Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4225-4230

Polymeric Complex of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with Schiff Bases Derived from Hydroquinone *bis*-(Acetylhydrazide) and Aromatic Aldehydes

VIVEKANAND* and N.S. BHANDARI†
Department of Chemistry, G.B. Pant University of Agriculture and Technology
Pantnagar-263 145, India
Fax: (91)(5944)233473; Tel: (91)(5944)235122; E-mail: imvivekanand@gmail.com

Complexes of the general formula, $M[C_6H_4\{OCH_2C(O)NH(N){=}CHR\}_2(AcO)_2]_n$ [where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and R = $-C_6H_4OH$, $-C_6H_4CH_3$ and $-C_6H_5$] were prepared by the reaction of divalent metal acetates with respective hydroquinone *bis*-(acetylhydrazide-2-arylaldehyde). These complexes have been characterized on the basis of the elemental analysis, magnetic susceptibility and infrared spectral studies. The magnetic moment data indicate an octahedral geometry for the metal complexes.

Key Words: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} Complexes, Schiff base.

INTRODUCTION

A survey of literature[1-4] indicated that no work has been done on 3*d*-bivalent metal complexes of the schiff base derived by the condensation of hydroquinone *bis*-(acetylhydrazide) and salicylaldehyde, benzaldehyde and anisaldehyde. Keeping this in view we report here preparation and characterization of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} complexes with hydroquinone *bis*-(acetylhydrazide-2-anisaldehyde) [HAHA-2] hydroquinone *bis*-(acetylhydrazide-2-benzaldehyde) [HAHB-2] and hydroquinone *bis*-(acetylhydrazide-2-salicyldehyde) HAHS-2).

EXPERIMENTAL

All chemicals used were of reagent grade and hydraquinone *bis*-(acetylhydrazie) was prepared by reported method[5]. Solvents were purified by standard methods.

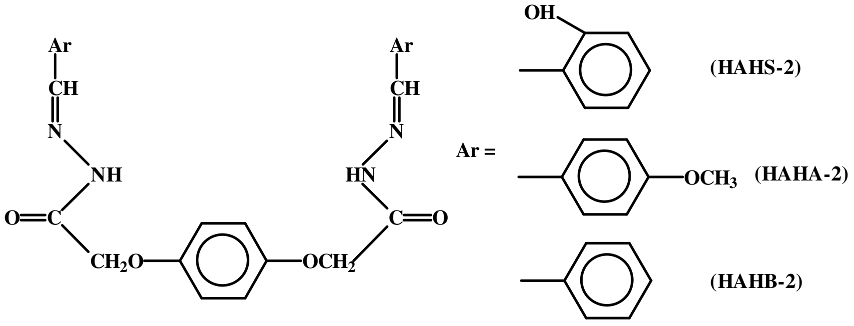
Metal contents in the complexes were estimated by standard methods[6]. Estimation of carbon, hydrogen and nitrogen was done by Perkin-Elmer-240C rapid element analyzer. The infrared spectra of the ligands

---

†Department of Chemistry, Kumaun University, Soban Singh Jeena Campus, Almora-263 601, India.

and polymeric complexes were recorded on PyUniCAM SP-1200 in the range 4000-400 cm^{-1} using KBr pellets. Magnetic susceptibility of the complexes was studied by Gouy's method using $Hg[Co(CNS)_4]$ as a reference substance.

Synthesis of ligands: Aryl aldehyde (0.02 mol) was added drop wise to a solution of hydroquinone *bis*-(acetylhydrazide) (0.01 mol) in 100 mL ethyl alcohol. The mixture was refluxed on a water bath for about 3 h. The resulting precipitate filtered, washed with alcohol and dried. The ligands were recrystallized from methanol. The ligands used in the present investigation have the following structure.



Synthesis of metal complexes: Metal acetate (0.003 mol) dissolved in methanol (40 mL) was added gradually to a solution of hydroquinone *bis*-(acetylhydrazide-2-aryl aldehyde) (0.003 mol) in the methanol (40 mL). The reaction mixture after adding 1 mL of glacial acetic acid was refluxed on sand-bath for about 1 h. The solution was allowed to cool and then poured into water (200 mL). The precipitate then obtained was filtered, washed with hot water and dried *in vacuo* over calcium chloride.

