(II), UO_2(II), Sb(III) and Mo(V) show a two-stage decomposition. The complexes are stable up to $\geqslant$ 190°C, which rules out the presence of any kind of water molecule, as is also evidenced by IR spectra. Above this temperature, the organic portion of the ligand in the complexes decomposes, resulting in the formation of the corresponding metal sulphates. Further heating results in the formation of a stable metal oxide [22]. Various thermal reactions for the above-mentioned complexes are represented as

$$\text{M-(4-Apdtc)}_2 \xrightarrow{\text{step I}} \text{MSO}_4 \qquad (1)$$

$$\text{MSO}_4 \xrightarrow{\text{step II}} \text{MO}$$

where M = Pb(II), Cd(II), Pt(II)

$$\text{UO}_2\text{-(4-Apdtc)}_2 \xrightarrow{\text{step I}} \text{UO}_2\text{SO}_4 \qquad (2)$$

$$\text{UO}_2\text{SO}_4 \xrightarrow{\text{step II}} \text{UO}_3$$

$$\text{Mo}_2\text{O}_3\text{(4-Apdtc)}_4 \xrightarrow{\text{step I}} \text{Mo}_2\text{O}_3(\text{SO}_4)_2 \qquad (3)$$

$$\text{Mo}_2\text{O}_3(\text{SO}_4)_2 \xrightarrow{\text{step II}} \text{MoO}_3$$

$$\text{Sb-(4-Apdtc)}_3 \xrightarrow{\text{step I}} \text{Sb}_2(\text{SO}_4)_3 \qquad (4)$$

$$\text{Sb}_2(\text{SO}_4)_3 \xrightarrow{\text{step II}} \text{Sb}_2\text{O}_3$$

The Ag(I)–4-Apdtc complex, however, is found to be thermally less stable. It starts to decompose at 160°C with a fast rate of weight loss with increase in temperature up to 430°C. At this stage the weight of the residue corresponds to the formation of Ag_2O which remains constant with further increase in temperature up to 900°C. The course of thermal reaction may be represented as

$$\text{Ag–4-Apdtc} \rightarrow \text{Ag}_2\text{O}$$

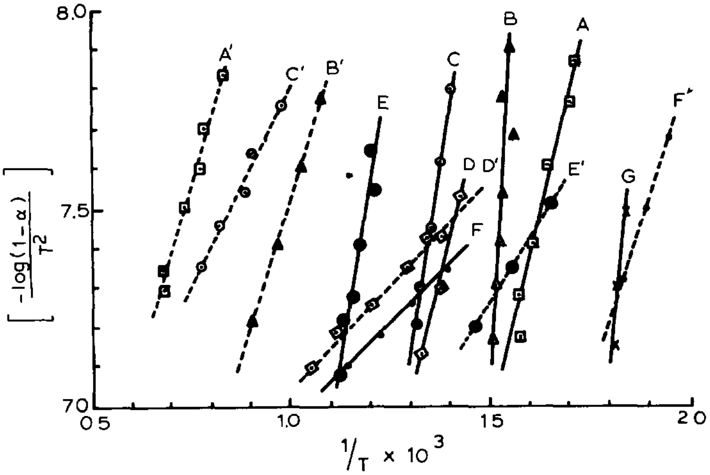


Fig. 1. 4-Aminophenazone dithiocarbamates of Pb (A,A′), Sb (B,B′), Cd (C,C′), UO_2 (D,D′), Pt (E,E′), Mo_2O_3 (F,F′) and Ag (G). The broken lines (A′, etc.) refer to the second step.

Thermal stability data and activation energy for both decomposition reaction steps in these complexes are given in Table 2. The plot of $-\log[\log(1-\alpha)/T^2]$ vs. $1/T \times 10^3$ results in a straight line of slope $= -E/2.303R$ (Fig. 1), indicating first order decomposition at each stage.

REFERENCES

1 H.W. Newman, Calif. Med., 73 (1950) 137.
2 J. Hald and G. Jacobsen, Lancet, 225 (1948) 1001.
3 A. Hulanicki and L. Shinshkova, Chem. Anal. (Warsaw), 10 (1965) 837.
4 C. Brinkhoff, Rec. Trav. Chim., 90 (1970) 377.
5 C. Preti and G. Tosi, J. Inorg. Nucl. Chem., 38 (1976) 1740.
6 P.E.B. Lindahl and S. Akerstrom, Lantbrakshoegsk. Ann., 31 (1965) 459.
7 B. Pradhan and D.V. Ramana Rao, J. Indian Chem. Soc., 58 (1981) 733.
8 H.B. Singh, S. Maheshwari, S. Srivastava and V. Rani, Synth. React. Inorg. Met.-Org. Chem., 6 (1982).
9 J. Grant, Quantitative Organic Microanalysis, Based on the Method of Fritz Pregl, Churchill, London, 1945.
10 A.I. Vogel, A. Textbook of Quantitative Inorganic Analysis, Longmans Green, London, 1964.
11 J.N. Smith and T.M. Brown, Inorg. Nucl. Chem. Lett., 6 (1970) 441.
12 A.N. Bhatt, R.C. Fay, D.F. Leneis, A.R. Lindmark and S.H. Strauss, Inorg. Chem., 13 (1974), 886.
13 A. Domenicano, A. Vaciago, L. Zanbonelli, P.L. Loader and L.M. Venanzi, Chem. Commun., (1966) 476.
14 P. Bonati and R. Ugo, J. Organomet. Chem., 1 (1964) 279.
15 D.C. Bradley and M.L.H. Green, J. Chem. Soc. A, (1969) 1152.
16 S. Mino and Z. Kecki, Rocz. Chem., 32 (1958) 1427.
17 L.H. Jones, Spectrochim. Acta, 10 (1958) 395.
18 J.E. Searbers and J.W. McDonald, Inorg. Chem., 13 (1974) 1100.
19 G. Gottow, A. Franks and A. Muller, Naturwissenschaften, 52 (1965) 42.
20 C.K. Jorgenson, J. Inorg. Nucl. Chem., 24 (1962) 1571.
21 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
22 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, London, 1963.