

Complexes of Zn(II), Cd(II) and Hg(II) with Schiff Bases Derived from Isatin and Derivatives of Aniline

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Abstract: Some new monochloro and bis, metal complexes containing Schiff bases of the types $[(Cl)M(SB)]$ and $[M(SB)_2]$ [where $M=Zn(II)$, $Cd(II)$ and $Hg(II)$, $SB=$ Isatin-aniline (SIA) and Isatin-3-nitroaniline (SIN)] have been synthesized by the interaction of MCl_2 with sodium salt of Schiff bases in different molar ratios in the presence of benzene/MeOH. The derivatives have been characterized by elemental analysis and spectral (UV-visible, IR, NMR & FAB-mass) studies.

Experimental

(A) Synthesis of Ligands :

The ligands Isatin-aniline (SIA) and Isatin-3-nitroaniline (SIN) have been synthesized according to established literature methods.^{1,2}

(B) Synthesis of Complexes

(I) Synthesis of monochloro Zn(II) complexes containing Schiff bases of the types $[(Cl)Zn(SIA)]$ and $[(Cl)Zn(SIN)]$.

To a benzene (20 cm³) solution of Na(SIA) (0.581g, 2.38 mmol), a suspension of $ZnCl_2$ (0.325g, 2.38 mmol) in methanol was added. The reaction mixture was refluxed for ~4h during which time the colour changed from orange to brown. The precipitated NaCl (0.139g, 2.38 mmol) was removed by filtration and filtrate was concentrated by distillation and stripped off the excess of solvent under reduced pressure to afford brown powdered solid $[(\mu-Cl)_2 Zn_2 (h^2-SIA)_2]$ (0.57g, 75%).

In a similar manner complexes $[(\mu-Cl)_2 Zn_2 (h^2-SIN)_2]$, $[(\mu-Cl)_2 Cd_2 (h^2-SIA)_2]$, $[(\mu-Cl)_2 Cd_2 (h^2-SIN)_2]$, $[(\mu-Cl)_2 Hg_2 (h^2-SIA)_2]$ and $[(\mu-Cl)_2 Hg_2 (h^2-SIN)_2]$ have been prepared and details are given in table-1.

Table-1
Synthetic and Analytical Details for Complexes of Zn(II), Cd(II) and Hg(II)
Containing Schiff Bases.

S.No.	Reactants (g, m mol)	Product (g, % yield)	% Analysis found (calcd)	
			M	Cl
1.	ZnCl ₂ + Na(SIA) (0.325, 2.38) (0.521, 2.38)	[(m-Cl) ₂ Zn ₂ (h ² -SIA) ₂] (0.57, 75)	19.2 (20.3)	11.4 (11.0)
2.	ZnCl ₂ + Na(SIA) (0.30, 2.20) (1.04, 4.40)	[Zn(h ² -SIA) ₂] (0.72, 65)	13.0 (12.8)	—
3.	ZnCl ₂ + Na(SIN) (0.250, 1.80) (0.465, 1.80)	[(m-Cl) ₂ Zn ₂ (h ² -SIN) ₂] (0.49, 81)	20.0 (19.4)	10.7 (10.5)
4.	ZnCl ₂ + Na(SIN) (0.250, 1.8) (0.930, 3.6)	[Zn(h ² -SIN) ₂] (0.76, 78j)	11.7 (12.1)	—
5.	CdCl ₂ + Na(SIA) (0.264, 1.44) (0.341, 1.40)	[(m-Cl) ₂ Cd ₂ (h ² -SIA) ₂] (0.32, 62)	—	10.0 (9.6)
6.	CdCl ₂ + Na(SIA) (0.332, 1.81) (0.884, 3.62)	[Cd(h ² -SIA) ₂] (0.76, 76)	—	—
7.	CdCl ₂ + Na(SIN) (0.40, 2.18) (0.563, 2.18)	[(m-Cl) ₂ Cd ₂ (h ² -SIN) ₂] 90.60, 72)	—	9.5 (9.2)
8.	CdCl ₂ + Na(SIN) (0.25, 1.36) (0.702, 2.72)	[Cd(h ² -SIN) ₂] (0.49, 62)	—	—
9.	HgCl ₂ + Na(SIA) (0.30, 1.1) (0.268, 1.1)	[(m-Cl) ₂ Hg ₂ (h ² -SIA) ₂] (0.41, 82)	—	8.0 (7.7)
10.	HgCl ₂ + Na(SIA) (0.20, 0.73) (0.356, 1.46)	[Hg(h ² -SIA) ₂] (0.29, 63)	—	—
11.	HgCl ₂ + Na(SIN) (0.25, 0.92) (0.475, 0.92)	[(m-Cl) ₂ Hg ₂ (h ² -SIN) ₂] (0.3, 86)	—	7.9 (7.5)
12.	HgCl ₂ + Na(SIN) (0.32, 1.17) (0.604, 2.34)	[Hg(h ² -SIN) ₂] (0.54, 69)	—	—

