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PREPARATION, STRUCTURE AND THERMAL DECOMPOSITION OF SOME METAL COMPLEXES OF 5-NITROSALICYLHYDRAZIDE (5NSH)

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ABSTRACT

Complexes of VO(II), Cu(II), Ni(II), Co(II), Zn(II) and Ca(II) with 5-nitrosalicylhydrazide (5NSH) have been prepared. Chemical, spectral and magnetic properties show that they have octahedral stereochemistry. Results of thermal decomposition studies (TG, DTG and DTA) of these complexes indicate that they decompose in the temperature range 100–460°C with explosion at ~ 250°C producing a low oxide content. The end products (oxides) were characterised by far-IR spectra.

INTRODUCTION

Since the discovery of antitubercular activity of acid hydrazides, many workers [1–9] have studied the coordination chemistry of these ligands. One of the rarely studied aspects of analytical and coordination chemistry of hydrazides is the thermal behaviour of their metal complexes. Recently [10–17], we reported the thermal decomposition of some transition metal complexes of salicylic (SA), 4-aminosalicylic (4-ASA), 5-sulphosalicylic (5-SSA) and 3,5-dinitrosalicylic (3,5-DNSA) acids with the intent of developing structure–activity relationships. The present paper describes the preparation of complexes formed between 5NSH (another derivative of salicylic acid) and VO(II), Cu(II), Ni(II), Co(II), Zn(II) and Ca(II), together with the results of thermal analysis (TG, DTG, DTA), visible spectra, infrared spectra, and magnetic measurements. The literature has shown that this type of study has not been attempted so far.

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TABLE 1

Abbreviated names, colour, percentage yield and elemental analysis of metal complexes of 5-nitro-salicylhydrazide (5NSH)

Complex	Colour	Yield (%)	Elemental analysis, observed(calculated) (%)			
			C	H	N	M
$VO(5NSH)_2 \cdot 2H_2O$	Grey	57.00	16.87(16.95)	1.58(1.62)	5.56(5.66)	13.49(15.52)
$Cu(5NSH)_2 \cdot 2H_2O$	Greenish blue	72.00	16.98(17.09)	1.60(1.66)	5.67(5.70)	12.63(12.93)
$Ni(5NSH)_2 \cdot 2H_2O$	Green	68.80	17.00(17.26)	1.59(1.64)	5.68(5.75)	11.83(12.06)
$Co(5NSH)_2 \cdot 2H_2O$	Brown	80.00	17.40(17.25)	1.54(1.64)	5.66(5.75)	11.90(12.10)
$Zn(5NSH)_2 \cdot 2H_2O$	Yellowish white	87.00	16.97(17.02)	1.57(1.62)	5.53(5.63)	13.00(13.27)
$Ca(5NSH)_2 \cdot 2H_2O$	Dirty white	65.25	17.82(17.95)	1.69(1.72)	5.78(5.98)	8.27(8.56)

EXPERIMENTAL

Chemicals

All the chemicals used were of BDH AnalaR or equivalent quality.

Preparation of the reagent

The reagent, 5-nitro-salicylhydrazide (5NSH), was prepared by a method described elsewhere [18]. The purity of the reagent was checked through TLC, melting point, elemental, UV and IR techniques.

Preparation of the complexes

The complexes were prepared following a method described previously [19]. A hot solution of 5NSH in methanol was added to the metal salt solution, which was made slightly alkaline by adding aqueous sodium acetate solution. A precipitate of the complex was formed immediately after the addition of 5NSH solution, and was allowed to settle. The addition of 5NSH was continued until the supernatant liquid was found to be clear. The mixture was refluxed for 4 h. The product was filtered, washed with methanol followed by water, to remove excess 5NSH and inorganic ions, respectively, and finally dried under vacuum.

The complexes prepared by this method are listed in Table 1.