RESULTS AND DISCUSSION

The metal acetates of Co(II), Ni(II), Cu(II), Zn(II) and Mn(II) react with hydroquinone *bis*(acetaldehydrazide-2-aryl aldehydes) according to the following equation.

$$C_6H_4(OCH_2CONHN{=}CHR)_2 + M(CH_3COO)_2 \xrightarrow[CH_3COOH]{CH_3OH} [(AcO)_2MC_6H_4(OCH_2CONHN = CHR)_2]_n \quad (1)$$

where $R = -C_6H_4OH, -C_6H_4OCH_3, -C_6H_5$

The physical properties of the polymeric complexes are compiled in Table-1. These complexes are found quite stable in air and are sparingly soluble in chloroform, acetonitrile and ethanol. All of these, however, are found reasonably soluble in DMSO and DMF.

TABLE-1
ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES FOR LIGANDS AND METAL COMPLEXES

Complexes/Colour	Yield (%)/m.p. (°C)	Analysis Found (Calcd.) %				μ_{eff} (BM)
		C	H	N	M	
HAHS-2	70	62.33	4.76	12.12	–	–
(Light yellow)	(195)	(62.28)	(4.85)	(11.49)	–	
Ni(II)HAHS-2$(AcO)_2$	76	51.79	4.29	8.87	8.90	2.47
(Yellow)	(260)	(52.60)	(4.38)	(8.76)	(9.19)	
Co(II)HAHS-2$(AcO)_2$	74	51.18	4.41	9.12	8.40	4.66
(Orange)	(280)	(52.59)	(4.38)	(8.76)	(9.22)	
Mn(II)HAHS-2$(AcO)_2$	77	51.59	4.31	8.18	8.17	5.69
(Light brown)	(265)	(52.92)	(4.41)	(8.82)	(8.65)	
Cu(II)HAHS-2$(AcO)_2$	75	51.32	4.52	8.98	9.25	1.79
(Green)	(290)	(52.21)	(4.35)	(8.70)	(9.87)	
Zn(II)HAHS-2$(AcO)_2$	73	51.50	4.56	9.01	9.92	–
(Green yellow)	(300)	(52.06)	(4.34)	(8.68)	(10.13)	
HAHA-2	74	62.67	5.31	11.43	–	–
(Brown)	(200)	(62.27)	(5.32)	(10.49)	–	
Ni(II)HAHA-2$(AcO)_2$	75	53.19	5.01	8.92	9.16	2.68
(White)	(285)	(54.00)	(4.80)	(8.40)	(8.80)	
Co(II)HAHA-2$(AcO)_2$	71	53.00	5.23	9.01	8.99	4.73
(Pink white)	(298)	(54.30)	(4.80)	(8.40)	(8.84)	
Mn(II)HAHA-2$(AcO)_2$	73	54.86	5.10	8.94	8.65	5.89
(Grey)	(300)	(54.30)	(4.83)	(8.45)	(8.29)	
Cu(II)HAHA-2$(AcO)_2$	77	52.98	5.11	8.75	10.02	1.75
(Light green)	(280)	(53.61)	(4.77)	(8.34)	(9.46)	
Zn(II)HAHA-2$(AcO)_2$	71	54.24	5.04	8.69	10.23	–
(Grey)	(310)	(53.46)	(4.75)	(8.32)	(9.71)	
HAHB-2	75	66.68	5.12	13.02	–	–
(White)	(194)	(67.78)	(5.65)	(13.95)	–	
Ni(II)HAHB-2$(AcO)_2$	75	53.93	5.15	9.63	9.98	2.60
(White)	(282)	(55.38)	(4.62)	(9.23)	(9.68)	
Co(II)HAHB-2$(AcO)_2$	69	55.65	4.97	9.60	9.99	4.86
(Pink white)	(290)	(55.36)	(4.61)	(9.23)	(9.71)	
Mn(II)HAHB-2$(AcO)_2$	71	56.01	5.21	9.78	9.85	5.63
(White brown)	(300)	(55.72)	(4.64)	(9.29)	(9.12)	
Cu(II)HAHB-2$(AcO)_2$	78	55.25	5.15	9.79	10.60	1.81
(Light green)	(292)	(54.94)	(4.58)	(9.16)	(10.39)	
Zn(II)HAHB-2$(AcO)_2$	80	55.83	5.22	9.65	11.01	–
(Pink white)	(304)	(54.78)	(4.56)	(9.13)	(10.66)	

