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Magnesium(II) and Calcium(II) Complexes of Some Azo Compounds

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Magnesium(II) and calcium(II) complexes of some azo compounds, *viz.*, phenyl azo-2-naphthol, *p*-methyl phenyl azo-2-naphthol, *o*-carboxy phenyl azo-2-naphthol or *o*-nitro phenyl azo-2-naphthol have been synthesised and characterised. The general formula of the complexes has been found to be $[ML_2]$, where M = Mg or Ca and HL = azo compound.

INTRODUCTION

Azo complexes of transition metal ions have been extensively studied[1, 2] with a view to trace their role in colour lakes in mordant dyeing. Azo ligands have also been used as indicators in complexometric titrations. A number of ligands containing the azo (—N═N—) group have been used[3, 4] as complexones. Azo complexes of non-transition metals, too, have been recently receiving attention. Banerjee *et al.*[5–7] have recently prepared and studied a number of mixed ligand azo complexes of alkali metals. In the present work, we have synthesised and characterised some azo complexes of magnesium and calcium of general formula ML_2, where M = Mg or Ca and

L = deprotonated phenyl azo-2-naphthol (Phan),

p-methyl phenyl azo-2-naphthol (CH_3-Phan),

o-carboxy phenyl azo-2-naphthol (COOH-Phan),

or *o*-nitro phenyl-azo-2-naphthol (NO_2-Phan).

EXPERIMENTAL

The azo compounds were prepared by the general method of diazotisation of calculated quantities of corresponding amine in 8 mL conc. HCl and 8 mL water, with an aqueous solution of 2 g of sodium nitrite at 0–5°C. Alkaline solutions of 3.9 g of β-naphthol were coupled with the diazotised solutions. The dyes separated were filtered, washed with water and dried.

The azo complexes were prepared by the general method of interaction of suspension of Mg/Ca acetates with the azo ligands in 1 : 2 mole ratios in acetone media. The reaction mixtures were refluxed with constant stirring on a hot plate magnetic stirrer for 1 h. The compounds separated were then filtered, washed with a little acetone and dried at 100°C in an air oven.

RESULTS AND DISCUSSION

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

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES OF COMPOUNDS

Compound	Colour	Melting/ Decomposition Temp. (°C)	Analysis %, found/(calcd)			
			Mg/Ca	C	H	N
H·Phan	Deep red	125(m)	— —	78.22 (77.41)	4.91 (4.83)	11.18 (11.29)
[$Mg(Phan)_2$]	Red	225(m)	4.52 (4.63)	74.61 (74.13)	4.33 (4.24)	11.21 (10.81)
[$Ca(Phan)_2$]	Red	260(d)	7.24 (7.49)	72.32 (71.91)	4.08 (4.11)	9.61 (10.48)
H·(CH_3-Phan)	Deep red	140(m)	— —	73.75 (74.04)	5.54 (5.34)	10.13 (10.72)
[$Mg(CH_3\text{-}Phan)_2$]	Red	230(d)	4.18 (4.39)	74.22 (74.72)	4.98 (4.76)	10.08 (10.25)
[$Ca(CH_3\text{-}Phan)_2$]	Red	250(d)	6.89 (7.11)	71.92 (72.58)	4.82 (4.62)	9.45 (9.96)
H·(COOH-Phan)	Deep red	260(m&d)	— —	69.44 (69.86)	4.23 (4.10)	10.12 (9.59)
[$Mg(COOH\text{-}Phan)_2$]	Deep red	300	3.68 (3.96)	67.11 (67.32)	3.42 (3.63)	9.46 (9.24)
[$Ca(COOH\text{-}Phan)_2$]	Maroon	300	6.26 (6.43)	65.18 (65.59)	3.61 (3.53)	9.08 (9.00)
H·(NO_2-Phan)	Reddish yellow	230(m)	— —	65.82 (65.52)	3.81 (3.76)	14.17 (14.33)
[$Mg(NO_2\text{-}Phan)_2$]	Reddish yellow	265(d)	3.69 (3.94)	63.32 (63.15)	3.47 (3.28)	15.91 (15.79)
[$Ca(NO_2\text{-}Phan)_2$]	Reddish yellow	300	6.36 (6.41)	61.72 (61.53)	3.68 (3.20)	14.85 (15.38)

Melting/decomposition of the complexes has been found to be higher than the corresponding azo ligands, suggesting that the complexes are genuine compounds and not the mixtures of reactants.

