

Synthesis and structural investigation of some mixed-ligand selenito complexes of cobalt(II)

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Abstract. Two complexes, $[\text{Co}(\text{An})_2(\text{O}_2\text{SeO})]$ and $[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2(\text{O}_2\text{SeO})]$, have been isolated and characterised by elemental analyses, IR spectra, magnetic measurements and thermogravimetric analysis. Their lattice constants have been determined with the help of X-ray powder diffraction data. Kinetic parameters like energy and entropy of activation for the thermal degradation process have been arrived at using Pilyan–Novikova, Coats–Redfern and Horowitz–Metzger equations. The mechanism of non-isothermal decomposition of complexes is by phase boundary nucleation. The probable structure for Co(II) complexes is six-coordinated octahedral in a high-spin electron configuration. The order of the thermal stability of complexes is $[\text{Co}(\text{An})_2(\text{O}_2\text{SeO})] > [\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2(\text{O}_2\text{SeO})]$.

Keywords Isoniazide; selenito; mixed-ligand/cobalt-complexes.

1. Introduction

Simple binary metal complexes of anthranilic acid (Wenger *et al* 1938), isoniazide (Foye and Duvall 1958; Shilakadze *et al* 1976) and selenite (Selivanova *et al* 1969) have been studied in the past, but the remarkable biological activity shown by these ligands has aroused significant interest in recent years. The literature survey reveals that mixed-ligand complexes involving the selenito group have not yet been widely investigated. The present paper deals with the investigation of new complexes of cobalt-selenite with anthranilic acid (An) and isoniazide (Iso). In these complexes the selenito (SeO_3^{2-}) group acts as a bidentate ligand.

2. Experimental

AR grade chemicals were used in the synthesis of complexes. $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ was prepared by the reported method (Koskenlinna *et al* 1976; Salib and Bucher 1983).

The mixed-ligand cobalt(II)-selenito complexes, $[\text{Co}(\text{An})_2(\text{SeO}_3)]$ and $[\text{Co}(\text{Iso})_2 \cdot (\text{H}_2\text{O})_2(\text{SeO}_3)]$, were prepared by refluxing the powdered $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ with anthranilic acid (10 h) and isoniazide (8 h), respectively, on a waterbath in the molar ratio 1:2 in an aqueous medium. The resulting solid, coloured complexes were washed

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with hot double-distilled water, followed by acetone, and dried over anhydrous CaCl_2 at 80°C .

3. Physical measurements

Physico-chemical characterization and the thermal studies of the synthesized complexes have been carried out. Elemental analysis was done at the Regional Sophisticated Instrumentation Centre (RSIC), Lucknow. Cobalt and selenium were estimated volumetrically (Vogel 1968; Salib *et al* 1986). IR spectra were recorded on a Perkin-Elmer-397 spectrophotometer (range $4000\text{--}400\text{ cm}^{-1}$). Magnetic measurements were performed on a Gouy's electrobalance, using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ($5.92 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$) as a calibrant and diamagnetic correction was made employing Pascal's constants (Lewis and Wilkins 1960). The X-ray powder pattern was recorded on a diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.54184\text{ \AA}$) radiation of intensity $35/20\text{ kV/mA}$, at the RSIC, Nagpur. The diffractograms were obtained at a scanning speed of $0.04^\circ/2\theta/\text{s}$. The TG analysis was done at the RSIC, Bombay, at a heating rate of 15 K min^{-1} , in the atmosphere of air. Piloyan-Novikova (P-N) (1966), Coats-Redfern (C-R) (1964) and Horowitz-Metzger (H-M) (1963) methods were employed for determining the kinetic parameters and mechanism. Due to the insolubility of the complexes, molar conductance could not be determined.

4. Results and discussion

The analytical data summarised in table 1, suggest the empirical compositions of $[\text{Co}(\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_4)(\text{SeO}_3)]$ and $[\text{Co}(\text{C}_{12}\text{H}_{14}\text{N}_6\text{O}_2)(\text{H}_2\text{O})_2(\text{SeO}_3)]$ for the $[\text{Co}(\text{An})_2\text{SeO}_3]$ and $[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2\text{SeO}_3]$ complexes, respectively.

