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STRUCTURAL AND THERMAL STUDIES ON MIXED LIGAND CO-ORDINATION COMPOUNDS OF Pd(II), Rh(III) AND Pt(II) WITH 3-(DIMETHYL-AMINOMETHYL)INDOLE AND SALICYLALDOXIME

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ABSTRACT

N-(ethyl, *m*-tolyl)dithiocarbomato complexes of Rh(III), Pd(II) and Pt(II) have been prepared and characterized [1]. A thermogravimetric study of these compounds under nitrogen has also been carried out. Teotia et al. [2] studied the reaction of Pd(II) and Pt(II) with picolinic acid hydrazide, *o*-hydroxyacetophenone picolinoylhydrazone and *o*-hydroxyacetophenone isonicotinoylhydrazone but the thermal behaviour of the isolated compounds has not been studied. A perusal of the literature reveals that no work seems to have been done on the co-ordination compounds of Pd(II), Rh(III) and Pt(II) with 3-(dimethylaminomethyl)indole and salicylaldoxime. In the present note, we report on the preparation of these compounds, determine their structure, and investigate their thermal behaviour.

EXPERIMENTAL

The platinum salts used were Johnson Matthey reagents. The ligands, 3-(dimethylaminomethyl)indole and salicylaldoxime were prepared as reported in the literature [3]. IR spectra of the co-ordination compounds in KBr pellets and in Nujol mull, for the far IR range (650–200 cm^{-1}), were recorded on a Beckmann IR-20 spectrophotometer. The thermogravimetric study was carried out on a thermobalance with a heating rate of 7 ° C min^{-1}.

Preparation of the chelates

The chelates were prepared by refluxing an aqueous solution of the appropriate metal chloride with an ethanolic solution of the ligands, 3-(dimethylaminomethyl) indole and salicylaldoxime, in a 1 : 1 : 2 molar ratio in

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the case of Rh(III), and in the ratio 1 : 1 : 1 in the cases of Pd(II) and Pt(II), for about an hour at 60–70 ° C. A slight excess of the reagents was added. The precipitated compounds were suction-filtered, washed with a little acetone and dry ether, and dried in vacuo over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The analytical results (reported in Table 1) suggest a stoichiometry of 1 : 1 : 2 (M : L : L′ where L is $C_{11}H_{14}N_2$ and L′ is $C_7H_7NO_2$) for the Rh(III) chelate, and of 1 : 1 : 1 for those of Pd(II) and Pt(II). The compounds are non-hygroscopic, decompose above 180 °, are orange-yellow in colour and are soluble in benzene, acetone, ethanol and chloroform. The compounds are stable and can be stored for quite a long time without decomposing. The chelates display electrolytic behaviour, as can be seen from their conductivity values [4], which correspond to 1 : 1 electrolytes, see Table 1. Molecular weight determinations support the above view. The compounds are diamagnetic.

Electronic spectra

The electronic spectra of Pd(11) and Pt(II) chelates in methanol exhibit bands at around 18 850, 23 400 and 27 300 cm^{-1}, and at 16 700, 20 350 and 24 200 cm^{-1}, respectively, which may be assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$. On the basis of the observed bands, a square-planar geometry is suggested for these compounds [5–8].

Two main bands have been observed in the electronic spectrum of Rh(III) chelates, at about 24 000 and 29 100 cm^{-1} which may be due to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. This suggests an octahedral co-ordination around the metal atom [5–7].

IR spectra

The comparative study of the IR spectra of the ligands and their chelates shows that both ligands act as bidentates in the chelate formation.

The N–H vibration band found at 3390 cm^{-1} in 3-(dimethylaminomethyl)indole shifts to a lower frequency, 3330–3320 cm^{-1}, in the chelates, due to the formation of metal–nitrogen bonds. A band of medium intensity observed at 1150 cm^{-1}, due to ν(C–N) of the aliphatic tertiary amine in the above ligand, appears in the spectrum of the chelates at around 1120 cm^{-1}. This suggests that the nitrogen atom of the C–N linkage of the *t*-amine plays a part in the co-ordination.

