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Studies of bi-valent complexes of Co(II), Ni(II), Mn(II) and Zn(II) with Hydrazine carboxylic acid and Formyl hydrazine carboxylic acid

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Abstract

Complexes of hydrazine carboxylic acid (Hhyc) and formyl hydrazine carboxylic acid (HCH=N-NH-COOH) abbreviated as (Hhyc) of Co(ll), Mn(II), Ni(II) and Zn(II) of composition M(hyc)$_2$ (NH$_2$-NH$_2$).H$_2$SO$_4$.2H$_2$O, M (fhyc) (H$_2$O)$_2$ SO$_4$ and Zn(Hhyc) (NH$_2$ – NH$_2$) SO$_4$ 2H$_2$O have been prepared and characterized by u-v, i.r., magnetic susceptibility and derivatographic studies of complexes. From above studies polymeric structure is assigned to both M(NH$_2$-NHCOO)$_2$N$_2$H$_4$ H$_2$SO$_4$.2H$_2$O and M(CH$_2$=N-NHCOOH)$_2$ (H$_2$O)$_2$ SO$_4$ type of complexes.

Keywords: hydrazine carboxylic acid, formyl hydrazine carboxylic acid complex Co(II), Ni(II), Mn(II), Zn(II), elemental analysis, magnetic moment, I.R., U.V., polymer.

Introduction

Undetailed studies on complexes of hydrazine carboxylic acid with some bi-valent metal ions have appeared in literature[1-5]. Substituted hydrazine carboxylic acid complexes due to their apparently prompted potential similarity to amino acids, have been studied by several workers and many transition metal complexes of these ligands have been synthesized, characterized and in few cases crystal structures [6-12] have been established. A few compounds of substituted hydrazine carboxylic acid have also been found to possess biological activities [13-15]. It was therefore, considered worthwhile to study the co-ordination ability of hydrazine carboxylic acid and formyl hydrazine carboxylic acid with Co(II), Mn(II), Ni(II) and Zn(II) salts. In present paper we report the preparation of complexes of Co(II), Ni(II), Mn(II), Zn(II) with hydrazine carboxylic acid (Hhyc) and formyl hydrazine carboxylic acid (fhyc) and their characterization by magnetic, electronic spectra, I.R. and thermogravimetric analysis.

Experimental preparation of hydrazine carboxylic acid (Hhyc)

It was prepared by saturating hydrazine hydrate with CO$_2$ in cold for 15 hrs. the product separated as white crystalline solid. It was filtered, washed with ethanol and dried over CaCl$_2$.
Found: N, 18.68; C, 8.24; H, 8.38; requires NH$_2$-NHCOOH.4H$_2$O:N, 18.91; C, 8.00; H, 8.10%.

Preparation of complexes

M(hyc)$_2$(N$_2$H$_4$)H$_2$SO$_4$.2H$_2$O(M=Co^{2+}, Mn^{2+}or Ni^{2+}) and Zn(Hhyc) NH$_2$NH$_2$SO$_4$ 2H$_2$O.

A saturated solution of hydrazine carboxylic acid (0.04 mol) was added with stirring to an aqueous solution of metal sulphate (0.01 mol in 30 ml) when a clear solution was obtained. The resulting solution was allowed to stand at room temperature when microcrystalline product separated slowly in a few days. The product was filtered, washed with ethanol and dried over CaCl$_2$.

M(fhyc)$_2$ (H$_2$O)$_2$ SO$_4$; (M = Co^{2+}, Ni^{2+} or Zn^{2+})

Aqueous solutions of hydrazine carboxylic acid (0.03 mol), formaldehyde (0.02 mol) and metal sulphate (0.01 mol) were mixed together when a clear solution was obtained. The solution was allowed to stand for 3-4 days when microcrystalline precipitate separated gradually. The product was filtered, washed with ethanol and dried over $CaCl_2$. The analytical results and μ_{eff} at 305^0 of complexes are given in table-I. The i.r and u.v spectra were recorded at Perkin elmer 577 and Unicame S.P. 500 spectrophotometer respectively. Magnetic susceptibility was measured by Gouy method. The TGA and DTA results were obtained at TG-750 Stompten Redroft make.