The IR spectra of the ligands and their complexes in the solid state were recorded and important IR absorption bands and their assignment are summarized in Tables 2-4. The IR spectra of ligands, HAHS-2, HAHB-2 and HAHA-2 show a strong intensity bands at 1680, 1700 and 1700 cm^{-1}, respectively and are assigned to ν(C=O) vibration[7]. These bands exhibit a negative shift of 25-60 cm^{-1} in metal complexes, which indicates that the ligands are ligated through O-atom of the carbonyl group[8]. The ligands HAHS-2, HAHB-2 and HAHA-2 show medium intensity band at 1620, 1615 and 1630 cm^{-1} attributable to ν(C=N) stretching vibration. These bands undergo a negative shift of 45-55 cm^{-1} on complexation[9,10]. It is further supported by a positive shift of 25-30 cm^{-1} in ν(N–N) vibration of metal complexes with respect to ligands[11].

TABLE-2
INFRARED SPECTRAL DATA OF HAHS-2 AND [HAHS-2](AcO)$_2$M(II)

HAHS-2	Ni	Co	Mn	Cu	Zn	Assignment
3220	3210	3210	3205	3215	3210	ν(OH)
3060	3025	3030	3030	3025	3025	ν(CH)
2900	2900	2900	2910	2900	2905	ν(CH$_2$)
2380	2370	2375	2370	2370	2370	ν(NH)
1680	1630	1635	1625	1630	1620	ν(C=O)
–	1645	1650	1635	1640	1650	ν(COO)
1620	1565	1570	1565	1575	1565	ν(C=N)
1510	1510	1510	1505	1510	1510	ν(CN) + δ(NH)
1440	1440	1435	1435	1440	1440	δ(CH)
1360	1365	1360	1355	1360	1355	δ(OH)
1040	1065	1065	1070	1065	1065	ν(N-H)
775	750	750	755	760	765	Disubsituted benzene
–	545	555	550	540	555	ν(M-O)
–	450	455	445	450	455	ν(M-N)

The presence of a band in the range 560-540 cm^{-1} in the spectra of complexes, which may be assigned to (M–O) vibration, further supports the interaction of metal with oxygen of carbonyl group[7]. A band in the range 445-455 cm^{-1} that is present in all the complexes and absent in the spectra of ligands may be assigned to (M–N) stretching vibration[7]. A medium intensity band is observed in the range 1655-1635 cm^{-1} in the spectra of metal complexes. It may be attributed to ν(COO) vibration which is coordinated through oxygen to metal atoms[12,13].

The room temperature magnetic moment values for Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) are tabulated in Table-1. The magnetic moment for Co(II) complexes fall in the range 4.66-4.86 BM which is close to the

TABLE-3
INFRARED SPECTRAL DATA OF HAHA-2 AND [HAHA-2]$(AcO)_2$M(II)

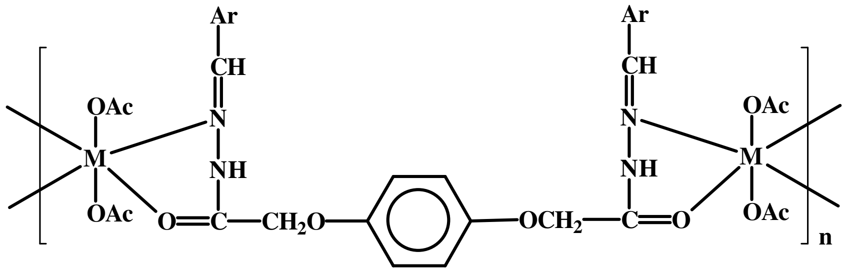
HAHA-2	Ni	Co	Mn	Cu	Zn	Assignment
2940	2940	2945	2935	2940	2940	ν(CH)
2850	2835	2830	2830	2835	2830	ν(CH_2)
2380	2370	2365	2370	2365	2365	ν(NH)
1700	1670	1665	1660	1665	1670	ν(C=O)
–	1640	1640	1635	1645	1650	ν(COO)
1615	1605	1600	1605	1610	1605	ν(C=N)
1510	1505	1505	1510	1500	1510	ν(CN) + δ(NH)
1440	1430	1425	1430	1430	1430	δ(C-H)
1040	1060	1065	1065	1060	1060	ν(N-N)
830	825	830	830	820	820	Disubsituted benzene
–	540	545	555	550	550	ν(M-O)
–	445	455	450	455	455	ν(M-N)

