

Synthesis & characterization of zinc(II), cadmium(II) & mercury(II) complexes with bis(bidentate) schiff bases

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A few Zn(II), Cd(II) and Hg(II) complexes of the bis(bidentate) Schiff bases derived from *p*-phenylenediamine and salicylaldehyde (H₂Salpphen), and *o*-phenylenediamine and *o*-vanillin (H₂Vanophen), of the type MCl₂.H₂L (H₂L = H₂Salpphen or H₂Vanophen) have been synthesised. The complexes have been characterized by elemental analysis, infrared, ¹H and ¹³C NMR and mass spectra.

The chemistry of group 12 metals with schiff bases is rather limited¹, more so with bis(bidentate) ones except a few^{2,3}. Therefore, in continuation of our studies on the chemistry of group 12 metal ions with nitrogenous ligands such as pyrazoles⁴, we now report here the results of the same with two bis(bidentate) schiff bases.

Experimental

p-Phenylenediamine, *o*-phenylenediamine and salicylaldehyde (all BDH, UK) were purified by standard methods. 2-Hydroxy-3-methoxybenzaldehyde (*o*-vanillin) (Lancaster, UK) was used as received. The schiff bases, H₂Salpphen and H₂Vanophen, were prepared from *p*-phenylenediamine and salicylaldehyde, and *o*-phenylenediamine and *o*-vanillin, respectively by literature methods^{5,6}. Infrared spectra for the range 4000-200 cm⁻¹ were recorded on a Perkin-Elmer 883 spectrophotometer, as KBr pellets and were calibrated with respect to the 1601 cm⁻¹ band of a polystyrene film. ¹H NMR spectra were recorded for solutions of the compounds in CdCl₂ or DMSO-*d*₆ on a Varian T-60A (60 MHz) (for the ligands only) or on a BRUKER AM 250 (250 MHz) (for the complexes), and ¹³C NMR spectra on a BRUKER AM 250 (62.9 MHz). Tetramethylsilane was used as internal standard for

both ¹H and ¹³C NMR spectra. Fast Atom Bombardment (FAB) mass spectra were recorded on a VG ZAB H Double Focussing mass spectrometer. Melting points were recorded on an electrical heating-coil melting point apparatus and are uncorrected. Elemental analyses for C, H and N were carried on a Perkin-Elmer 240C or 2400 II elemental analyser.

Synthesis of the complexes

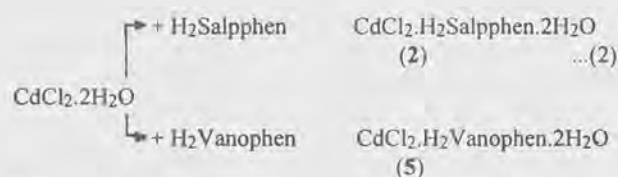
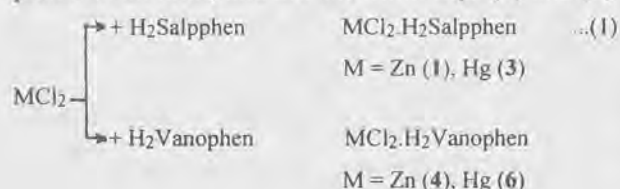
General procedure

An appropriate schiff base, H₂Salpphen (SBI) (0.56 g, 2 mmol) or H₂Vanophen (SB2) (0.75 g, 2 mmol) and absolute ethanol (100 ml) were taken in a three-neck round-bottomed flask equipped with a reflux condenser and the mixture refluxed till the reagent dissolved. To this hot solution, a solution of ZnCl₂ (0.27 g, 2 mmol) or CgCl₂.2H₂O (0.45 g, 2 mmol) or HgCl₂ (0.54 g, 2 mmol) in 100 ml absolute ethanol was added and stirred. Precipitation started in about half-an-hour and was complete within an hour. The precipitate was filtered, collected and washed several times with absolute ethanol and finally dried *in vacuo*. They are all coloured solids. The data are presented in Table 1.