Results and Discussions

Analytical result indicate that hydrazine carboxylic acid, with metal sulphate gave complexes of composition $M(hyc)_2$ $(NH_2\text{-}NH_2)$ $H_2SO_4.2H_2O$ ($M=Co^{2+}$, Ni^{2+} or Mn^{2+}). However in presence of formaldehyde the formyl complexes $M(fhyc)$ $(H_2O)_2SO_4$ were obtained. The complexes are insoluble in ethanol, methanol, and water and stable at room temperature. The complexes, $M(fhyc)_2$ $NH_2\text{-}NH_2$ $H_2SO_4.2H_2O$ gradually lose water molecules above 80^0C but $M(fhyc)$ $(H_2O)_2.SO_4$ retains water molecule below $120\text{-}130^0$. The insolubility of complexes suggests their polymeric or dimeric structure. Co(II), Mn(II) and Ni(II) complexes are paramagnetic. The room temperature magnetic moment value of $Ni(hyc)_2$ $(NH_2\text{-}NH_2)$ H_2SO_4 $2H_2O$ (3.28 B.M.) and $Ni(fhyc)_2$ $(H_2O)_2.SO_4$ (2.88 B.M.).

The magnetic moment value of Mn(II) complexes (5.92 – 5.96 B.M.) and Co(II) complexes (4.92 – 5.01 B.M.) are similar to spin free octahedral Mn(II) and Co(II) complex[16] respectively.

The electronic absorption spectra of complexes were determined as nujole mull, Zn(II) and Mn(II) complexes do not display distinct band in visible region. Co(II) complexes display a medium absorption band at 19000 and soulder at 21500 cm^{-1} in case of $CO(fhyc)_2$ $(H_2O)_2.SO_4$. The absorption bands of Co(II) complexes are attributed to transitions $^4T_{1g}\rightarrow{}^4T_{2g}$ and $^4T_{1g}\rightarrow A_{2g}$ (P) in approximately octahedral field[17]. Ni(II) complex $Ni(hyc)_2$ $(NH_2\text{-}NH_2)$ H_2SO_4 $2H_2O$ shows a weak band at 15500 and a medium band at 25000 cm^{-1}. In case of $Ni(fhyc)_2$ $(H_2O)_2SO_4$ the electronic absorption bands are observed at 15400 and 25300 cm^{-1} assignable to transitions $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and $^3A_{2g}\rightarrow{}^3T_{1g}$ (P) respectively in approximately octahedral field[18,19]. The other electronic band of Ni(II) and Co(II) complexes could not be observed due to limitation of range of the instrument.

The derivatographic studies of some of the complexes were performed in N2 atmosphere at heating rate of 100C per minute between 40 -650^0C. The complexes $M(NH_2\text{-}NH\text{-}COO)_2$ H_2SO_4 $2H_2O$ ($M = Ni^{2+}$ or Mn^{2+}) starts losing weight at $80\text{–}120^0$ with an endothermic step in DTA curve. The loss of H_2O is completed between $240\text{-}290^0C$. Above 290^0C one molecule of NH_2NH COOH is lost rapidly with an exothermic step and loss is completed by 3000C. The product $M(NH_2\text{-}NHCOOH)$ (N_2H_4) H_2SO_4 is stable between $300\text{-}350^0$ and after that one coordinated hydrazine carboxylic acid decomposes to give CO_2 molecule with an exothermic step between $360\text{-}450^0$ forming $M(NH_2\text{-}NH_2)SO_4$. The product is quite stable indicating the polymeric nature of $M(NH_2\text{-}NH_2)_2SO_4$ in which hydrazine probably bridges the metal atoms. The product $M(NH_2\text{-}NH_2)SO_4$ decomposes above 450^0C with an exothermic step to form metal sulphate. In case of Co(II) and Mn(II) metal sulphate formed is quite stable but $NiSO_4$ decomposes slowly with exothermic step. The retainsion of hydrazine in derivatographic studies of complexes $M(NH_2\text{-}NHCOO)^2$ $(NH_2\text{-}NH_2)$ H_2SO_4 $2H_2O$ even at 350 – 400^0C form $M(NH_2\text{-}NH_2)_2SO_4$, clearly indicates bridging nature of hydrazine molecules in these polymeric complexes.