TABLE-4
INFRARED SPECTRAL DATA OF HAHB-2 AND [HAHB-2]$(AcO)_2$M(II)

HAHB-2	Ni	Co	Mn	Cu	Zn	Assignment
2985	2980	2975	2975	2980	2980	ν(CH)
2875	2870	2875	2870	2865	2870	ν(CH_2)
2370	2360	2360	2355	2355	2360	ν(NH)
1700	1675	1670	1675	1675	1670	ν(C=O)
–	1650	1645	1645	1635	1635	ν(COO)
1630	1600	1605	1600	1610	1600	ν(C-N)
1510	1505	1505	1505	1500	1505	ν(CN) + δ(NH)
1415	1405	1410	1410	1405	1410	δ(CH)
1080	1100	1105	1105	1100	1105	ν(N-N)
825	815	810	810	815	810	Disubsituted benzene
–	550	555	560	565	550	ν(M-O)
–	445	445	455	450	450	ν(M-N)

spin only values expected for octahedral geometry[14,15]. The Ni(II) complexes show magnetic susceptibilities in between 2.47-2.68 BM. Low values of magnetic moments are attributed to polymeric behaviour of complexes with octahedral arrangement around metal atom[16,17]. The magnetic moment values 5.63-5.89 of Mn(II) complexes favour to the high spin octahedral structure of the complexes[18]. The Cu(II) complexes have BM values in the range 1.75-1.81 supporting a octahedral structure[17,18]. Zn(II) complexes are found diamagnetic in nature[17,18].

On the basis of the elemental composition, infrared spectral studies and magnetic susceptibility behaviour the following structures were proposed for the complexes.



M = Ni(II), Co(II), Cu(II), Zn(II), Mn(II); Ar = C_6H_5OH, $C_6H_5OCH_3$, C_6H_5

ACKNOWLEDGEMENTS

The authors are thankful to Prof. C.S. Mathela, Head, Department of Chemistry, Kumoun University, Nanital for encouragement and suggestion for the work and Prof. K.N. Mathpal, Head, Department of Chemistry, Kumaun University, S.S.J. Campus for facilities.

REFERENCES

1. R.S. Batoi and C.P. Mackeson, *J. Inorg. Nucl. Chem.*, **32**, 2645 (1971).
2. P.L. Maurya, B.P. Agarwal and A.K. Day, *Polym. Bull.*, **1**, 631 (1979).
3. A.K. Day, *J. Indian Chem. Soc.*, **63**, 357 (1986).
4. H. Upadhya, P. Patel and M.N. Patel, *Proc. Ind. Acad. Sci.*, **101**, 371 (1989).
5. R. Rautela, Docteral Thesis, Kumaun University, Nanital (1993).
6. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longmans, London, edn. 3 (1961).
7. K. Nakamotto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1986).
8. M. Schafer and B. Najjar, *J. Inorg. Nucl. Chem.*, **5**, 265 (1966).
9. R.K. Agarwal and J. Prakash, *Polyhedron*, **10**, 2399 (1991).
10. R.K. Agarwal and I. Chakraborti, *Polish J. Chem.*, **68**, 1085 (1994).
11. H.D. Juneja and K.N. Munshi, *Indian J. Chem.*, **27A**, 452 (1988).
12. L.J. Bellamy, The Infrared Spectra of Organic Molecules, John Wiley Sons, Inc. New York (1958).
13. I.S. Ahuja, C.L. Yadav and S. Tripathi, *Asian J. Chem.*, **1**, 195 (1989).
14. B.N. Figgis and Lewis, Progressive Inorganic Chemistry, Interscience, New York, edn. 1 (1964).
15. A.K. Rana and J.R. Shah, *J. Indian Chem. Soc.*, **63**, 281 (1986).
16. B.K. Arora, K.V. Pande and R.P. Singh, *J. Indian Chem. Soc.*, **56**, 656 (1979).
17. A.K. Day, *J. Chem. Soc.*, **48**, 641 (1971).
18. G. Narain, P.R. Shukla, V.K. Singh and A.M. Jaiswal, *J. Indian Chem. Soc.*, **60**, 321 (1983).

(*Received*: 25 February 2006; *Accepted*: 2 April 2007) AJC-5544