Elemental analyses

The composition of the complex was determined by elemental analysis. The metal content was estimated by standard procedures [20] while carbon, hydrogen and nitrogen analyses were carried out on a Colemann 29 CHN analyser. Analytical data are given in Table 1.

IR spectra

Infrared absorption spectra (KBr discs) of 5NSH and its complexes were investigated employing a Perkin-Elmer Model 377 spectrophotometer. The 4000–400 cm^{-1} region was scanned at 5 min per resolution. Far-IR spectra were recorded in the range 650–50 cm^{-1} employing a Polytec FTR 30 Fourier far-IR spectrometer. The characterization of IR band positions is given in Table 2.

Magnetic measurements

The effective magnetic moments of the complexes were determined by the Guoy method using $Hg[Co(SCN)_4]$ as calibrant. The room temperature

TABLE 2

Characteristic IR band positions (cm^{-1}) for 5-nitrosalicylhydrazide (5NSH) and its complexes [a]

Compound	νN–H	δN–H + νC–N (amide II)	νC=O (amide I)	νC–O	νM–O	νM–N
5NSH [b]	3350(sb)	1505(m)	1630(s)	1255(s)	–	–
	3155(s)		1535(s)			
Cu(II)–5NSH	3345(m)	1528(m)	1540(s)	1300(s)	485(m)	500(m)
	3150(m)					
Ni(II)–5NSH	3340(m)	1530(m)	1550(m)	1290(s)	475(m)	490(m)
	3150(m)					
Co(II)–5NSH	3340(m)	1525(m)	1565(s)	1290(s)	465(m)	495(m)
	3145(m)					
VO(II)–5NSH	3345(m)	1520(m)	1535(s)	1300(m)	490(m)	515(m)
Zn(II)–5NSH	3340(m)	1535(m)	1530(s)	1280(m)	475(m)	500(m)
Ca(II)–5NSH	3345(m)	1510(m)	1540(sb)	1275(m)	465(m)	500(m)
	3140(m)					

[a] s = sharp, m = medium, w = weak, sh = shoulder, sb = sharp and broad, ms = medium and sharp.

[b] O–H = 3320(sb), δO–H = 1345(s), C–O = 1145(s), 1255(s); N–H = 700–755(sb).

TABLE 3

Observed band positions (electronic) and effective magnetic moments for metal complexes of 5-nitro-salicylhydrazide (5NSH)

Complex	Temp. (K)	Band position (KK)	μ_{eff} (B.M.)
$VO(5NSH)_2 \cdot 2H_2O$	298	25.32, 16.94, 12.50	1.85
$Cu(5NSH)_2 \cdot 2H_2O$	301	40.25 [a], 15.38	1.39
$Ni(5NSH)_2 \cdot 2H_2O$	303	40.00 [a], 30.76, 16.13, 10.98	3.54
$Co(5NSH)_2 \cdot 2H_2O$	303	37.04 [a], 19.61	4.97

[a] Charge transfer band.

magnetic moments (μ_{eff}) are presented in Table 3.

Optical spectra

Reflectance spectra for VO(II), Cu(II), Ni(II) and Co(II) complexes of 5NSH were obtained on a VSU-2P spectrophotometer and are given in Fig. 1. The characteristic band positions (KK) are presented in Table 3.

Thermal analysis

Thermogravimetry (TG) of 100-mg samples was carried out on a Stanton-Redcroft recording thermobalance (HT model) of 1-mg sensitivity in static