IR Spectra

The prominent ir bands of ligand hydrazine carboxylic acid $N_2H_3COOH.4H_2O$ and its complexes are shown in table-II. The ligand shows a broad band between 3340-2550cm^{-1} attributable to v(OH) + v(NH) + $v(NH_2)$ and $v(H_2O)$ [20]. The complexes shows a broad band at 3350 – 3050 cm^{-1} indicating the absence of carboxylic (OH) hydrogen bonding in the complex. The ligand displays very broad and strong band at 1695-1540 cm^{-1} and attributed to combination of v(COO) and $\delta(NH_2)$ + $\delta(H_2O)$ of ligand molecule. The $v_s(COO)$ [21] is assigned to a strong band located at 1370-1310 cm^{-1}. The prominent i.r. band observed at 1265 – 1228, 830 and 780 cm^{-1} are attributed to v(C-N), NH_2 wagging and NH out of plane bending of ligand molecule. The strong bands located at 655 – 585 and 512 cm^{-1} in ligand are attributed to (COO), (C-N-N) and (N-C-O) deformation bands of the molecule. The complex $M(hyc)_2$ $(NH_2\text{-}NH_2)$ H_2SO_4 $2H_2O$ displays distinct bands for $v_s(COO)$ $\delta(NH_2)$, $\delta(H_2O)$ and $\beta(NH_2)$ indicating degree of hydrogen bonding in complexes. The $v_{as}(COO)$ is shifted to lower and $v_s(COO)$ at higher wave number in complexes, indicate coordination of carboxylic oxygen to metal atom. The $v_3(SO_4)$ of sulphate group is located as strong and broad band at 1180 and $v_1(SO_4)$ at 990 ± 5 cm^{-1} and splitting of band could not be observed indicating that SO_4 is ionic in complexes [22,23]. The different i.r. bands of ligand are also affected on bonding with metal atom. The new band located at 375 – 435 cm^{-1} in complexes are assigned to v(M-N) stretch. The v(M-O) assigned [25] to a band at 600–560 cm^{-1}. Formaly hydrazine carboxylic acid complexes display broad band at 3600 – 3080 cm^{-1} attributable to v(OH), $v(NH_2)$ and $v(H_2O)$. A broad band at 2320-2000 cm^{-1} in complexes is attributed to uncoordinated carboxylic (OH). The sulphate is also ionic in these complexes which is indicated by broad and strong $v_3(SO_4)$ and $v_1(SO_4)$ vibration of ionic sulphate group in these complexes [24]. The complexes displays a broad and strong band at 1650 – 1620 cm^{-1}, is attributed to v(COO), $\delta(H_2O)$ + v(C=N) vibration. The $\beta(NH_2)$ is observed at 1365 ± 5 cm^{-1}. The band at 1015 ± 5 cm^{-1} is assigned to v(N-N) vibration. The ρ_wH_2O of coordinated water molecule is observed at 660 ± 10 cm^{-1}. The i.r. band located at 550 ± 10 cm^{-1} is assigned to (M-O) and at 420 ± 5 cm^{-1} to (M-N) vibration [25].

From above studies polymeric structure is assigned to both $M(NH_2\text{-}NHCOO)_2$ $N_2H_4H_2SO_4$ $2H_2O$ and $M(CH_2{=}N\text{-}NHCOOH)_2$ $(H_2O)_2$ SO_4 type of complexes.

Table I: Analytical results and physical data

Complex	Colour	μ_{eff} in BM	Analysis in % Found/(calc)		
			M	N	SO_4
$Ni(hyc)_2N_2H_4H_2SO_4\ 2H_2O$	Blue	3.28	16.32	14.89	3.02
			(15.71)	(15.27)	(3.27)
Co(hyc)2N2H4H2SO4 2H2O	Brick-Red	5.01	16.49	15.36	3.09
			(15.85)	(15.26)	(3.27)
Mn(hyc)2N2H4H2SO4 2H2O	Light Pink	5.96	14.36	15.74	3.36
			(14.80)	(15.43)	(3.50)
Ni(hyc)2 (H2O)2 SO4	Bluish Green	2.88	16.60	22.82	4.01
			(16.01)	(22.60)	(4.20)
Co(hyc)2 (H2O)2 SO4	Brick Red	4.92	16.66	22.14	4.34
			(16.06)	(22.40)	(4.20)
Mn(hyc)2 (H2O)2 SO4	Light Yellow	5.92	16.21	25.00	4.16
			(15.13)	(25.30)	(4.31)