Results and discussion

Schiff bases derived from salicylaldehyde such as N,N'-ethylene-bis(salicylideneimine) (H₂Salen) are well-known as polydentate ligands⁷ coordinating in three ways. In the first, the ligand is ionised by removal of phenolic protons giving complexes such as M(Salen)₂ (M = U(IV), Th(IV) (ref.8). In the second, the schiff base (e.g., H₂Salen or related base such as N,N'-propylenebis(salicylideneimine), salicylidene aniline or its aniline substituted derivative is apparently unionised⁸⁻¹², and forms adducts in which the metal is coordinated only through azomethine nitrogen atoms, leaving the unionised phenolic group uncoordinated. A third type of bonding has been proposed with H₂Salen or related bases, where the metals such as lanthanoids or actinoids are

coordinated through the phenolic oxygen atoms of the charge-separated (zwitterionic) form rather than through the nitrogen atoms^{2,13}. The complexes of the Schiff base H₂Salophen (derived from *o*-phenylenediamine and salicylaldehyde) with Zn, Cd and Hg were reported as coordinated through both azomethine nitrogen and phenolic oxygen without replacement of phenolic hydrogen³. In this work, the Schiff bases, H₂Salpphen (SB1) and H₂Vanophen (SB2) have been reacted with Zn(II), Cd(II) and Hg(II) chlorides in absolute ethanol, by adding the latter to the hot ethanolic solutions of the former. As the reactions are carried out in the absence of any base in ethanol, adduct formation takes place and no phenolic hydrogen is replaced. The reactions are completed in an hour, and are shown in Eqs. (1) and (2).



Compounds 1-6 are obtained in good yields and are coloured solids (Table 1). They are thermally stable, but hydrolyse slowly in the presence of moisture.

They are moderately soluble in chloroform, but highly soluble in DMSO.

In the infrared spectra of the Schiff bases, broad absorptions found in the range 3050 - 2600 cm⁻¹ owing to intramolecular hydrogen bonding (O-H...N)¹³ shift to the range 3550 - 3321 cm⁻¹ for the metal complexes. Compounds 1, 2 and 3 show two types of -OH bands, one at 3420, 3340 and 3350 respectively for complex formation side (compartment I) and the other at 3020, 3055 and 3056 cm⁻¹ respectively being almost at the same positions as in the ligand owing to the intramolecularly hydrogen bonded -OH group (compartment II). This indicates that the other side remains unaffected. Compounds 4, 5 and 6 show -OH bands at higher values (3321, 3507 and 3525 cm⁻¹) after complex formation. The 1623 cm⁻¹ band assigned to $\nu(\text{C}=\text{N})$ of H₂ Vanophen (SB2), on complex formation, is shifted to 1611, 1617 and 1626 cm⁻¹ respectively for the complexes 4, 5 and 6, indicating coordination of azomethine nitrogen to metal. For H₂Salpphen (SB1), the $\nu(\text{C}=\text{N})$ occurs at 1611 cm⁻¹, while two types of $\nu(\text{C}=\text{N})$ bands occur for its complexes, viz., 1610 and 1559 cm⁻¹ for the complex 1, 1617 and 1558 cm⁻¹ for the complex 2 and 1609 and 1559 cm⁻¹ for the complex 3.

In the ¹H NMR spectra of the ligands, the resonance signals owing to the aryl -OH protons in the free ligands occur at δ 13.23 and 13.57 for SB1 and SB2 respectively. For their metal complexes, there appears a signal for each between δ 13.05 and 13.27

Table 1 -- Characterization data of the complexes of schiff bases^{a,b}

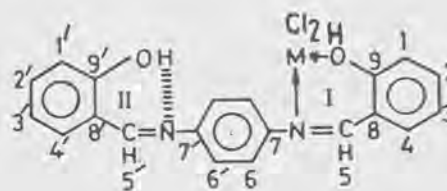
Sl.No.	Empirical form.	Colour Yield(%)	M.pt. (°C)	Found (Calcd), %		
				C	H	N
1	ZnCl ₂ .SB1	Yellow	230-232	52.92	4.01	5.75
	C ₂₀ H ₁₆ Cl ₂ N ₂ O ₂ Zn	87		(53.07)	(3.56)	(6.18)
2	CdCl ₂ .SB1.2H ₂ O	Red	> 260	45.25	3.91	5.71
	C ₂₀ H ₂₀ Cl ₂ N ₂ O ₂ Cd	82		(44.84)	(3.76)	(5.22)
3	HgCl ₂ .SB1	Red	230-232	41.25	2.59	5.02
	C ₂₀ H ₁₆ Cl ₂ N ₂ O ₂ Hg	85		(94.86)	(2.74)	(4.76)
4	ZnCl ₂ .SB2	Yellow	242 (d)	50.98	3.48	5.79
	C ₂₂ H ₂₀ Cl ₂ N ₂ O ₄ Zn	50		(51.53)	(3.93)	(5.46)
5	CdCl ₂ .SB2.2H ₂ O	Red	236(d)	44.64	3.64	4.11
	C ₂₂ H ₂₄ Cl ₂ N ₂ O ₆ Cd	88		(44.35)	(4.05)	(4.70)
6	HgCl ₂ .SB2	Red	148	40.42	2.95	4.39
	C ₂₂ H ₂₀ Cl ₂ N ₂ O ₄ Hg	84		(40.79)	(3.19)	(4.32)

^aSB1 = H₂Salpphen; ^bSB2 = H₂Vanophen.

