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2-Imino-4-oxo-1,3-thiazolidine Complexes of Silver(I), Zinc(II), Cadmium(II) and Mercury(II)

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Complexes of the types [MXL_2], [MX_2L_2] and [MX_2L] (where M = Ag^I, Zn^{II}, Cd^{II} or Hg^{II}; X = Cl, Br, I, SCN, NO_3, ClO_4 or $^1/_2SO_4$; L = 2-imino-4-oxo-1,3-thiazolidine) have been prepared as white, diamagnetic non-electrolyte compounds. The infrared spectral studies suggest that silver and zinc derivatives are N-bonded, cadmium complex is S-bonded and mercury derivatives are both N- and S-bonded.

Introduction

Recently studies have been made[1] on the complexation of sterically hindered heterocyclic compounds containing nitrogen, oxygen and sulphur donor atoms with several metals in order to find out the competivity among the donor atoms in coordination to the metal. These ligands behave both as soft and hard bases depending on the metal ions employed. 2-Imino-4-oxo-1,3-thiazolidine, $\overset{1}{S}$–$\overset{2}{C}$:NH–$\overset{3}{N}$H–$\overset{4}{C}$:O–CH_2, L, is one such ligand containing four different reaction centres, namely, sulphur, carbonyl oxygen, exocyclic and cyclic nitrogen atoms. In an earlier communication[2] we have reported N-bonded cobalt(II) halide complexes of L and Singh and Sukla[3] claimed O-bonding in their nickel(II) derivatives. The behaviour of this ligand with Group II B metals is therefore of interest as it is well known that the tendency of these metals to coordinate to nitrogen or oxygen decreases on passing from zinc to mercury whereas the tendency to coordinate through sulphur increases. In this paper we report the isolation and characterization of silver(I), zinc(II), cadmium(II) and mercury(II) derivatives of L containing different anions.

Experimental

The ligand L was prepared[4] by the condensation of monochloroacetic acid with thiourea. All other reagents used were AnalaR or chemically pure grade.

Preparation of Silver Complexes

To aqueous solutions of silver salts containing small amount of respective acids was added an aqueous solution of the ligand in approximately 1:2 molar ratio. The contents were stirred and kept aside. The crystallized complexes were filtered, washed with acetone and dried.

Preparation of Zinc and Cadmium Complexes

To an ethanolic solution of MX_2 was added an alcoholic solution of ligand in 1:2 molar ratio. The mixtures were refluxed for 4–6 hr whereby the separated complexes were filtered, washed with acetone and dried.

Preparation of Mercury Complexes

The thiocyanato derivative was obtained from alcoholic medium by following the method of zinc complexes whereas other mercury complexes were obtained by following the method of silver complexes.

Analysis

The complexes were analysed for nitrogen, sulphur, halogens and metals by standard methods[5–6]. The analytical results are given in Table I.

Physical Measurements

Magnetic susceptibility measurements of the complexes were carried out by the Gouy method. Conductivity measurements were made with Philips 9600 conductivity bridge in $10^{-3}M$ NN-dimethylformamide and dimethylsulphoxide solutions. Infrared spectral measurements of all the compounds were examined in the region 4000–200 cm^{-1} using Perkin–Elmer 257 and Beckman IR-12 spectrophotometers. Both KBr pellet and nujol mull techniques have been employed.

Results and Discussion

All the complexes are colourless and diamagnetic consistent with a d^{10} configuration. The silver and mercury complexes decompose in water to give the respective deprotonated derivatives[7], whereas zinc and cadmium derivatives dissociate to give metal salts and free ligand. They are insoluble in ethanol, ether, acetone, carbon tetrachloride, benzene and are soluble in NN-dimethylformamide and dimethylsulphoxide. The low conductivity values (below 30 ohm^{-1} cm^2) in these solvents show that they behave as non-electrolytes. The complexes decompose in the temperature range 140–170° C. The principal infrared frequencies of the complexes and the ligand are given in Table II. The assignment of the bands are in accordance with the previous paper[2]. The cyclic ν(NH) appears as medium intensity band at 3380 cm^{-1} and as a strong and broad band around 3100 cm^{-1}. The appearance of this band at low frequency region is attributed to the intermolecular hydrogen bonding in the ligand[8]. The exocyclic ν(NH), ν(C=O) and ν(CS) appear in the free ligand at 3230, 1650 and 700 cm^{-1} respectively. If coordination occurs through the exocyclic nitrogen, exocyclic ν(NH) should decrease; coordination through carbonyl oxygen on the other hand results in the decrease of C=O stretching frequency and an increase in the CN stretching frequency as in the O-bonded urea complexes[9]. Coordination of the cyclic nitrogen to a metal causes a negative shift of 200–300 cm^{-1} in the ν(NH) vibration as observed in the metal morpholine complexes[10, 11]. Coordination of the sulphur to a metal causes both a decrease in the frequency and a marked lowering of intensity in the ν(CS) modes.

