GEOLOGICAL APPLICATION OF Co(II), Ni(II), Cu(II) Cr(III), Mn(III), Fe(III), VO(IV), Zr(IV) and UO_2(VI) WITH SCHIFF BASE METAL COMPLEXES

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Abstract:
The newly Schiff base have been synthesized by condensing 2-hydroxy-5-bromo acetophenone with ethylene diamine. The metal complexes were obtained as a result of interaction of Schiff base ligand and metal ions: Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI). The complexes have been characterized on the basis of elemental analysis, infrared, molar conductance, magnetic Susceptibilities and electronic spectra. The application of metal complex used for comparative study of the qualitative investigations of the rocks and minerals contains the percentage of these metals. The technique is high-performance liquid chromatography (HPLC) is widely used for the separation, determination, and in the preparation of organometallic compounds and metal coordination compounds.
Keywords: Schiff base, Molar conductance, Application

Introduction

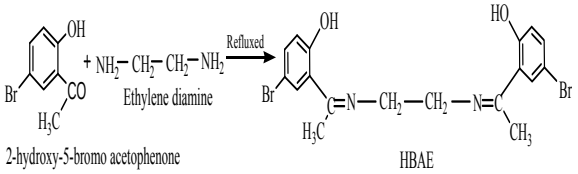
The Schiff bases play a significant role in the area of coordination chemistry and applicable in geological chemistry. The common Schiff bases are crystalline solids, which are in basic nature. In the area of bioinorganic, biotechnology and biochemistry the interest in the Schiff base complexes shows to provide synthetic models for the metal-containing sites like metalloproteins/enzymes and also contributed enormously to the development of the research in radio immunotherapy, cancer diagnosis medicinal chemistry, and treatment of tumor [1,2]. Schiff base ligands have lot of significant importance in all branches of chemistry especially in the development of Schiff base complexes of transition metal, because Schiff base ligands are potentially capable of forming stable complexes with metal ions [3]. The Schiff base complexes and derivatives of Coumarin, thiazolidinone and triazoles so far reported as anti-inflammatory[4], antioxidant[5]. The mathematical calculating of thermal decomposition activation parameters can be obtained.[6]. This paper discusses the metal complexes, molar conductance, geological application for Schiff base complexes of Co (II), Ni (II), Cu (II), Cr (III), Mn (III), Fe (III) VO (IV), Zr (IV) and UO_2 (VI).

Experimental

All the chemicals were of A.R. grade and used as received ethylene diamine and 2-hydroxy-5-bromo acetophenone (HBA) was prepared by known methods.[7] The solvents were purified by standard methods.[8]

Synthesis of 2-Hydroxy-5-bromoacetophenone-N,N'-ethylenediimine (HBAE).

A hot ethanolic solution of ethylene diamine (0.05 mol) was added to an ethanolic solution of respective acetophenone (0.05 mol). The reaction mixture was refluxed in a water-bath for 4-5 h. The colour product was filtered off and recrystallised. Yield 70%. M. P. 270^0C



2-hydroxy-5-bromo acetophenone HBAE

Preparation of complexes:

All the metal complexes were prepared in a similar way by following method. To a hot solution of ligand HBAT (0.02M) in 25ml of ethanol a suspension of respective metal salts was added drop wise with constant stirring. The reaction mixture was refluxed on a water bath for 4-6 h. The precipitated complexes were filtered, washed with ethanol followed by ether and dried over fused calcium chloride.

Yield : 45-50%

Table 1. Analytical data and molar conductance of the compounds.

Compounds	Colour	Mol.wt.	Analysis % Found (calc.)					μ_{eff} B. M.	Λ_M (Ω^{-1} cm^2 mol^{-1})
			M	C	H	N	Cl		
$C_{18}H_{18}N_2O_2Br_2$	Yellow	453.8	--	47.83 (47.59)	3.85 (3.96)	6.07 (6.17)	--	--	--
$[CoL(H_2O)_2]$ H_2O	Brown	564.7	10.32 (10.43)	38.12 (38.25)	3.72 (3.89)	4.80 (4.95)	--	4.27	6.1
$[NiL]$ H_2O	Black	528.5	11.02 (11.10)	40.72 (40.87)	3.25 (3.40)	5.17 (5.29)	--	Dia	5.6
$[CuL(H_2O)_2]$ $2H_2O$	Brown	587.3	10.61 (10.81)	36.61 (36.77)	3.95 (4.08)	4.62 (4.76)	--	2.02	18.8
$[CrL(H_2O)Cl]$ $2H_2O$	Yellow	593.3	8.66 (8.76)	36.22 (36.40)	3.52 (3.70)	4.58 (4.71)	5.77 (5.98)	3.86	21.2
$[MnL(OAc)]$ $2H_2O$	Brown	601.7	9.02 (9.12)	39.78 (39.88)	3.62 (3.82)	4.53 (4.65)	--	5.6	12.8
$[FeL(H_2O)Cl]$ H_2O	Green	579.2	9.58 (9.65)	37.13 (37.29)	3.32 (3.45)	4.72 (4.83)	6.02 (6.12)	6.0	18.8
[VOL]	Green	518.8	9.41 (9.83)	41.12 (41.63)	3.01 (3.08)	5.09 (5.39)	--	1.78	14.5
$[ZrL(OH)_2]$ $2H_2O$	Yellow	613.0	14.72 (14.87)	35.08 (35.23)	3.47 (3.58)	4.38 (4.56)	--	Dia	31.9
$[UO_2L]$	Orange	721.9	32.87 (32.98)	29.82 (29.92)	2.08 (2.21)	3.75 (3.87)	--	Dia	23.6