The IR spectrum of salicylaldoxime has a strong band at 3310 cm^{-1} and a medium one at 3205 cm^{-1}, assigned to symmetric and antisymmetric

TABLE 1

Analytical, conductivity and molecular weight data of Pd(II), Rh(III) and Pt(II) chelates of 3-(dimethyl-aminomethyl)indole and salicylaldoxime

Chelate [a]	Analysis [b]										Conductivity ΛM (Ω^{-1} cm^2)	Mol. wt.	
	Metal		C		H		N		Cl			Found	Calcd.
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.			
[PdL.L′]Cl	23.08	23.59	48.20	47.77	4.40	4.42	9.19	9.28	7.81	7.84	78.8	220	452.15
[RhL.2L′]Cl	17.49	17.61	50.80	51.33	4.43	4.44	9.48	9.58	6.10	6.06	82.3	285	584.36
[PtL.L′]Cl	36.58	36.10	39.41	39.94	3.70	3.69	7.80	7.76	6.51	6.55	81.2	278	540.68

[a] Where L is $C_{11}H_{14}N_2$ and L′ is $C_7H_6NO_2$.

[b] Reported percentages.

TABLE 2

Thermal decomposition data for Pd(II), Rh(III) and Pt(II) co-ordination compounds of 3-(dimethyl-aminomethyl)indole and salicylaldoxime

Chelate [a]	Decomp. temp. (°C)		Wt. loss(%)		Decomp. product
	Initial	Final	Found	Calcd.	
[PdL.L′]Cl	185	230	37.49	38.48	[PdL′]Cl
	400	430	74.85	72.86	PdO
[RhL.2L′]Cl	185	250	29.70	29.77	[Rh.2L′]Cl
	400	480	57.51	56.56	Rh_2O_3
[PtL.L′]Cl	185	240	31.78	32.18	[PtL′]Cl
	400	440	61.99	60.93	PtO

[a] L is $C_{11}H_{14}N_2$ and L′ is $C_7H_6NO_2$.

stretching vibrations of –OH in the N–OH group [9]. These modes of the oxime group are, however, not disturbed, showing the non-involvement of the group in complexation reactions. A sharp band at 1650 cm^{-1} due to the ν(C–N) mode of the oxime group [10,11] is considerably lowered to 1625–1615 cm^{-1} in the spectra of the chelates, indicating that the azomethine nitrogen is involved in the chelate formation. A broad band observed at 3560 cm^{-1}, characteristic of ν(OH) (phenolic) is not traceable in the spectra of the co-ordination compounds, indicating the deprotonation and subsequent participation of phenolic oxygen in the bond formation with the metal ion. Thus, the co-ordinates sites in the ligand are azomethine nitrogen and phenolic oxygen.

New bands at approximately 500–510 and 420–410 cm^{-1} may be assigned to M–N and M–O stretching frequencies respectively. The low frequency band appearing in the range 240–230 cm^{-1} in the chelates is tentatively assigned to the ν(M–Cl) mode.

Thermal behaviour

All the co-ordination compounds are stable up to 180 °C. The absence of any peak below 160 °C in the DTA thermograms of these compounds clearly indicates the absence of water molecules both in the co-ordination sphere and outside it. The thermal decomposition studies of these compounds reveal loss of the heterocyclic ligand in the temperature range 185–250 °C. The weight losses and the analysis of the products after decomposition support the above fact. An endothermic peak is observed at about 230 °C in the DTA thermograms of these chelates. The sharp decomposition of the products takes place in the range 400–480 °C resulting from the loss of the oxime ligand, as expected for phenolic oxime chelates [12]. The final products of decomposition computed from the TG curves correspond, in each case, to metallic oxides.

The decomposition of the co-ordination compounds is represented as follows

$$[Pd(C_{11}H_{14}N_2)(C_7H_6NO_2)]Cl \xrightarrow{185\text{-}230\,^\circ C} Pd(C_7H_6NO_2)Cl \xrightarrow{400\text{-}430\,^\circ C} PdO$$

$$\begin{aligned}[Rh(C_{11}H_{14}N_2)(C_7H_6NO_2)_2]Cl &\xrightarrow{185\text{-}250\,^\circ C} Rh(C_7H_6NO_2)_2Cl \\ &\xrightarrow{400\text{-}480\,^\circ C} Rh_2O_3\end{aligned}$$

$$[Pt(C_{11}H_{14}N_2)(C_7H_6NO_2)]Cl \xrightarrow{185\text{-}240\,^\circ C} Pd(C_7H_6NO_2)Cl \xrightarrow{400\text{-}440\,^\circ C} PtO$$

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