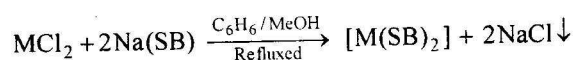
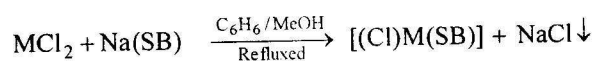
(II) Synthesis of Zn(II) complexes containing Schiff bases of the types $[Zn(SIA)_2]$ and $[Zn(SIN)_2]$.

The bis-complexes of Zn(II) have been prepared as described for monochloro-complexes by using 1:2 stoichiometric ratio of metal chloride and Schiff bases (SIA & SIN).

Similar procedure was adopted for the synthesis of bis-complexes of Cd(II) and Hg(II).

Results and Discussion

The complexes of Zn(II), Cd(II) and Hg(II) containing Schiff bases have been prepared by the reaction of anhydrous metal chloride (MCl_2) with sodium salt of isatin-aniline (SIA) and isatin-3-nitroaniline (SIN) in 1:1 and 1:2 molar ratios of the types $[(\mu-Cl)_2 M_2 (h^2-SB)_2]$ and $[M_2(\eta^2-SB)_2]$ (where $M=Zn(II)$, $Cd(II)$, $Hg(II)$ and $SB=SIA$ and SIN).



(where $M=Zn(II)$, $Cd(II)$ and $Hg(II)$ and $SB=SIA$ and SIN).

These complexes are white solids and are soluble in common organic solvents. These complexes have been purified by recrystallization in C_6H_6 /EtOH mixture.

Electronic Spectra

The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes formed by SIA and SIN do not show any significant band which could help in elucidating their structure.

The bands observed at 24330 ± 260 , 28310 ± 150 and 32000 ± 281 cm^{-1} may be due to their $n-\pi^*$, $\pi-\pi^*$ and $n-\sigma^*$ transitions.³

I.R. Spectra

The presence of Schiff base moiety indicated by the appearance of absorption band in the range $1625-1628$ cm^{-1} , which is shifted to lower frequency region by $10-35$ cm^{-1} suggesting participation of azomethine group on complexation. The ν_{∞} (phenolic) stretch observed at $1261-1276$ cm^{-1} in the free Schiff bases, shifted to higher frequency region $1310-1353$ cm^{-1} in complexes suggesting bond formation between metal and phenolic oxygen. The monochloro complexes showed characteristic I.R. frequency ν_{M-Cl} for around $\sim 293(m)$, $\sim 285(s)$ cm^{-1} .

The strong band observed around 285 cm^{-1} suggesting bridging between two metal centre via chlorine.