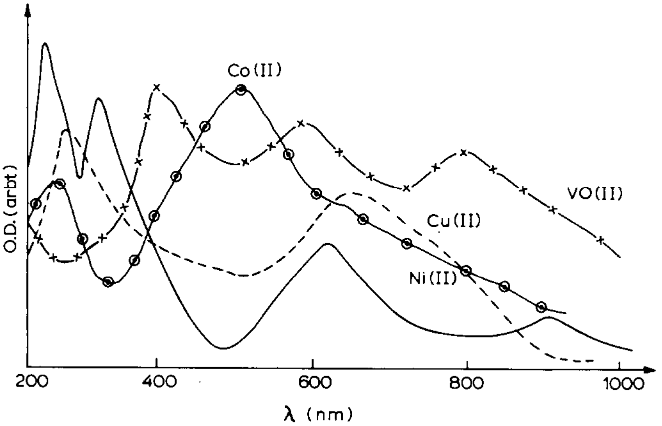

Fig. 1. Optical spectra of metal complexes of 5-nitrosalicylhydrazide (5NSH): (× —— ×) VO(II)-5NSH; (— — —) Cu(II)-5NSH; (——) Ni(II)-5NSH; (O —— O) Co(II)-5NSH.

air with a heating rate of 4°C min^{-1}. The chart speed was maintained at 7.5 cm h^{-1}. The sample was homogenised by sieving below 100 mesh and was packed as uniformly as possible in a platinum crucible of appropriate size.

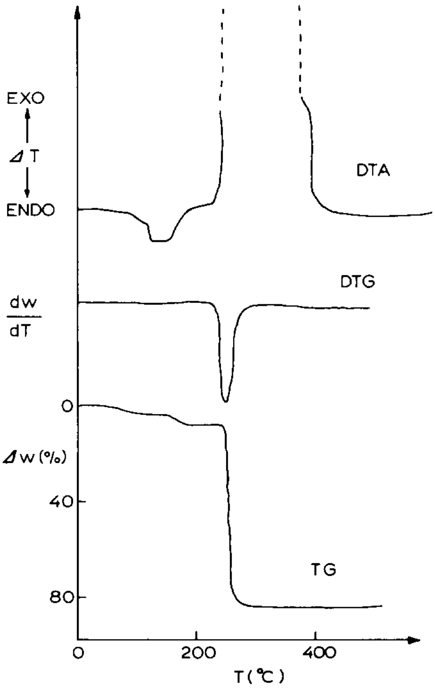

Fig. 2. TG, DTG and DTA curves for Cu(II)-5-nitrosalicylhydrazide.

The same platinum crucible was used throughout all the experiments.

A differential thermal analysis (DTA) assembly with an F and M Scientific, Hewlett-Packard temperature programmer and a Platinet-II thermocouple (Engelhard, U.S.A.) was used. DTA curves for 40-mg samples were recorded with a Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as standard reference material.

A typical set of TG, DTG and DTA curves for Cu(II)–5NSH is given in Fig. 2.

RESULTS AND DISCUSSION

Stoichiometry and behaviour

The prepared complexes, their analysis, colour, percentage yield and abbreviated names are reported in Table 1. The complexes are stable in air, and insoluble in water and common organic solvents, except DMF in which they are slightly soluble. Because of the insolubility of the complexes in common organic solvents, single-crystal growth is not possible. Without an X-ray structure analysis it is hoped that the IR spectral study will throw some light on the structure of these complexes.

The analytical data recorded in Table 1 indicate that the stoichiometry of all the complexes is $ML_2 \cdot 2H_2O$ (M = VO(II), Cu(II), Ni(II), Co(II), Zn(II), Ca(II); L = anion of 5NSH).

Streochemistry of the complexes

The visible reflectance spectrum of Ni(II)–5NSH resembles that normally found for octahedrally coordinated nickel(II), although the true environment will be of lower symmetry than O_h [21]. The observed transitions are

$$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F),\ {}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F),\ {}^3A_{2g}(F) \rightarrow {}^1E_g(G).$$

The broadening of the band for the transition $^3A_{2g}(G) \rightarrow {}^3T_{2g}(F)$ reflects the lowering of symmetry in the compound and is probably due to spin–orbit coupling. A study of magnetic moments [22] further supports an octahedral environment for the nickel atom (Table 3).

The magnetic moment of 1.39 B.M. for the blue-green complex formed between 5NSH and copper(II) ions would suggest an octahedral or square-planar evironment for the copper(II). Thus, the evidence for stereochemical assignment is from spectral data (Fig. 1, Table 3).

