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Study of Interaction between N-Aralkylsalicylaldimines and Halides of Cadmium(II) and Mercury(II)

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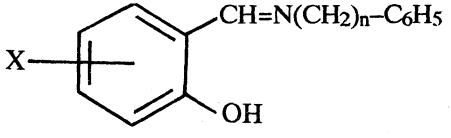
The interaction between N-aralkylsalicylaldimines and halides of cadmium(II) and mercury(II) in dry methanol/ethanol yielded a series of interesting complexes conforming with 1 : 1 or 1 : 2 metal halide ligand stoichiometry, depending upon the nature of substituents on the aldehyde moiety and the molecular size of metal halides. Probable structures have been proposed for the resulting complex species based on analytical and spectroscopical evidences. Reaction between mercuric chlorides and ligands in 95% aqueous ethanol, on the other hand, led to the decomposition of the latter with simultaneous formation of dimeric metal amine complexes of 1:1 stoichiometric ratio.

INTRODUCTION

Despite the enormous attention that the metal complexs of Schiff bases have evinced in general, analogous compounds of cadmium and mercury have remained practically unexplored. Isolated reports that we find in literature[1–3], incidentally relate to Schiff bases derived from aliphatic or aromatic amines while no attention appears to have been focused on N-aralkylamines as constituents of Schiff bases even though the latter happen to be relatively stronger bases. This investigation was therefore devoted exclusively to the study of interaction between N-aralkylsalicylaldimines and halides of Hg(II) and Cd(II) in different solvent conditions.

EXPERIMENTAL

The various N-aralkylsalicylaldimines (L_1–L_8) employed as ligands in this study were prepared and characterised as already reported by these authors[4]. The ligands can be represented by the following general structural formula:



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wherein

L_1; n = 1, X = H; L_2; n = 2, X = H; L_3; n = 1, X = 3–OCH_3;
L_4; n = 2, X = 3–OCH_3; L_5; n = 1, X = 5–NO_2; L_6; n = 2, X = 5–NO_2;
L_7; n = 1, X = 3–NO_2; L_8; n = 2, X = 3–NO_2

Reaction between the metal halides and ligands were studied in dry methanol/ethanol under reflux conditions. Use of 95% aqueous ethanol as solvent was restricted to the study of interaction between mercury (II) chloride complexes only. Requisite quantities of the reactants were accurately weighed and dissolved separately in minimum quantities of the solvent prior to mixing and subsequent refluxing on a water bath for varying intervals of time (5–30 min). The complexes that precipitated/crystallized out on cooling the reaction mixtures were filtered and repeatedly washed using small volumes of the solvent and then crystallized from methanol or chloroform, wherever possible.

Characterisation of the metal complexes was done based on metal halide and nitrogen estimations performed according to standard procedures. The halide ions were determined as the corresponding silver salts from extracts prepared by refluxing sodium carbonate and the complexes in 5 : 1 w/w ratio for 1 hr in water as medium. Aldehydes were separated out, wherever possible, by chilling and filtering the extracts. Nitrogen was estimated by the Kjeldhal's method.

RESULTS AND DISCUSSION

Reactions between the metal halides and the ligands in dry methanol/ethanol yielded complexes of typical pale yellow to deep yellow colour which showed remarkable stability under ambient conditions of temperature and pressure. Analytical data (Table 1) was found to be consistent with MLX_2 or ML_2X_2 stoichiometries where MX_2 and L stand for the metal halide and ligand respectively. Use of insufficiently dried solvents gave products of variable composition apparently due to hydrolysis of the ligands or the metal halides or both. The complexes showed poor solubility in common organic solvents, pointing to polymeric nature. Extrermely low conductance (Table 1) ruled out an ionic structure.

The I.R. spectra of the complexes resembled the parent ligand strikingly. A very conspicuous feature was the retention of very broad band in the 3200–2500 cm^{-1} region, attributable to the intramolecularly hydrogen-bounded phenolic group. Additionally, the OH deforming mode (1350–1325 cm^{-1}) did not show an appreciable shift either. These observations suggested that the phenolic group remained intact during complexation. This conjecture received further support from the observed displacement of the C–O stretching mode by 45–20 cm^{-1} on chelation. A marginal downward shift of ν(C=N) was taken as a proof of the involvement of azomethine nitrogen on coordinate bond formation[5–7]. Weak bands observed in 480–450 cm^{-1} and 445–420 cm^{-1} regions were tentatively assigned to $\nu_M \leftarrow O$ and $\nu_M \leftarrow N$ respectively.

TABLE 1

ANALYTICAL DATA OF CADMIUM(II) AND MERCURY(II) COMPLEXES OBTAINED WITH DRY METHANOL/ETHANOL.

