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Thermal, Spectral and Magnetic Studies on Fluorenone Thiosemicarbazone Complexes of Cobalt(II) and Nickel(II)

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Fluorenone thiosemicarbazone (FTSC) forms 1 : 2 complexes with cobalt(II) and nickel(II). Both of these complexes are found to be non electrolytes in nitrobenzene and dimethyl formamide. Square planar structures are assigned for the complexes based upon spectral and magnetic measurements. IR studies reveal that these complexes are formed by the replacement of the hydrogen atom of the SH group by metal ion with N and S coordinating to the metal. On the basis of thermal studies, the relative thermal stabilities of the chelates can be given as $[CoL_2] > [NiL_2]$.

INTRODUCTION

Metal complexes of thiosemicarbazone have been known for their pharmacological applications[1]. Significant antitubercular[2], fungicidal[3] and antiviral[4] activities have been reported for thiosemicarbazides and their derivatives. In continuation of our earlier work on transition metal complexes[5–8], we report here in the preparation and characterization of cobalt(II) and nickel(II) complexes of a novel ligand, fluorenone thiosemicarbazone (FTSC).

EXPERIMENTAL

Fluorenone thiosemicarbazone was prepared according to the procedure described in the literature[9].

The complexes were synthesized by the following general method.

A methanolic solution of metal salt was added drop wise to a hot solution of the ligand in methanol (1 : 2 ratio). The complexes separated were filtered, washed with methanol and dried in a desiccator.

RESULTS AND DISCUSSION

The complexes are found to be coloured. They are insoluble in water and alcohols, but are soluble in DMF, ketones, dimethyl sulfoxide etc. The analytical data in Table 1 show metal to ligand ratio 1 : 2 and are stable in air. DMF and nitrobenzene solution of these complexes have low conductance values in the range of 0–10 ohm^{-1} cm^2 $mole^{-1}$ indicating a non electrolytic nature.

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TABLE 1
ANALYTICAL DATA OF COMPLEXES

Complex	% Found (Calc)				μ_{eff} (BM)
	C	H	N	M	
[NiL2]	60.01 (59.71)	3.67 (3.58)	14.82 (14.93)	14.50 (14.30)	0
[CoL2]	61.5 (59.62)	3.66 (3.58)	14.66 (14.92)	14.31 (14.25)	2.64

The magnetic moments of the complexes calculated from the corrected magnetic susceptibilities support a square planar geometry[10] for Co(II) complex (2.64 B.M.). Though not very common, such complexes have been reported by Burger *et al.*[11]. Diamagnetism in the case of Ni(II) complex indicates square planar configuration.

The ligand and the complexes have been characterized on the basis of their infrared spectra recorded in CS_2 and KBr. On complex formation most of the bands in the spectrum of FTSC undergo frequency shifts and in many cases intensity changes. The most marked change is that of the 850 cm^{-1} band which is shifted almost 100 ml^{-1} to lower frequencies. The band at 850 cm^{-1} is attributed to $\nu C = S$. In Co(II) and Ni(II) complexes this band disappears and instead new bands around 700 cm^{-1} characteristic of $\nu C–S$ could be taken as evidence of the ligand coordinating via thioenol[12]. The shift of the bands at 1595 cm^{-1} ($C = N^3$) in the complexes indicate the participation of N^3 in coordination. The absence of bands in the region 2800–2550 cm^{-1} in the free ligand indicates absence of SH grouping in the free ligand[13].

Thermogravimetric Analysis

The thermal behaviour of the above chelates were studied in detail. The TG traces exhibit a two stage decomposition pattern. The DTA traces at 20°C min^{-1} also exhibit two exothermic peaks corresponding to the above decomposition temperatures. The decomposition temperature ranges in DTA and DTG traces for the Co(II) and Ni(II) chelates are given in Table 2.

TABLE 2
THERMAL DECOMPOSITION DATA

Substance	Peak Temp. in DTG °C	Temp. ranges in DTG °C	Peak Temp. in DTA °C	Temp. ranges in DTA °C	% loss of mass		From independents pyrolysis
					From TG	Theoretical	
CoL_2							
Stage I	245	100–270	259 (w)	150–300	45.5	44.96	
Stage II	510	280–540	580 (s)	300–650	86.2	85.75	85.5
NiL_2							
Stage I	245	100–300	241 (w)	200–275	44	44.94	
Stage II	495	300–520	512 (s)	400–700	86	86.74	86.95

The overall loss of mass from the TG curve is 85.5% for CoL_2 and 87.4% for NiL_2 while the calculated loss in mass for these conversions are

$$CoL_2 \rightarrow Co_3O_4 \qquad 85.75\%$$

$$NiL_2 \rightarrow NiO \qquad 86.74\%$$

These complexes do not contain any water molecule and there is no detectable change in both DTA and TG curves upto almost 100°C. The mass loss data at the end of the first stage of both complexes indicates that one ligand group is detached from the molecule. Between 300 and 500 °C there is a mass loss of about 41% indicating the loss of second ligand group. The loss of thiosemicarbazone groups appear as exothermic peaks on the DTA curve. The residual materials at the end of the second stage of decomposition were identified as oxides from their X-ray powder patterns, (Table 3). Both complexes show similar TG and DTA profiles.

