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NOTE

Magnesium(II) and Calcium(II) Complexes of Some Schiff Bases

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Magnesium(II) and calcium(II) complexes of some Schiff bases, *viz.*, salicylidene *p*-toluidine, salicylidene sulphanilic acid, vanilidene *p*-toluidine or vanilidene sulphanilic acid have been synthesised and characterised.

Magnesium and calcium are biologically important metals.[1] Studies in their coordination behaviour would be helpful in understanding the mechanism of their storage and transport in plants and animals. Banerjee *et al.*,[2–5] have synthesised a number of magnesium and calcium complexes and studied their mode of bonding. In the present work we have synthesised and characterised magnesium and calcium complexes of some schiff bases of the general formula $[ML_2]$, where M = Mg(II) or Ca(II), L = deprotonated salicylidene *p*-toluidine (Satd), salicylidene sulphanilic acid (Sasa), vanilidene *p*-toluidine (Vatd) or vanilidene sulphanilic acid (Vasa).

The Schiff bases were prepared by the general method of reaction of calculated quantities of the aldehydes (salicylaldehyde or vaniline) and amines (*p*-toluidine or sulphanilic acid) in methanol. The reaction mixtures were refluxed with constant stirring over a hot plate magnetic stirrer for 1 h. The compounds were cooled, filtered and washed with the solvent and dried at 100°C.

Complexes of Schiff bases were prepared by the general method of interaction of a suspension of magnesium or calcium hydroxide with the Schiff base in 1 : 2 mole ratios in acetone media. The reaction mixtures were refluxed with constant stirring over a hot plate magnetic strirrer for 1 h. The compounds separated were filtered, washed with the solvent and dried at 100°C.

The complexes have been found to be stable when stored under dry conditions. The colour, melting/decomposition temperatures and analytical results of the complexes are mentioned in Table-1.

Melting/decomposition temperatures of the complexes have been found to be higher than that of the corresponding ligands suggesting the genuinity of the compounds.

Selected infrared bands of the ligands and complexes are recorded in Table-2. In the spectra of salicylidene *p*-toluidine, a medium band appearing at 1640 cm^{-1} may be assigned to $\nu(CH{=}N)$ stretching vibration. This band shows down at 1620 cm^{-1} in the spectra of magnesium and calcium complexes. This negative shift of $\nu(CH{=}N)$ band suggests its coordination to the metal.

TABLE-1: ANALYTICAL DATA OF Mg(II) AND Ca(II) COMPLEXES

Compound colour	m.p/decomp./ temp. (°C)	Mg/Ca	Analysis % Found (calcd.)		
			C	H	N
H. Satd	110 (m)	—	79.81	6.34	6.52
(Deep yellow)		—	(79.60)	(6.16)	(6.95)
[Mg(Satd)$_2$]	180 (d)	5.20	75.18	5.62	6.21
(Deep yellow)		(5.40)	(75.67)	(5.40)	(6.30)
[Ca(Satd)$_2$]	219 (d)	8.23	73.36	5.46	5.81
(Brick red)		(8.69)	(73.04)	(5.21)	(6.08)
H . Sasa	262 (d)	—	56.62	4.16	4.81
(Yellow)		—	(56.31)	(3.97)	(5.05)
[Mg(Sasa)$_2$]	264 (d)	3.92	54.81	3.56	4.34
(Reddish brown)		(4.16)	(54.16)	(3.47)	(4.86)
[Ca(Sasa)$_2$]	270 (d)	6.71	53.67	3.62	4.83
(Light yellow)		(6.75)	(52.70)	(3.37)	(4.72)
H . Vatd	140 (d)	—	74.91	6.83	5.42
(Pale yellow)		—	(74.68)	(6.22)	(5.80)
[Mg(Vatd)$_2$]	190 (d)	4.34	71.81	5.62	5.18
(Brown)		(4.76)	(71.42)	(5.55)	(5.55)
[Ca(Vatd)$_2$]	210 (d)	7.45	69.81	5.56	5.16
(Black)		(7.69)	(69.23)	(5.38)	(5.38)
H. Vasa	256 (d)	—	54.98	4.62	4.24
(Yellow)		—	(54.72)	(4.23)	(4.56)
[Mg(Vasa)$_2$]	259 (d)	3.51	52.63	3.92	4.15
(Pale yellow)		(3.77)	(52.83)	(3.77)	(4.40)
[Ca(Vasa)$_2$]	265 (d)	5.92	51.86	3.98	4.16
(Brownish yellow)		(6.13)	(51.53)	(3.68)	(4.29)

m—melted, d—decomposed

TABLE-2: SELECTED IR BANDS (cm^{-1}) OF Mg(II) AND Ca(II) COMPLEXES

Compound	ν(CH=N)	ν(OCH$_3$)	ν(C—O)
H. Satd	1640		
[Mg(Satd)$_2$]	1620		
[Ca(Satd)$_2$]	1620		
H. Sasa	1640		
[Mg(Sasa)$_2$]	1615		
[Ca(Sasa)$_2$]	1620		
H. Vatd	1620	1030	1280
[Mg(Vatd)$_2$]	1620	1020	1290
[Ca(Vatd)$_2$]	1620 (br)	1020	1300(br)
H. Vasa	1660	1020	1180
[Mg(Vasa)$_2$]	1660	1005	1170
[Ca(Vasa)$_2$]	1660	1005	1170

br—broad

In the spectra of salicylidene sulphanilic acid, the ν(CH=N), once again, appears at 1640 cm^{-1}. This band shows down at *ca.* 1620 cm^{-1} in the complexes suggesting the involvement of azomethine group in coordination. The —OH group, *ortho* to the CH=N, most likely gets deprotonated during complexation. It is not possible to pinpoint from the spectra because the ligand has two—OH groups, one phenolic—OH and the other sulphonic acid—OH. Spectra of ligand and complexes both contain ν(OH) bands, SO_3H group is not suitably oriented to the CH=N group so as to deprotonate and form chelate ring; as such the OH bands in complexes might be due to sulphonic acid—OH group.

In case of vanilidene *p*-toluidine the ν(CH=N) band has been spotted at 1620 cm^{-1}. This band mostly remains undisturbed in the spectra of its magnesium and calcium complexes suggesting that the CH=N group does not participate in coordination to the metal. A reason for this may be its unavailability in suitable stereochemical orientation to the other groups. A medium band at 1030 cm^{-1} (in the ligand) may be assigned to $\nu(OCH_3)$. This shifts down by 10 cm^{-1} in complexes suggesting coordination through the $—OCH_3$ group. The ν(C—O) at 1280 cm^{-1} in the ligand has been found to show up at *ca.* 1300 cm^{-1} in the complexes.

In case of vanilidene sulphanilic acid, the ν(CH=N) appears at 1660 cm^{-1}, which remains unaffected upon complexation suggesting its non-participation in coordination to the metal. The $\nu(OCH_3)$ band, spotted at 1020 cm^{-1} in the ligand, shifts down to *ca.* 1005 cm^{-1} in the complexes, suggesting coordination of OCH_3 group to the metal. The ν(C—O) band at 1180 cm^{-1} also shifts down by about 10 cm^{-1} upon complexation. The phenolic OH, which is *ortho* to the $—OCH_3$, most likely gets deprotonated to bind to the metal as it would help chelate formation.

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