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Synthesis and Spectral Properties of Cd(II), Pb(II) and Bi(III) Complexes of Furan-2-Aldoxime and Thiophene-2-Aldoxime

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The furan-2-aldoxime and thiophene-2-aldoxime were used to prepare Cd(II), Pb(II) and Bi(III) complexes by two different methods. The crystalline products were characterised by analytical parameters which suggest the molecular stoichiometry as $M(L)_n$ where n = 2 for Cd(II) and Pb(II) while n = 3 for Bi(III) complexes for precipitation method while refluxion method gave complexes with formula $MCl_2(L)_2$ where M = Cd(II) or Bi(III). Each of these complexes was characterised by IR spectral data.

INTRODUCTION

The modification of heterocyclic molecule can alter the chemical and physical properties of metal complexes which leads to the discovery of new substance having increased potential for their commercial applications.[1,2] The oximes of furan-2-aldehyde and thiophene-2-aldehyde were used to synthesise the metal complexes. We have prepared complexes of Cd(II), Pb(II) and Bi(III) with the ligand furan-2-aldoximes (L_1) and thiophene-2-aldoxime (L_2). The metal complexes were prepared by precipitation and refluxion method. The metal complexes were analysed for physico-chemical parameters and assigned molecular stiochiometry to each of them. The detail IR investigation was carried out to ascertain different types of vibrational bonds.

EXPERIMENTAL

The ligands furan-2-aldoxime and thiophene-2-aldoxime were prepared by the method reported in the literature.[3] Both the ligands were characterised by their elemental analysis and physico-chemical properties.

(A) Preparation of complexes by precipitation method

Metal complexes of these ligands were synthesised by using aqueous solution of cadmium sulphate, lead nitrate and bismuth nitrate (1000 ppm). The ligand solutions (1% w/v) in ethanol were mixed with metal ion solutions in stiochiometric proportion at the optimum pH of 10.8. The metal complexes were digested, filtered and washed with distilled water followed by ethanol. The solid complexes were dried at 110°C. Each of these complexes was analysed and experimental results are tabulated in Table-1.

TABLE-1
ANALYTICAL PARAMETERS OF METAL COMPLEXES OBTAINED BY PRECIPITATION METHOD

Metal complex	% Analysis, found (calcd.)					
	C	H	N	S	Cl	M
$Cd(L_1)_2$	35.63 (35.88)	2.86 (2.99)	8.15 (8.37)	—	—	33.04 (33.61)
$Pb(L_1)_2$	27.52 (27.96)	2.17 (2.33)	6.13 (6.52)	—	—	47.60 (48.28)
$Bi(L_1)_3$	32.80 (33.21)	2.16 (2.77)	7.98 (7.75)	—	—	38.46 (38.56)
$Bi(L_1)_2Cl$	26.04 (25.74)	2.07 (2.15)	6.26 (6.01)	—	7.82 (7.61)	45.56 (44.86)
$Cd(L_2)_2$	32.07 (32.75)	2.27 (2.73)	7.05 (7.64)	17.08 (17.47)	—	30.75 (30.68)
$Pb(L_2)_2$	26.48 (26.02)	2.12 (2.17)	6.21 (6.07)	13.38 (13.88)	—	45.15 (44.93)
$Bi(L_2)_3$	29.68 (30.51)	2.11 (2.54)	6.88 (7.12)	16.55 (16.27)	—	35.43 (35.42)
$Bi(L_2)_2Cl$	23.86 (24.08)	2.07 (2.01)	5.56 (5.62)	12.41 (12.84)	7.30 (7.11)	41.90 (41.82)

(B) Preparation of Metal complexes by refluxing method

Hydrated cadmium chloride (10^{-2} M) and the respective oxime (2×10^{-2} M) were refluxed in ethanol medium for 2 h on a water bath. The solid compound separated on cooling was filtered and washed with hot water containing 10% of ethanol. The compounds were dried at 110°C. Similarly Bi(III) complexes were prepared by refluxing hydrated bismuth trichloride (10^{-2} M) and the respective oxime (3×10^{-2} M) in ethanol. Refluxion of anhydrous bismuth chloride and oxime in ethanol gave the same compound $Bi(L)_2Cl_2$ as obtained above using hydrated $BiCl_3$.