The compound shows one broad adsorption band at 15.38 KK. This suggests an octahedral environment for the copper atom since square planar copper(II) complexes show two bands of nearly equal intensity at about 15.0 and 18.00 KK [23–25]. The observed band at 15.38 KK is due to the

$^2E_g \rightarrow {}^2T_{2g}$ transition. The broadness of the band is due to Jahn–Teller distortion involving the ^2E_g ground state.

The observed magnetic moment (4.99 B.M.) for cobalt(II)–5NSH is slightly less than usual for high-spin octahedral cobalt(II) complexes. This may be due to incomplete quenching [26] of the orbitals of the metal ion during chelation leading to low-spin octahedral stereochemistry for the complexes. Like most of the high-spin octahedral complexes [27], a single, broad band is observed at 19.61 KK for Co(II)–5NSH. The band may be assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ [21].

The room-temperature magnetic moment value (1.85 B.M.) of VO(II)–5NSH is well within the range of an oxovanadium(IV) complex of symmetry lower than octahedral [28,29]. This value also suggests that there are no significant anti-ferromagnetic interactions between pairs of oxovanadium(IV) ions in the complex in the solid state. The complex exhibits *d–d* bands at 12.50, 16.49 and 25.32 KK, possibly due to $d_{xy} \rightarrow d_{yz}$, d_{xz}; $d_{xy} \rightarrow d_{x^2-y^2}$; and $d_{xy} \rightarrow d_{z^2}$ transitions [30,31], indicating distorted octahedral geometry, elongation occurring in the *xy*-plane.

Structure of the complexes

The important IR spectral bands of 5NSH and its complexes are given in Table 2. 5NSH shows bands at 1630, 1505 and 1255 cm^{-1} and a broad band at 650–750 cm^{-1}, which are assigned to amide-I, (νC=O), -II (νCN + δNH), -III (δNH) and -IV (ϕC=O) vibrations, respectively [32,33]. On complexation, the amide-I band shifts to lower frequencies ~ 1550 cm^{-1}, while the amide-II, -III and -IV bands exhibit a 10–30 cm^{-1} shift to higher frequencies. These observations indicate that the amide group coordinates to the metal atom through the oxygen atom of the keto group. The low-field shift in carbonyl carbon resonance in complexes compared to 5NSH shows a reduction in electron density of the –C=O bond due to coordination of the carbonyl oxygen atoms to metal ions.

The ligand also shows bands at 3320, 1345, 1145 and 1255 cm^{-1}. The appearance of broad band around 3320 cm^{-1} is due to an intramolecular hydrogen bonded –OH stretch. The other two bands are assigned to –OH in-plane bending and a C–O stretch due to the phenolic –OH group of 5NSH. A shift of this band to higher frequency (1300 cm^{-1}) for the complexes indicates the involvement of phenolic oxygen in complex formation.

N–H stretching and coupled primary amine (hydrazide) bands occurred at 3350 and 3155 cm^{-1} in the ligand. In the complexes, these bands are not greatly affected and they appear in the same region, whereas the lower frequency band around 1615 cm^{-1}, a doublet of the carbonyl band, appears at a lower frequency (~ 1530–1506 cm^{-1}) in the complexes, indicating that at least one of the nitrogen atoms of the ligand is coordinated to a metal atom. The lowering observed in νN–H vibration is comparatively less than that observed for other amino-group coordinated complexes [34].

The involvement of one of the nitrogen atoms in complex formation is also supported by the appearance of two bands in the region 980–1030 cm^{-1}. The lower frequency band may be attributed to the uncoordinated (–N–N–) moiety whereas that occurring at ~ 1030 cm^{-1} may be due to coordinated nitrogen. This observation supports involvement of the $-NH_2$ group of 5NSH in coordination to the metal atom.