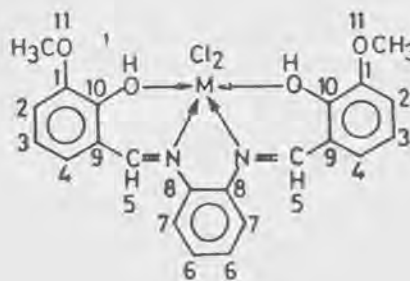
suggesting that the aryl -OH protons still exist. The $\delta(^1\text{H})$ of azomethine (HC=N) protons of the ligands (SB1 and SB2) occurring at 8.68 is either shifted downfield or remains almost unchanged in the complexes being δ 8.7, 9.5 and 8.65 for the complexes **1**, **2** and **3** respectively, and δ 9.28, 8.92 and 8.96 for the complexes **4**, **5** and **6** respectively. For the SB2 complexes, the singlets appearing at δ 3.8-3.84 (δ 3.96 for the ligand itself) are due to -OCH₃ groups. For the complexes the phenyl group appear at δ 7.18-7.58 as multiplets compared to δ 7.23 and 6.98 for the ligands SB1 and SB2 respectively.

In the ¹³C NMR spectra of the metal complexes of H₂Salpphen (SB1), two types of C-5 centres (structure A) are expected if the metal is bonded to one of the bidentate sites, which is suggested from the results of infrared spectra (*vide supra*). Thus, the C-5 centres appear as pairs of signals at (δ 162.15, 161.05), (δ 163.45, 160.15) and (δ 162.35, 161.54) for the complexes **1**, **2** and **3** respectively, supporting the above suggestion. On the hand, the C-5 centres for the complexes **4**, **5** and **6** (structure B) and singlets only, respectively, at (δ 162.95, 164.26 and 164.74). The C-1 to C-4 centres for the complexes **1**, **2** and **3** occur at δ 116.56-133.45, while for the complexes **4**, **5** and **6** at δ 112.05-153.0. For the latter three complexes δ (C-1) values are quite high being 153.0, 150.48 and 150.81, as the C-1 centres are attached to OCH₃ group. The C-11 centres owing to OCH₃ occur in their usual positions at δ 55.16 - 56.05. The signals for other carbon centres excepting the tertiary carbon centres occur in the usual positions in consonance with literature values¹⁴. The tertiary carbon centres, however, are not found always, thus all the signals for C-7, C-8 and C-9 centres for the complexes **1**, **2** and **3** and C-8, C-9 and C-10 for the complexes **4**, **5** and **6** could not be detected. The data, however, amply support the formation of complexes as depicted in structures A and B.

FAB mass spectra of H₂ Vanophen and its cadmium complex (**5**) (range m/z 600-460) were recorded. Elemental analysis for C, H and N and infrared and NMR spectra support the composition CdCl₂·H₂ Vanophen·2H₂O. This formulation is also supported by mass spectral data. The molecular ion (M⁺) peak at m/z 596 (20%) corresponds to the suggested formulation. Other peaks are at m/z 525 [M⁺ - (2H₂O + Cl)] (100%) and m/z 489 [M⁺ - (2H₂O + 2Cl)]-1, i.e. [CdH Vanophen]⁺ (65%). The ligand



(A)

[M=Zn, Cd(2H₂O), Hg]

(B)

[M=Zn, Cd(2H₂O), Hg]

also shows important peaks at m/z 377 (M⁺ + 1) (15%), m/z 243

+

[H₃NC₆H₄N=CH(OH)(OCH₃)C₆H₃] (100%), and m/z 119 [C₈H₇O⁺] (82%).

Thus from the analytical and spectral data, it is assumed that for compounds **1-3**, derived from H₂Salpphen (SB1), only one side of the bis(bidentate) ligand is coordinated to the metal (structure A), while for compounds **4-6**, derived from H₂Vanophen (SB2) both sides of the bis(bidentate) ligand are coordinated to the metal (structure B), behaving as a tetradentate ligand. The water molecules in the cadmium complexes are probably present in the crystal lattice, as evident from the infrared spectra [$\nu(\text{OH})_{\text{H}_2\text{O}}$ -3507 cm⁻¹].

Acknowledgement

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