4.1 Infrared spectral studies

A comparison of IR spectra of ligands with their metal complexes, show virtual similarities along with some important differences, which are owing to coordination of ligand with the metal ion at some bonding sites. The solid-state (KBr) IR spectra of both the complexes exhibited four characteristic absorption bands (Fowlers and Stranks 1977) derived from the oxygen-coordinated selenito ligand in the region $850\text{--}450\text{ cm}^{-1}$. A free selenite anion has C_{3v} symmetry and absorbs in the region $900\text{--}250\text{ cm}^{-1}$ giving only four IR active fundamental frequencies (Fowlers and Stranks 1977). Previous workers (Fowlers and Stranks 1977; Nakamoto 1986; Maeda *et al* 1988) have reported the appearance of four absorption bands (three stretch and one bending, in the region $850\text{--}400\text{ cm}^{-1}$) i.e. ν_1 , $805\text{--}835$; ν_2 , $755\text{--}770$; ν_3 , $510\text{--}530$ and ν_5 , $580\text{--}690$, in the oxygen-chelated bidentate selenito (O_2SeO) moiety. In the present studies, the similar IR bands at ν_1 , 830 ± 10 ; ν_2 , 715 ± 15 ; ν_3 , 520 ± 10 and ν_5 , 670 ± 20 , have been recorded which favours the bidentate behaviour of the selenito ligand coordinated through oxygen, in both the complexes (Wilkinson 1987).

The ligand anthranilic acid shows the principal characteristic IR bands at 3440 , 1605 and 1710 cm^{-1} which may respectively be assigned to N-H stretching, N-H bending and C=O stretching (Silverstein *et al* 1981). In the spectra of the metal complexes, these characteristic bands were observed at 3390 , 1580 and 1670 cm^{-1} ,

Table 1. Analytical and magnetic data of complexes.

Complex	Colour	Analysis %: Exp. (calcd.)				Mol. wt.	$\chi_M (\times 10^{-6})$ cgs units	$\chi'_M (\times 10^{-6})$ cgs units	μ_{eff} (BM)
		C	H	N	Co				
[Co(An) ₂ SeO ₃]	Light violet	36.78 (36.53)	2.96 (3.04)	5.99 (6.18)	12.90 (12.80)	459.893	10576.25	10772.42	5.15
[Co(Iso) ₂ (H ₂ O) ₂ SeO ₃]	Light brown	29.49 (29.04)	3.50 (3.63)	16.01 (16.93)	11.95 (11.88)	495.893	10090.92	10292.97	5.03

respectively, showing downward shift and suggesting chelation through $-\text{NH}_2$ and $-\text{COOH}$ groups of the anthranilic acid moiety (Nakamoto 1986; Dey and Ray 1973). Two new bands at 525 and 410 cm^{-1} in the metal complex may tentatively be assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ respectively. The vibrations at frequencies 3400, 1405, 1295 and 910 cm^{-1} are assigned to H-O stretching, H-O in-plane bending, C-O stretching and H-O out-of-plane bending, respectively.

The IR spectrum of the ligand isonicotinic acid hydrazide, shows characteristic absorption bands at 3240, 1640, 1550, 1290, 750 and 670 cm^{-1} due to N-H stretching, C=O stretching, mixed C-N stretching and N-H deformation, N-H bending, C=O in-plane deformation and C=O out-of-plane deformation. The stretching vibrations due to the nitrogen in the pyridine ring are observed at 1490 and 1060 cm^{-1} , while N-N stretching appears at 925 cm^{-1} (Dey 1986). A comparative study of IR spectra of ligand and its complex reveals the mode of coordination of the ligand. Strong stretching and deformation N-H bands are observed in the complex at 3200 and 1510 cm^{-1} ; and a new band at 465 cm^{-1} . This negative shift of N-H frequencies and a new band corresponding to $\nu(\text{M}-\text{N})$ suggest the coordination through $-\text{NH}_2$ group of isoniazide (Yadav *et al* 1987). Further the positive shift in N-N stretching frequency (at 1015 cm^{-1} in complex) indicates a reduction in repulsion between the lone-pair electrons of the nitrogen atoms and substantiates the same view (Monaci and Tarli 1977). The absorption bands which correspond to carbonyl group ($-\text{C}=\text{O}$) and pyridine ring nitrogen ($-\text{N}=\text{N}$) remain practically unchanged in the spectrum of the complex revealing non-involvement of these groups in coordination. The IR bands in the spectrum of the complex at 3540 and 1610 cm^{-1} may be assigned to ν_{OH} and $\delta_{\text{H}_2\text{O}}$, respectively, and indicate the presence of coordinated water (Nakamoto 1986; Das *et al* 1983).

4.2 X-ray studies

The complexes showed characteristic X-ray powder diffraction patterns. The data are summarized in tables 2 and 3.