Reactants	Colour	M. pt. (°C)	Molecular formula	Chemical Analysis (%)			Molar conductance (mhos cm^2. $mole^{-1}$)
				N	Halogen	Metal	
$CdCl_2$ and L_3	Light-yellow lustrous crystals	154–6	$C_{30}H_{30}O_4N_2 \cdot CdCl_2$	4.47 (4.21)	10.76 (10.67)	16.96 (16.89)	1.59
$CdBr_2$ and L_3	Bright-yellow thin needles	217–18	$C_{30}H_{30}O_4N_2 \cdot CdBr_2$	4.02 (3.71)	20.94 (21.21)	14.55 (14.90)	0.31
CdI_2 and L_3	Deep-yellow crystals	250 (decomp)	$C_{15}H_{15}O_4N \cdot CdI_2$	2.40 (2.27)	39.82 (40.14)	15.58 (18.20)	0.20
$CdCl_2$ and L_7	Yellow powder	—	$C_{28}H_{24}N_4O_6 \cdot CdCl_2$	8.20 (8.00)	9.88 (10.21)	16.45 (16.16)	0.35
$CdBr_2$ and L_7	Yellow powder	—	$C_{28}H_{24}N_6O_6 \cdot CdBr_2$	7.00 (7.14)	20.03 (20.40)	13.95 (14.33)	0.55
CdI_2 and L_7	Yellow granules	184–6	$C_{28}H_{24}N_4O_6 \cdot CdCl_2$	6.22 (6.37)	28.44 (28.92)	12.39 (12.80)	2.02
$CaCl_2$ and L_5	Light-yellow granules	—	$C_{28}H_{24}N_4O_2 \cdot CdCl_2$	8.45 (8.87)	9.76 (11.25)	16.66 (17.74)	0.21
$CdCl_2$ and L_6	Light-yellow granules	—	$C_{30}H_{28}N_4O_6 \cdot CdCl_2$	7.48 (7.44)	9.42 (9.81)	16.11 (15.54)	0.15
$HgCl_2$ and L_3	Light-yellow granules	164–7	$C_{15}H_{15}NO_2 \cdot HgCl_2$	3.01 (2.37)	13.94 (13.85)	38.75 (39.13)	0.41
$HgCl_2$ and L_4	Light-yellow granules	141–45	$C_{16}H_{17}NO_2 \cdot HgCl_2$	2.60 (2.66)	13.35 (13.48)	37.80 (38.09)	0.45
$HgCl_2$ and L_5	Light-yellow granules	158–60	$C_{28}H_{24}N_4O_6 \cdot HgCl_2$	7.33 (7.15)	9.22 (9.06)	25.37 (25.60)	0.39
$HgCl_2$ and L_7	Light-yellow granules	174–76	$C_{28}H_{24}N_4O_6 \cdot HgCl_2$	6.96 (7.15)	8.82 (9.06)	25.19 (25.60)	0.39

Note: Calculated values have been reflected in parenthesis.

TABLE 2
ANALYTICAL DATA OF MERCURY(II) COMPLEXES OBTAINED IN 95% AQUEOUS ETHANOL MEDIUM.

Reactants	Colour	M.P. (°C)	Molecular formula	Chemical Analysis (%)			Molar conductance (mhos $cm^2 \cdot mole^{-1}$)
				N	Cl	Hg	
$HgCl_2$ and L_1	Lustrous white	Sublimes	$(C_7H_9N \cdot HgCl_2)$[a]	4.10 (3.70)	18.36 (18.75)	52.60 (52.98)	Negligible
$HgCl_2$ and L_2	-do-	-do-	$(C_8H_{11}N \cdot HgCl_2)$[b]	3.75 (3.57)	17.83 (18.09)	50.84 (51.09)	-do-

[a]Identical complexes formed when ligands L_3, L_5 and L_7 were used in place of L_1.
[b]Identical complexes formed when ligands L_4, L_6 and L_8 were used in place of L_2.