All the above complexes were diagnosed for their physico-chemical parameters and IR spectral data. The analytical parameters are tabulated in Table-2. The IR spectra were recorded using KBr pellet technique on IR spectrometer supplied by M/s Schimadzu Corporation, Japan. The salient features of IR spectra are summarised in Table-3.

TABLE-2
ANALYTICAL PARAMETERS OF METAL COMPLEXES OBTAINED BY REFLUXION METHOD

Metal complex	% Analysis, found (calcd.)					
	C	H	N	S	Cl	M
$Cd(L_1)_2Cl_2$	30.07 (29.46)	2.26 (2.46)	6.70 (6.87)	—	17.21 (17.41)	27.97 (27.60)
$Bi(L_1)_2Cl_2$	24.55 (23.82)	1.70 (1.99)	5.18 (5.56)	—	14.33 (14.07)	41.44 (41.47)
$Cd(L_2)_2Cl_2$	27.55 (27.32)	2.16 (2.28)	6.86 (6.37)	15.06 (14.57)	15.73 (16.14)	25.69 (25.59)
$Bi(L_2)_2Cl_2$	22.41 (22.39)	1.98 (1.87)	6.06 (5.24)	11.84 (11.94)	12.98 (13.23)	40.10 (39.00)

TABLE-3
SALIENT FEATURES OF IR SPECTRA (cm^{-1}) OBTAINED BY PRECIPITATION METHOD

Metal complex	ν(OH)	ν(C=N)	ν(N—O)	ν(M—N)
L_1	3230	1638	960	—
$Cd(L_1)_2$	3330	1650	955	530
$Pb(L_1)_2$	3330	1655	955	525
$Bi(L_1)_2$	3330	1655	960	490
L_2	3180	1657	942	—
$Cd(L_2)_2$	3580	1650	980	455
$Pb(L_2)_2$	3580	1630	975	460
$Bi(L_2)_2$	3375	1640	955	460
SALIENT FEATURES OF IR SPECTRA (cm^{-1}) OBTAINED BY REFLUXION METHOD				
$Cd(L_1)_2Cl_2$	3325	1650	970	535
$Bi(L_1)_2Cl_2$	3325	1638	970	570
$Cd(L_2)_2Cl_2$	3320	1650	950	580
$Bi(L_2)_2Cl_2$	3340	1640	1025	615

RESULTS AND DISCUSSION

All the metal complexes are crystalline in nature. It can be seen from the table that metal : ligand stiochiometry is very well in agreement with molecular formulae $M(L)_n$ where n = 2 for Cd(II) and Pb(II) complexes while n = 3 for Bi(III) complexes. A compound with the formulae $Bi(L)_nCl$ was obtained when the bismuth salt was used in the above preparation with $BiCl_3$. All the complexes are stable at room temperature and isothermal heating experiments indicate their stability up to 160°C. Most of the complexes are yellow in colour but a few of them vary in colour shade from light brown to even brown.

It can be seen that the hydrogen bonded –OH are observed in the spectra of the complexes in the region 3330–3180 cm^{-1}. It shows that there is a strong intra and intermolecular hydrogen bonding[3,4] due to which the actual frequency of OH is lowered.[5,6] The very small change in ν(C=N) is in accordance with the extended conjugation C—C=C—C—N present in the molecules.[7] The symmetric N—O bands are shifted to higher frequencies in the complexes indicating the coordination of metal ion through oximic nitrogen atom.[8] The additional band pointed in the region 460–350 cm^{-1} may be assigned to ν(M—N) stretching vibrations. Similar assignment was made for such stretching vibrations on the basis of reported data from the literature.[9,10]

The infrared spectra of the complexes obtained by refluxion method suggested that the metal corordination with ligand takes place only through the oximic N atom. It is proposed that these compelexes may be represented as $MCl_2(L)_2$ where M = Cd or Bi(III) and L is either furan-2-aldoxime or thiphene-2-aldoxime ligand.

Conclusively, both the oximic ligand molecules act as a unidentate ligand if complexes are prepared by refluxion method while it behaves as bidentate ligand during precipitation method. The following structure is proposed for the compounds involving intramolecular H-bonding, interchelate ring resonance and a *trans* MCl_2.

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