The cell parameters have been calculated using the following equations (Henry *et al* 1951). For tetragonal:

$$\sin^2\theta_{hkl} = A(h^2 + k^2) + Cl^2, \quad (1)$$

where $A = B = \lambda^2/4a^2$ and $C = \lambda^2/4c^2$.

For hexagonal:

$$\sin^2\theta_{hkl} = A(h^2 + hk + k^2) + Cl^2, \quad (2)$$

where $A = B = \lambda^2/3a^2$ and $C = \lambda^2/4c^2$.

The values of $\sin^2\theta$ for each peak have been calculated with the help of the cell parameters and the corresponding hkl in all cases are in good agreement with observed $\sin^2\theta$ values. The number of molecules per unit cell and the density of the complex have been calculated by using the formula:

$$n = \rho VN/M,$$

where n is the number of molecules in the unit cell, ρ , density of the complex compound,

Table 2. X-ray data of $[\text{Co}(\text{An})_2\text{SeO}_3]$.

Crystal system: tetragonal;
 $A = B = 0.00210$; $C = 0.00120$;
 $a = b = 16.8916 \text{ \AA}$; $c = 22.2545 \text{ \AA}$;
 Cell volume $V = 6349.7972 \text{ \AA}^3$;
 $D(\text{obs.}) = 1.6873 \text{ g cm}^{-3}$; $n = 14$;
 $D(\text{calcd.}) = 1.6836 \text{ g cm}^{-3}$; ($D = \text{density}$).

Peak no.	d spacing (\AA)	Rel. Int.* ($I/I_0 \times 100$)	$\text{Sin}^2 \theta$		hkl
			Obs.	Calcd	
1	16.7368	2.3041	0.0021	0.0021	(100)
2	15.2391	2.6294	0.0025	0.0025	(100)
3	13.2044	100.00	0.0034	0.0033	(101)
4	6.6813	4.7980	0.0132	0.0132	(202)
5	6.6135	2.8191	0.0135	0.0132	(202)
6	4.4755	6.0178	0.0296	0.0297	(214)
7	4.4654	12.0357	0.0298	0.0298	(303)
8	4.4146	7.2919	0.0305	0.0306	(333)
9	4.3383	4.9064	0.0315	0.0319	(913)
10	4.0164	1.3553	0.0368	0.0370	(411)
11	3.8540	2.1686	0.0399	0.0391	(331)
12	3.4673	2.7920	0.0490	0.0489	(305)
13	3.4208	1.8433	0.0507	0.0511	(915)
14	3.3690	6.5058	0.0523	0.0527	(500)
15	3.3373	2.7703	0.0533	0.0535	(216)
16	2.8371	6.5600	0.0738	0.0730	(531)
17	2.3691	2.2228	0.1058	0.1056	(209)

* Rel. Int. – Relative intensity

V is the unit cell volume and N is Avogadro's number. The density of the examined complex has been measured by making a pellet under 7 ton pressure.

4.3 Magnetic measurements

The complexes were paramagnetic at 308 K. Molar susceptibility (X_m) and corrected molar susceptibility (X'_m) values were determined (table 1). The observed magnetic moment [$\mu_{\text{eff}} = 2.83(X'_m T)^{1/2}$] lie in the range 5.03–5.15 BM, in agreement with the reported values for the octahedral outer-orbital complexes of bivalent cobalt (Shaw and Saltoni 1969; Figgis 1976).

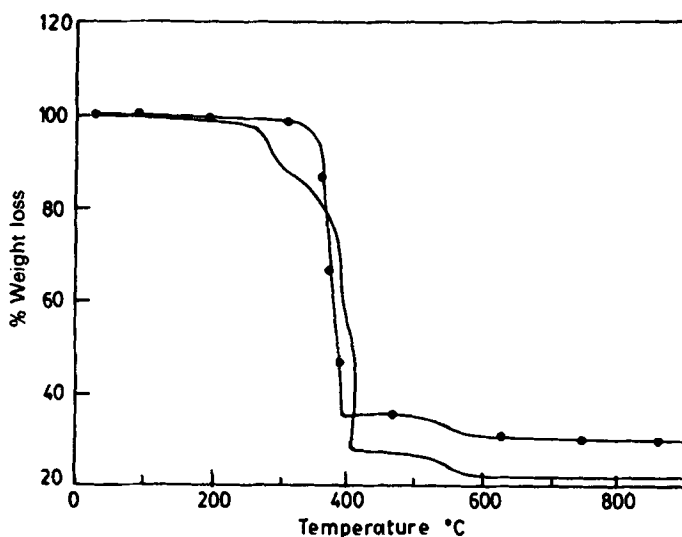
4.4 Thermal decomposition

4.4a $[\text{Co}(\text{An})_2\text{SeO}_3]$: The thermogram of this complex is shown in figure 1. The complex is stable upto 340°C and shows no mass loss, which is also indicative of absence of water molecules. Above 340°C , a gradual mass loss was observed upto 385°C , which may probably be due to the decomposition of the organic ligand part of the complex in one step (% wt. loss, obs./calcd., 62.0/59.6); the remaining weight corresponds probably to the species CoSeO_3 . Above 385°C degradation occurs upto 550°C and beyond this temperature, a constant weight curve has been recorded,