Infra-red spectra of all the complexes showed characteristic I.R. frequencies in the region 500 ± 15 and $405 \pm 10 \text{ cm}^{-1}$, assigned for $\nu_{(M-O)}$ and $\nu_{(M-N)}$ stretch respectively.^{4,7}

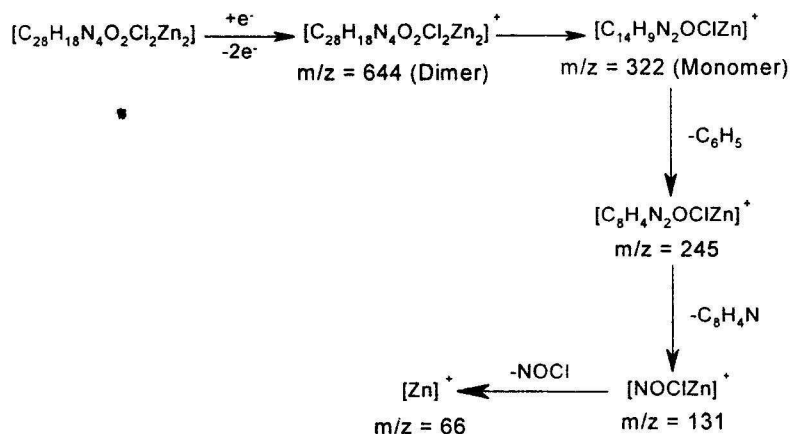
Nuclear Magnetic Resonance (NMR) Spectra

On comparing the ^1H -NMR spectra of ligands with those of complexes, it was found that the peak due to NH of isatin ring appears at $\delta 11.2$ ppm in the spectra of the ligands disappeared in the complexes further confirming the enolization of keto group. The signals due to aromatic ring protons appear at $\delta 7.8$ - 8.4 ppm in the ligands shifts slightly downfield in the complexes. This may be due to decrease in electron density after formation of complexes.⁸

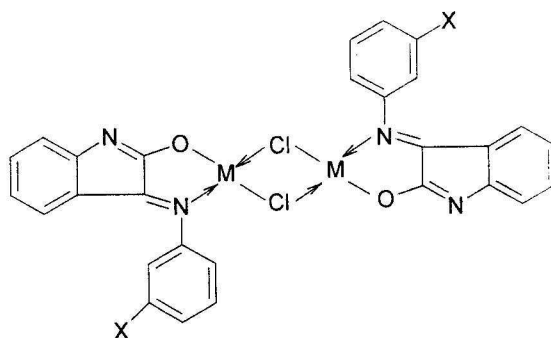
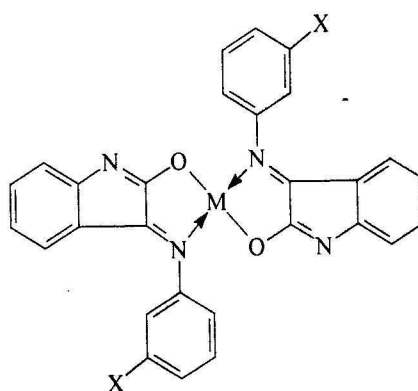
The ^{13}C -NMR spectral data showed the shifting the carbon signals of C=N group $\delta 159$ ppm to down field in the complexes confirming the bonding of azomethine group to metal atom. However, sharp decrease of signals in CS_2 ($\delta 135.0$) showed the bidentate nature of the $-\text{CS}_2$ ligand group and downfield shifting of band of amido carbon (NH-C=) from 166 to 170 ppm clearly indicated that covalent bond formation may occur with enolic oxygen of isatin derived ligand.⁹

FAB-mass Spectra

The FAB-mass spectrum of mono (Isatin-aniline) Zinc(II) chloride $[(\mu\text{-Cl})_2\text{Zn}_2(\text{h}^2\text{-SIA})_2]$ showed a peak at $m/z = 644$ corresponded to the molecular weight of the complex suggesting dimeric nature. Other peaks obtained at m/z 322, 247, 131 showed fragmentation of ligand from complex by formation of radical cations. The fragmentation pattern is given in scheme.



Scheme : Fragmentation pattern of $[(\mu\text{-Cl})_2\text{Zn}(\text{h}^2\text{-SIA})_2]$.

Fig. 1 : Proposed structure of $[(m-Cl)_2 M_2(h^2-SB)_2]$ Fig. 2 : Proposed structure of $[M_2(h^2-SB)_2]$

where : $M = \text{Zn(II), Cd(II) and Hg(II)}$

and $X = \text{H}$ for Isatin-aniline (SIA) and NO_2 for Isatin-3-nitroaniline (SIN)

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