TABLE 3
X-RAY POWDER DIFFRACTION DATA

Substance	*d*-spacing (observed) Å	Intensity order (observed)	Substance	*d*-spacing ASTM data file Å	Intensity grading from ASTM data file
Final product from CoL_2	2.45	1	Co_3O_4	2.49	100
	1.42	2		1.43	45
	2.87	3		2.86	40
Final product from NiL_2	2.09	1	NiO	2.09	100
	2.41	2		2.41	91
	1.49	3		1.48	57

Thermal decomposition kinetics

Kinetic parameters, *viz.* activation energy E, pre-exponetial factor A and order parameters n, for the thermal decomposition of the cobalt(II) and nickel(II) complexes were evaluated from the TG data. The fractional decomposition α, for the respective temperature was calculated from the TG curves. Using a computer, the best fit value of n was determined for the decomposition of the two complexes and it was found to be 1 for both stages in both complexes. Using this value of n the kinetic parameters were calculated from the four non mechanistic integral equations.

Coats-Redfern equation[14]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (1)$$

Horowitz-Metzger equation[15]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \ln\frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \qquad (2)$$

Freeman-Carroll equation[16]

$$\frac{\Delta \log (\frac{dw}{dt})}{\Delta \log w_r} = \frac{-E^*/2.303R\Delta(T^{-1})}{\Delta \log w_r} + n \qquad (3)$$

The left hand side of the above equations was plotted against reciprocal absolute temperature (1/T) for equations (1) and (3) and against $\theta = (T - T_s)$ for equation (2). From the slope and intercept, E and A were calculated.

Zsako's modified Doyle method[17]

The trial and error method of Doyle was modified by Zsako by introducing the standard deviation instead of curve fitting g method for the calculations. The values of the integral

$$P(x) = \frac{e^{-x}}{x} - \int_x^{\infty} \frac{e^{-u}}{u} du \qquad (\text{where } u = \frac{E^*}{RT}) \qquad (4)$$

were calculate and tabulated by Doyle for x values covering a range from 10 to 50 and these values were used in calculating **B**. The average of **B** values, as obtained at different temperatures was taken and $\partial = \frac{(B_i - \bar{B})^2}{r}$ where Bi is any value, **B** is arithmetical mean and **r** is number of values. ∂ values for various **B** values are calculated and given in Table 4.

TABLE 4
ZSAKO MODIFIED METHOD ∂ VALUES

Substance	E*	n = 0	n = 1	n = 2
CoL_2	18	0.0004	0.00920	0.0649
	20	0.0006	0.00960	0.0490
	22	0.0089	0.02120	0.0283
	24	0.0086	0.00008	0.0506
	26	0.0075	0.00290	0.0499
	28	0.0096	0.00219	0.0417
NiL_2	18	0.0007	0.0042	0.0649
	20	0.0074	0.0048	0.0490
	22	0.0118	0.0003	0.0283
	24	0.1603	0.0038	0.0506
	26	0.0123	0.0038	0.0499
	28	0.0119	0.0100	0.0417

The ∂ value is minimum if the apparent order of reaction is taken as 1, *i.e.* first order reaction. Thus from tested n values, n = 1 is the best.

The analysis of data using the Freeman-Carroll equation and Zsako's modified Doyle method by calculation of standard deviation gives the order of the decomposition reaction near unity for both stages in all cases. Based on this value of the order of reactions, the kinetic parameters are evaluated. Thus all the methods appear to be satisfactory for the calculation of E* within the limits of accuracy required. In the case of differential methods, the most accurate data are calculated from the medium-steep parts of the curve. The slight deviation of E values obtained by Freeman-Carroll method is due largely to the determination of three different functions over short temperature intervals. One of these involves the tangents dw/dt; therefore any inaccuracy in determining a single value affects the position of two points in the plot used to determine the activation energy. For the approximation method, the accuracy depends on the determination of curve inflection point temperature. The Coats-Redfern method seems to be more accurate but considerably time consuming.

The values of activation energy E* obtained by the three methods for the two complexes are given in Table 5. The negative values of ΔS^* in these complexes indicate that the activated complexes has a more ordered structure than the reactants and that the reactions are slower than the normal.

TABLE 5
KINETIC DATA

Substance		Parameters	Freeman-Carroll Equation	Coats-Redfern equation	Horowitz-Metzger Equation
CoL_2	Stage I	E^*, kJ mol^{-1}	119.7	106.4	102.7
		Z, s^{-1}	2.26×10^{10}	9.76×10^{8}	3.52×10^{8}
		ΔS^*, J mol^{-1} K^{-1}	–51,2	–77.4	–85.9
	Stage II	E^*, kJ mol^{-1}	95.8	119.7	130.5
		Z, s^{-1}	7.16×10^{4}	1.82×10^{6}	4.27×10^{6}
		ΔS^*, J mol^{-1} K^{-1}	–179.2	–133.2	–126.0
NiL_2	Stage I	E^*, kJ mol^{-1}	76.6	72.3	85.6
		Z, s^{-1}	1.81×10^{6}	1.86×10^{5}	5.49×10^{6}
		ΔS^*, J mol^{-1} K^{-1}	–129.6	–148.7	–120.5
	Stage II	E^*, kJ mol^{-1}	106.4	83.3	102.7
		Z, s^{-1}	1.77×10^{5}	3.94×10^{3}	6.68×10^{4}
		ΔS^*, J mol^{-1} K^{-1}	–155.2	–184.1	–160.5

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