Table 3. X-ray data of $[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2\text{SeO}_3]$.

Crystal system: hexagonal;
 $A = B = 0.0011$; $C = 0.0032$;
 $a = b = 26.8393 \text{ \AA}$; $c = 13.6924 \text{ \AA}$;
 Cell volume = 4931.6441 \AA^3 ;
 $D(\text{obs.}) = 1.8368 \text{ g cm}^{-3}$; $n = 11$;
 $D(\text{calcd.}) = 1.8366 \text{ g cm}^{-3}$ ($D = \text{density}$).

Peak no.	d spacing (\AA)	Rel. Int. ($I/I_0 \times 100$)	$\text{Sin}^2 \theta$		hkl
			Obs.	Calcd.	
1	9.4943	82.4320	0.0064	0.0064	(111)
2	7.6618	100.000	0.0099	0.0099	(300)
3	5.7194	7.7962	0.0180	0.0176	(400)
4	5.4872	10.4989	0.0194	0.0200	(212)
5	4.8674	7.6923	0.0251	0.0258	(222)
6	4.7518	49.3762	0.0262	0.0262	(411)
7	4.4992	12.9937	0.0293	0.0295	(330)
8	4.2546	12.2661	0.0328	0.0328	(331)
9	4.0804	21.6216	0.0356	0.0357	(412)
10	3.8336	20.5821	0.0404	0.0402	(502)
11	3.7850	32.8482	0.0414	0.0417	(223)
12	3.5782	27.7546	0.0464	0.0462	(610)
13	3.4478	8.4199	0.0499	0.0494	(611)
14	3.2767	10.6029	0.0550	0.0551	(204)
15	3.0068	81.3929	0.0650	0.0650	(314)
16	2.6537	6.6528	0.0836	0.0836	(460)
17	2.5956	5.3014	0.0882	0.0890	(900)
18	2.1839	11.0187	0.1238	0.1240	(724)
19	2.0693	13.9293	0.1391	0.1391	(910)
20	2.0002	10.7068	0.1477	0.1471	(514)

**Figure 1.** Thermograms of $[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2\text{SeO}_3]$ (—), and $[\text{Co}(\text{An})_2\text{SO}_3]$ (---).

which results in the ultimate pyrolysis product Co_3O_4 in air (% wt. loss, obs./calcd., 69.5/82.6) (Duval 1963; Muldagalieva *et al* 1969).

4.4b $[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2\text{SeO}_3]$: The thermal degradation curve of the complex is shown in figure 1. There is a negligible mass loss upto 250°C , which also indicates the thermal stability of the complex. The thermogram witnesses the loss of the co-ordinated water molecules from the complex in the temperature range $250\text{--}280^\circ\text{C}$ (% wt. loss obs./calcd., 8.0/7.3). Further, a gradual mass loss occurs upto 410°C , which may be due to the thermal degradation of the organic ligand part of the complex (% wt. loss, obs./calcd., 69.0/62.5); the remaining intermediate may be cobalt selenite. The residue starts decomposing further after 410°C and ultimately gives a constant weight curve above 560°C . The final pyrolysis product is determined as Co_3O_4 in air (% wt. loss, obs./calcd., 78.0/83.8) (Duval 1963; Muldagalieva *et al* 1969).

A slight variation in the observed and calculated weight losses at some stages may be attributed to disproportionation of the expected products due to certain oxidation–reduction reactions or some carbon ash formation.