TABLE I. Analytical Data and Some Physical Properties of the Complexes.

Compound	Analytical Data (%) Found (Calculated)								Conductance (ohm^{-1} cm^2)		Dec. Temp. (° C)
	N		S		X		M		DMSO	DMF	
$AgNO_3L_2$	16.9	(17.4)	15.1	(15.6)	–		27.2	(26.8)	31.4	28.9	162
$AgClO_4L_2$	12.2	(12.7)	13.8	(14.5)	–		25.3	(24.6)	26.0	28.5	152
$Ag_2SO_4L_4$	14.0	(14.4)	19.9	(20.6)	–		27.0	(27.8)	28.9	31.2	170
$ZnCl_2L_2$	14.8	(15.2)	16.9	(17.4)	18.7	(19.2)	18.1	(17.7)	3.5	8.1	168
$ZnBr_2L_2$	12.2	(12.3)	13.7	(14.0)	34.2	(34.9)	14.1	(14.3)	18.6	23.4	157
ZnI_2L_2	9.52	(10.2)	11.4	(11.6)	45.5	(46.0)	11.5	(11.9)	19.5	22.8	155
$CdCl_2L_2$	12.9	(13.5)	14.8	(15.4)	16.8	(17.1)	27.8	(27.1)	9.3	13.8	161
$HgCl_2L$	6.95	(7.23)	7.91	(8.27)	17.7	(18.3)	50.8	(51.7)	1.1	3.1	172
$HgBr_2L$	5.92	(5.88)	7.21	(6.73)	32.9	(33.6)	42.0	(42.1)	3.2	3.8	158
$Hg(SCN)_2L$	12.4	(12.9)	21.8	(22.2)	–		45.8	(46.5)	9.1	9.9	165
$Hg(NO_3)_2L$	12.1	(12.7)	6.80	(7.27)	–		44.9	(45.5)	1.9	2.9	148
$HgSO_4L$	6.45	(6.79)	14.9	(15.5)	–		47.9	(48.6)	2.9	4.1	140

TABLE II. Principal Infrared Bands of the Ligand and Its Complexes (cm^{-1}).[a]

Compound	ν(NH) cyclic	ν(NH) exocyclic	ν(CO)	ν(CS)	ν(M–N)	ν(M–S)	ν(M–X)
L	3380 m 3100 s, b	3230 s	1650 s	700 s	–	–	–
$AgNO_3L_2$	3080 s	3230 s	1650 s	710 m	270 m	–	–
$AgClO_4L_2$	3120 s	3260 s	1645 s	700 m	290 m	–	–
$Ag_2SO_4L_4$	3090 s	3230 s	1650 s	710 m	270 m	–	–
$ZnCl_2L_2$	3160 s	3260 s	1680 s	700 m	240 m	–	300 m
$ZnBr_2L_2$	3160 s	3260 s	1680 s	700 m	240 m	–	228 s
ZnI_2L_2	3160 s	3260 s	1680 s	700 m	245 m	–	–
$CdCl_2L_2$	3580 s	3230 s	1650 s	680 m	245 m	–	215 m
$HgCl_2L$	3110 s	3230 s	1680 s	660 m	280 m	235 m	290 m
$HgBr_2L$	3170 s	3230 s	1680 s	650 m	290 w	230 m	210 m
$Hg(SCN)_2L$	3160 s	3260 s	1675 s	650 m	290 m	230 m	–
$Hg(NO_3)_2L$	3080 s	3240 s	1680 s	670 m	280 m	235 m	–
$HgSO_4L$	3080 s	3260 s	1680 s	650 m	270 m	240 m	–

[a] s = strong, m = medium, b = broad.