Additional bands observed for the complexes in the region 650–50 cm^{-1} are supposed to be metal sensitive. These vibrations are either pure or are coupled with other vibrations. The bands showing greatest sensitivity to metal are probably νM–O and νM–N, which are the purest.

The fact that nitrogen of the $-NH_2$ group and oxygen of the –C=O group are coordinating is further evidenced by the appearance of νM–N and νM–O bands around 500 and 475 cm^{-1}, respectively [35].

Perusal of Table 3 shows that the νM–N and νM–O bands, in general, follow the sequence VO(II) > Cu(II) > Ni(II) ~ Zn(II) > Co(II) ~ Ca(II), which, except for Zn(II) and Ca(II), follows the spectrochemical series [36].

Thermal behaviour

All the metal chelates of 5NSH undergo almost explosive decomposition in the temperature range 240–260°C. The complexes exploded with fire and smoke at ~ 250°C. A typical set of TG, DTG and DTA curves for Cu(II)–5NSH is given in Fig. 2. A close look at this figure indicates that it is impossible to investigate the composition and thermal behaviour of the complexes quantitatively due to the occurrence of a sharp inflection in the TG curve. It is worthwhile to note that below the decomposition range (240–260°C) only 1.5–3.0% decomposition of the complexes takes place. At the explosion temperature (~ 200°C) about 92% decomposition occurred rapidly. Due to this rapid, explosive decomposition some of the decomposing material could have easily been ejected from the thermobalance pan, thus leaving a very low oxide content after complete decomposition. Because the oxide content was very much in doubt, it was impossible to establish the composition of metal–5-nitrosalicylhydrazide complexes from thermal data.

It is interesting to note that all the metal–5-nitrosalicylhydrazides began to lose weight (1.5–3.0%) in the temperature range 60–80°C. First, the weight loss is gradual but it becomes extremely rapid in the temperature range 240–260°C. The oxide level began to increase at 300–320°C. Weight loss is almost constant above the oxide level. However, as stated earlier, the exact amount of oxide is very much less due to ejection of the metal hydrazides. In general, the oxide content was found to be about 14–15% lower than the theoretical value. Thus, a constant oxide level is of no use in determining the composition and kinetic parameters for the thermal decomposition. These findings are in accordance with the results obtained previously by us [15] and Wendlandt [37]; explosive decomposition takes place in the case of nitro-compounds.

The DTA curve (Fig. 2) indicates a discontinued exothermal peak in the temperature range 240–300°C corresponding to decomposition of the complexes. However, the position and shape of the exothermal peak could not be exactly determined due to the explosive nature of the thermal decomposition.

It is worthwhile noting that during thermal decomposition of the metal chelates of SA, 4ASA and 5SSA [10–17] no such explosive decomposition was observed while in the present case explosion was noted, which may be due to the formation of various nitro-compounds during thermal decomposition. Further, in the case of metal complexes of 3-5DNSA, explosive decomposition takes place after dehydration, while in the present case, dehydration and explosive decomposition follow simultaneously.

Composition of end products

Analysis of the final decomposition products (residue) indicated the formation of a metal oxide in each case. The composition of the oxides is estimated by estimation of the metal and also by observing the far-IR spectrum of the residue. The appearance of bands at 610(m), 500(s), 410(m); 595(vb), 390(w), 288(w); 650(w), 465(sb); 655(s), 635(sh), 560(s), 460(mb), 350(w); 450(wb); and 465(m) cm^{-1} indicated the formation of CuO, V_2O_5, NiO, Co_3O_4, ZnO and CaO, respectively, in the corresponding metal complexes of 5NSH [35].

CONCLUSION

Results of this study on the thermal decomposition of metal complexes of 5NSH showed that the complexes decompose in the range 240–260°C with explosion at ~ 280°C giving a low oxide content. Far-IR spectra indicated the formation of CuO, V_2O_5, NiO, Co_3O_4, ZnO and CaO as end products.

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