4.5 Kinetics of decomposition

The fractions of the reaction $[\alpha = (W_t - W_f)/(W_0 - W_f)]$ were calculated from the TG curve at different temperatures. The α - T curves were constructed on the basis of TG data for the two compounds (figures not shown). The decomposition reaction of the compounds were subjected to non-isothermal kinetic studies (Kaul and Sharma 1991) and the weighted least-squares method (LSM) was used for obtaining the best linear plots by applying the data to various equations (Horowitz and Metzger 1963; Coats and Redfern 1964; Piloyan and Novikova 1966). The values of slope, intercept and energy of activation were obtained from plots (figures 2, 3 and 4). The values of frequency factor Z and entropy of activation S^* , were calculated from (4) and (5).

$$Z = (E/RTm)\beta \exp(E/RTm^2), \quad (4)$$

$$Z = (KTm/h) \exp(\Delta S^*/R). \quad (5)$$

A perusal of table 4 reveals that the values of the kinetic parameters obtained by

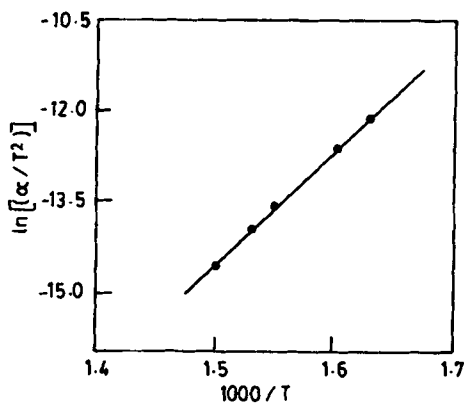


Figure 2. Piloyan–Novikova (1966) plot of $[\text{Co}(\text{An})_2\text{SeO}_3]$.

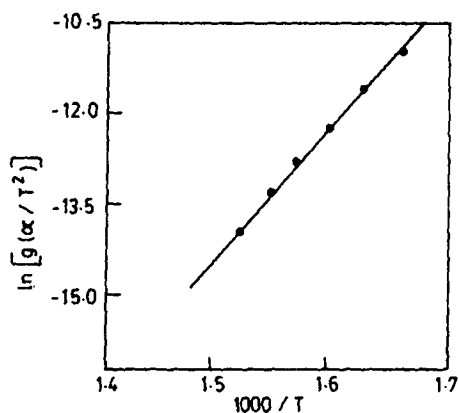


Figure 3. Coats-Redfern (1964) plot of $[\text{Co}(\text{An})_2\text{SeO}_3]$.

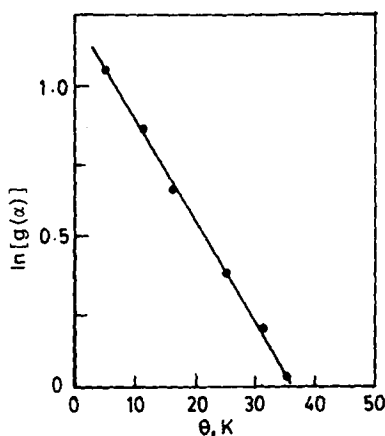


Figure 4. Horowitz-Metzger (1963) plot of $[\text{Co}(\text{An})_2\text{SeO}_3]$.

Table 4. Kinetic parameters of Co(II) selenito complexes.

Calculated kinetic results are given. The mechanism involved in decomposition is phase boundary contracting sphere nucleation. It is found that the best linear fit (for two complexes) for $n = 2/3$, $g(x) = 3[1 - (1 - x)^{1/3}]$ by both C-R and H-M methods.

Complex	Equation due to*	Decomp. stage	E^* (kJ mol^{-1})	$Z(\text{s}^{-1})$ ($\times 10^2$)	ΔS^* ($\text{JK}^{-1} \text{mol}^{-1}$)
$[\text{Co}(\text{An})_2\text{SeO}_3]$	P-N		84.588	5.107	-100.634
	C-R	Ist	80.640	4.4858	-100.844
	H-M		60.023	3.539	-102.208
$[\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2(\text{SeO}_3)]$	P-N		41.496	2.879	-102.386
	C-R	Ist	40.000	2.772	-102.545
	H-M		24.472	1.611	-104.980

* P-N = Piloyan-Novikova (1966); C-R = Coats-Redfern (1964); H-M = Horowitz-Metzer (1963);

C-R and P-N methods are quite consistent while those obtained by the H-M method differ. The order of the thermal stabilities of the two cobalt complexes is the same on the basis of first decomposition potential and energy of activation i.e. $[\text{Co}(\text{An})_2\text{SeO}_3] > [\text{Co}(\text{Iso})_2(\text{H}_2\text{O})_2\text{SeO}_3]$. Generally, the value of Z increases with decrease in E^* , however, there are some more inherent physical and chemical factors which may cause a change or deviation in this trend (Benson 1976). The negative values obtained for entropy of activation indicate that the activated complexes have more ordered structures than the reactants and that the reactions are slower than normal (Mishra *et al* 1993).

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