Silver Complexes

The results of the infrared study show a negative shift of the order of 250–300 cm^{-1} in the cyclic ν(NH) and not much significant change in the positions of the other bands of the free ligand. This large negative shift of cyclic ν(NH) suggests that the cyclic nitrogen atom is involved in the coordination to the metal atom. In N-bonded metal complexes bands due to ν(M–N) interaction are observed[10–12] in the region 300–200 cm^{-1}. In our spectra, in the far-infrared region medium intensity bands located in the region 270–290 cm^{-1}, which are absent in the free ligand spectrum, are assigned to ν(Ag–N) interaction. The oxyanions of silver complexes are all coordinated to the metal as indicated by their low conductance. The ν(NO) bands of nitrate are observed for the nitrato complex at 1412, 1315 and 820 cm^{-1} which are characteristic of unidentate nitrato groups[13, 14] and not bidentate as the separation between the first two bands in the latter case is much larger[14]. In the sulphato complex the triply degenerate ν(SO) appears at 1170, 1090, 1065 and 970 cm^{-1} which can be assigned to bidentate sulphato groups of C_{2v} symmetry. The absence of a band around 1220 cm^{-1} suggests that the sulphato group is bridging rather than chelating group[15, 16]. The perchlorato complex shows four bands at 1140, 1095, 1050 and 930 cm^{-1} due to ν(Cl–O) which are attributed to bidentate perchlorate group of C_{2v} symmetry[14]. Depending on the nature of ligand and anion, silver(I) is known to form variety of complexes due to the possibilities of sp, sp^2 and sp^3 hybridization. In the present study, silver in the nitrato complex, [AgL_2ONO_2] is 3-coordinated through two cyclic nitrogen atoms of the ligand and one oxygen atom of the nitrate. In the sulphato complex, [$L_2AgOSO_3AgL_2$] the metal is probably three coordinated with the sulphato group bridging the two silver atoms coordinated through two nitrogen atoms of the ligand. On the other hand, in the perchlorato complex [AgL_2OClO_3], the metal is 4-coordinated with two nitrogen atoms of the ligand and two oxygen atoms of the perchlorate group. However, it should be remembered that this conclusion is only from the infrared spectral data and the exact stereochemistry of silver(I) in these complexes could be had from the X-ray crystal structure analysis.

Zinc Complexes

As in the case of silver complexes the cyclic ν(NH) suffers a negative shift of approximately 200 cm^{-1} and there is no significant change in the positions of exocyclic ν(NH) and ν(CS) bands. As far as ν(C=O) vibration is concerned, this band occurs at 1650 cm^{-1} in the spectrum of the free ligand and is shifted towards higher frequency region, 1680 cm^{-1} in these complexes. This suggests that the coordination takes place through the cyclic nitrogen atom. In the low lying absorption spectra, the bands observed around 240 cm^{-1} are assigned to ν(Zn–N) vibration according to literature data[10]. The bands at 300 and 234 cm^{-1} for chloro- and bromo-complexes are assigned to Zn–X stretching vibrations according to the reported values for ν(Zn–X) vibrations in tetrahedral ZnX_2L_2 complexes[10, 17]. The ratio ν(Zn–Br)/ν(Zn–Cl), 0.78, agrees well with the expected value[18]. The ν(Zn–I) band could not be identified as it is expected below 200 cm^{-1} which is beyond the limit of the spectrophotometer used. The spectral data suggest that in these complexes the halide atoms are not bridged as for bridged halides ν(Zn–X) values fall[18] below 220 cm^{-1}.

Cadmium complex

The cyclic ν(NH) vibration in the spectrum of CdX_2L_2 appears with greater intensity at 3400 cm^{-1} and ν(CS) observed at 700 cm^{-1} for free ligand is lowered to 680 cm^{-1} with reduced intensity. There is not much change in the positions of exocyclic ν(NH) and ν(CO) from that of free ligand. This suggests that the ligand is coordinated to cadmium through the sulphur atom. The frequencies due to Cd–Cl[16] and Cd–S[19, 20] occur for cadmium complexes in the region 270–210 and 240–200 cm^{-1} respectively. The bands observed at 245 and 215 cm^{-1} in our complex are assigned to ν(Cd–S) and ν(Cd–Cl) vibrations respectively.

Mercury Complexes

In the preparation of these complexes even with the metal:ligand ratio over 1:4, only 1:1 complexes separated out. The results of infrared spectral studies show that the exocyclic ν(NH) has not changed its position from that of free ligand and ν(CO) has slightly shifted to higher frequency region. The cyclic ν(NH) has suffered a negative shift of the order of 200–250 cm^{-1} which suggests the bonding of cyclic nitrogen to mercury. Furthermore, there is lowering of ν(CS) band from 700 to 650 cm^{-1} indicating S-coordination to the metal. All the complexes exhibit medium intensity bands around 280 and 240 cm^{-1} which are assigned to ν(Hg–N)[10–12] and ν(Hg–S)[21] vibration respectively. The bands at 290 and 210 cm^{-1} for chloro- and bromo-complexes are assigned to ν(Hg–X) according to the literature values[16] of tetrahedral mercury(II) halide complexes. In the metal thiocyanato complexes ν(CN) vibration occurs in the range 2060–2100 cm^{-1} for N-bonded and 2100–2120 cm^{-1} for S-bonded terminal NCS groups[14, 22], whereas for bridging thiocyanate[14, 23] it occurs in the range 2140–2180 cm^{-1}. Our complex $Hg(SCN)_2L$, exhibits CN stretching vibration at 2115 cm^{-1} suggesting S-bonded terminal thiocyanato group. The nitrato complex exhibits NO stretching bands at 1435, 1315 and 815 cm^{-1} which clearly suggests the unidentate ONO_2 group[13, 14]. The sulphato complex absorbs at 1245, 1120, 1085 and 960 cm^{-1} due to triply degenerate ν(SO), suggesting bidentate chelating sulphato group[14, 16].

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