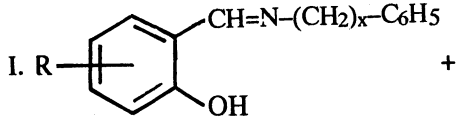
Steric Factors

The molecular size of the metal halide and the substituent at 3 position of aldehyde moieties were found to have steric implications. For example, reaction between CdI_2 and L_3 resulted in a 1 : 1 type adduct as against 1 : 2 type normally expected. $HgCl_2$ and L_3 also gave a product of identical stoichiometry. However, presence of $-NO_2$ group in place of $-OCH_3$ group at 3 position (L_7) did not exert steric effect sufficient enough to force a 1 : 1 stoichiometry with either of the aforesaid metal halides. It was concluded, therefore, that the steric effects became significant only when the molecular size of the metal halide exceeded certain limits. Another possibility also existed in that the Schiff bases from *o*-vanillin could form complexes through the participation of phenolic and methoxy oxygen atoms[8]. But that did not really happen as confirmed by PMR spectral measurements. Bond formation through methoxy oxygen was expected to cause deshielding of the associated protons which incidentally was not the case since the methoxy protons appeared at 3.98 both in the ligand and complexes thereof. This and other evidences discussed above amply demonstrated that the complexation did take place through the azomethine and phenolic oxygen atoms only and that the primary valencies were satisfied by the halide ions situated within the coordination sphere. In contrast, the transition metals are known to form chelates essentially via deprotonation of the phenolic group with the type of the ligands used in this study. Going by the various evidences presented and in view of both tetra and hexa covalencies shown by Cd(II) and Hg(II), tetrahedral and octahedral geometries are being assigned for complexes of MLX_2 and ML_2X_2 respectively.

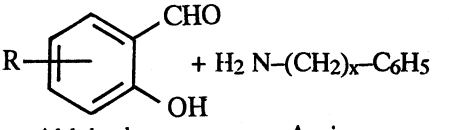
Effect of Water

As already stated elsewhere, presence of extraneous moisture led to products of variable composition, presumably due to hydrolysis of the ligands or the salt or both. In order to discern the role of water on the reaction course, interaction between the ligands and $HgCl_2$ was studied using 95% aqueous ethanol as solvent under reflux conditions. Interestingly enough, regardless of the nature of the aldehyde moiety, all the Schiff bases formed from benzylamine gave an identical lustrous white, flaky, compound that sublimed above 150°C. Its analytical data was found to be concordant with the empirical composition, $C_6H_5CH_2NH_2 \cdot HgCl_2$. Likewise, β-phenyl-ethylamine analogues yielded complexes of similar physical characteristics, but analysing as $C_6H_5CH_2CH_2NH_2 \cdot HgCl_2$. Formation of such amine complexes is difficult to explain without pre-supposing hydrolytic type of decomposition of the ligands into respective constituents. The cleavage of the azomethine double bond was probably facilitated by the metal ion electrophiles through inducing a sufficiently strong electronic shift away from the double bond involved and thus enabling water to attack[9,10]. If that were the case, substituents on the aldehyde ring ought to modify the degree of susceptibility to hydrolysis which, in fact, was the observation. As expected

from the resonance stabilization effect, the Schiff bases corresponding to 3-nitro-salicylaldehyde displayed maximum resistance (longer reflux times) to hydrolysis[11]. Formulation of $HgCl_2$-amine complexes is believed to proceed according to the following scheme:



Schiff base



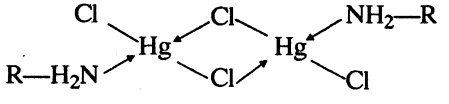
Aldehyde Amine

II. $C_6H_5(CH_2)_xNH_2 + HgCl_2 \rightarrow [C_6H_5(CH_2)_xNH_2HgCl_2]$

Complex x = 1 or 2

Mishra *et al* (1966)[12], reported 1 : 2 $HgCl_2$-amine complexes prepared via a direct interaction between the constituents. But the complexes obtained by these authors following exactly the conditions employed by Mishra *et al*[12] were found to have a 1 : 1 stoichiometry instead. Further, these complexes resembled those obtained in this study using Schiff base ligands in every detail.

The mercuric chloride-amine complexes under dicussion had extremely poor solubility in most common organic solvents—a characteristic of polymeric organic compounds. Conductance value of the order of 4×10^{-5} Mhos, as recorded on 1% solutions in DMF, further supported a polymeric structure besides ruling out an ionic one. Infrared spectra provided unambiguous information that these compounds were coordination complexes rather than loose adduct. The most conspicuous feature was the downward displacement of N–H stretching modes by as much as 100 cm^{-1} seemingly, resulting from the drainage of electrons from the nitrogen atom in the process of coordinating with the metal ion.[13,14] Weak absorption bands appearing around 300 cm^{-1} were tentatively assigned to Hg–Cl terminal stretches. However, bridging modes couldn't be resolved. Based on the evidences presinted and in agreement with Brill *et al*[15] and Marcotrigiano *et al.*[16] Chlorobridged, dimeric structures, as shown below, are being proposed for the amine complexes.



R = $C_6H_5CH_2$ or $C_6H_5CH_2CH_2NH_2$

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