The complexes are soluble in DMSO and DMF but insoluble in water and common organic solvents. The metal chloride content of complexes were analyzed by standard methods[11]. The ^1H NMR spectra of ligand was recorded and obtained from RSIC Chandigarh. IR spectra of the compounds were recorded on Perkin Elmer 842 spectrophotometer in the region 400-4000cm^{-1}, carbon, hydrogen and nitrogen analysis were carried out at RSIC, Punjab University, Chandigarh. The molar conductance of the complexes at 10^{-3} M dilution in DMF were determined using equiptronic digital conductivity meter EQ-660 with a cell constant 1.00 cm^{-1} at room temperature. The magnetic moment measurement were made on a Gouy balance at room temperature using $[HgCo(SCN)_4]$ as the calibrant. The thermogravimetric analysis was performed on laboratory set up apparatus in air atmosphere at 10^0 C min^{-1} heating rate. The molecular weights of the complexes were determined by Rast method.

Result and Discussion

The Schiff base ligand HBAE and its complexes have been characterized on the basis of ^1H NMR, IR spectral data, elemental analysis, molar conductance, magnetic susceptibility measurements and thermogravimetric analysis data. All these values and analytical data is consistent with proposed molecular formula of ligand. All the compounds are coloured solid and stable in air. The ^1H NMR spectra of ligand HBAE shows signals at: 15.97 (1H, s, phenolic OH); 8.06(1H, s, phenyl); 7.67 and 7.31 (2H, m, phenyl), 3.29(4H, s, CH_2CH_2); 2.51 ppm (3H, s, methyl) [9-18]

Table 2. IR spectra of ligand and metal complexes.

Compound	(OH) hydrogen bonded	(C=N) imine	(CO) phenolic	(MO)	(MN)	
$C_{18}H_{18}N_2O_2Br_2$	2900	1614	1480	--	--	----------
$[CoL(H_2O)_2]$ H_2O	--	1589	1440	520	455	3400, 1640, 815, 770
[NiL] H_2O	--	1586	1460	510	495	3326, 1630
$[CuL(H_2O)_2]$ $2H_2O$	--	1595	1440	590	490	3406, 1642, 818, 780
$[CrL(H_2O)Cl]$ $2H_2O$	--	1600	1436	570	460	3390, 1635, 830, 745
[MnL(OAc)] $2H_2O$	--	1590	1446	580	495	3330, 1628
$[FeL(H_2O)Cl]$ H_2O	--	1602	1463	530	425	3395, 1638, 845, 740
[VOL]	--	1600	1455	525	480	----------
$[ZrL(OH)_2]$ $2H_2O$	--	1601	1440	565	460	3335, 1628
$[UO_2L]$	--	1590	1420	560	470	----------

Recent applications of HPLC to some metal complexes-

The first reported use of HPLC for the separation of organometallic complexes was made by Veening et al. in 1969 [19]. An increasing variety of detection techniques have made it suitable for the separation and determination of metal complexes. Metal complexes of Cu(II), Co(II) and Ni(II) chelates with diethyldithiocarbamic acid used for many types of samples including alloys [20]. Ni(II), Co(II) and Cu(II) as diethyl dithiocarbamate complexes for Nickel and copper in real samples[21]. Cobalt(II), copper(II), iron(II) and vanadium(IV) complexes for Crude petroleum oils [22]. Cu(II), Fe(II) and U(VI) complexes of [M(HPO)] and their neutral complexes Chromium(III)–diphenylcarbazone for Synthetic mixtures and Standard Reference Materials[23], Geological samples[24]. Uranium, iron, nickel and copper complexes for Mineral ore samples and phosphate rock residue [25].

Conclusion:

It is assumed that dehydration of the complexes containing water occurs within an active reaction interface. This metal complexes used in geological field sample studies for sepration, determination, reaction and complexation of the metal complexes by HPCL. The technique has been shown to be an effective tool in many such applications

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