Table II: IR bands in Cm-1 their assignments ($NH_2NHCOOH$) H2O

M(hyc)	$M(hyc)_2\ (NH_2NH_2)SO_42H_2O$	$M(fhyc)_2\ (H_2O)_2SO_4$	
3340–2520	3310–3180 Sbr	360–3080 Shr	$v(NH)+v(H_2O)+(OH)$
2100 m		2320–2000 mbr	v(OH)
1695–1540	1680–1640 Sbr	1650–1620 Sbr	$v(COO)+v(H_2O)+v(NH_2)+v(C=N)$
1480 m	1412 m	1470±5 S	vs(COO)
1370–1360	1170–1060 Sbr	1180–1080 Sbr	v_3SO_4
1265–1228	1012±5 m	1015±5m	v(N–N) Ligand
830	990±5 m br	985±5 m	$v_1(SO_4)$
780	690±5 m br	660±10 m br	$\rho_w(H_2O)$
655	620±5 m	620±5 m	$v_4(SO_4)$
580	600–560 m	510±10 m	v(M–O)
512	375 – 435 m	420±5 m	v(M–N)

References

1. Ferrari A, Braibanti A. Nature 1966;211:1174.
2. Battistoni G, Mattagno G, Mongci A, Tarei F, J Inorg. Nucl. Chem 1970;32(7):2313.
3. Brainbanti A, Tripiecho A, Mariaanna, Lanfredi Mannoti, Dallavalie F. RIC. Sci 1960;36(II):1210.
4. Bottomley F, Cand. J Chem 1970;48:350.
5. Ferrari A, Braibanti A, Bigliardi G, Lenfredi AM, Krist Z 1965;122:259.
6. Qing-bao S, Zhong-lin L, Xiao-li W, Young_xing M. Transition Met. Chem 1994;19:503.
7. Srivastava AK, Agarwal RK, Kapur V, Sharma S, Srivastava M, Jain PC. Transition Met. Chem 1982;7: 41.
8. Howlader MBH, Islam MS. Indian J Chem sec A 2007;46:440.
9. Inkander MF, El-Sayed L, El-Toukchy A, Tawfik M. Transition Met. Chem 1982;7:135.
10. Kuppusamy K, Govindranjan S. Thermochim. Acta 1996;274:125.
11. Vikram L, Sivasankar BN. Indian J Chem Sect A 2006;45:864.
12. Sravanam N, Sivasankar BN, Rajan SG, Yusuff MKK. Synth. React., Inorg. Metal-Org. Chem 1994;24:703.
13. Ratnam J. J Chem. Soc., Dalton Trans 1994,787.
14. Singh KN, Singh DK, Singh SB. Synth. React. Inorg. Metal-Org. Chem 2001;32:703.
15. Zhang L, Tang N, Wu JC, Tan MU, Wang Q, Han Y, Synth. React. Inorg. Metal-Org. and Nano Met. Chem 2003;33:847.
16. Figgis BN, Lewis J. Progress in Inorg. Chem., (F.A. Gotton Ed) Interscience 1964;6:185.
17. Carlin RL. Transition metal chemistry (R.L. Carlin Ed.) Edward Arnold Ltd., Longdon 1965;I:6.
18. Lever ABP. "Inorganic electronic spectroscopy", Elsevier Amgsterdam 1968.
19. Lever ABP, Mantvani E, RS. Ramaswamy, Inorg. Chem 1967;8:107.
20. Beliamy LJ. "Infranced Spectra of complex molecules", Willey, New York 1957.
21. Nakamoto K. "Infrared and Raman spectra of inorganic and co-ordination compound", Wiley New York 1970.
22. Earnsaw A, Larkworthy LF, Pater KC. J Chem. Coc. 1969A,1339.
23. Khepekar AV, Lewis J, Mabbs FE, Weigold H. "J Chem. Soc 1967,1561.
24. Fujita J, Nakamoto K, Kobayashi. "Spectro Chem. ACTA 1956,1249.
25. Adams DM. "Metal Ligand and related vibrations". E. Arnold Publication, London 1967.