Analytical results of 1:2 mole ratio between metal and ligand suggest the following scheme of reaction:

$$[M(OAc)_2] + 2HL \rightarrow [ML_2] + 2HOAc$$

where HOAc = acetic acid and HL = azo ligand.

Apart from M—O bonding, all the azo ligands that we have studied have —N=N— and other suitable stereochemically available donor groups (in some cases) to form chelate rings by additional metal-ligand bonding.

Infrared Studies

Selected infrared bands of ligands and complexes are recorded in Table-2. In the spectra of H·Phan and H·(CH_3-Phan) weak bands at 1540 cm^{-1} may be assigned to —N=N— stretching vibration. In the spectra of complexes this band splits into two and shows down at *ca.* 1530 (as a double headed peak) and *ca.* 1515 cm^{-1}, suggesting a weak coordination of —N=N— group to the alkaline earth metals.

TABLE-2
KEY IR BANDS (cm^{-1}) OF METAL COMPLEXES OF AZO LIGANDS

Compound	ν(N = N)	ν(OH)	$\nu_{asym}(NO_2)$	ν(C = O)	$\nu_{asym}(COO^-)$
H-Phan	1540	2720	—	—	—
		2340	—	—	—
[Mg(Phan)$_2$]	1530	—	—	—	—
	1515	—	—	—	—
[Ca(Phan)$_2$]	1530	—	—	—	—
	1515	—	—	—	—
H·(CH_3-Phan)	1540	3170	—	—	—
[Mg(CH_3-Phan)$_2$]	1530	—	—	—	—
	1515	—	—	—	—
[Ca(CH_3-Phan)$_2$]	1530	—	—	—	—
	1515	—	—	—	—
H·(COOH-Phan)	1515	3400	—	1710(m)	—
[Mg(COOH-Phan)$_2$]	1560	3380	—	1710(w)	1585
	1535	3160	—		
[Ca(COOH-Phan)$_2$]	1550	3380	—	1710(w)	1585
	1535	3160	—		
H·(NO_2-Phan)	1555	3340	1570	—	—
		3160			
		2400			
[Mg(NO_2-Phan)$_2$]	1550	—	1565	—	—
	1535	—			
[Ca(NO_2-Phan)$_2$]	1550	—	1565	—	—
	1535	—			

The ν(OH) does not appear at its usual position in the spectra of H-phan and H·(CH_3-Phan). However, it shows as two broad humps at 2720 and 2340 cm^{-1} in case of H·Phan and as a broad weak band at *ca.* 3170 cm^{-1} in case of H·(CH_3-Phan). The low position of ν(OH) may be due to the involvement of OH in hydrogen bonding. In the spectra of complexes the νOH bands disappear suggesting deprotonation of phenolic OH during complexation.

In the spectra of COOH·Phan a weak band at 1555 cm^{-1} may be assigned to ν(N=N) vibration. In the spectra of magnesium and calcium complexes of H·(COOH-Phan) this ν(N=N) band splits into two and shows down at 1550 and

1535 cm^{-1} in case of calcium complex, and at 1560 (with a shoulder at 1555) and 1535 cm^{-1} in case of magnesium complex, suggesting coordination through tne —N=N—.

The ν(C=O) of COOH group shows at 1710 cm^{-1} as a medium and sharp band in H·(COOH-Phan). In complexes, the ν(C=O) appears undisturibed but as a weak band at 1710 cm^{-1}. The indicates that C=O does not coordinate with the metal. However, appearance of sharp band at 1585 cm^{-1} in the spectra of complexes, which may be assigned to ν_{asym} (COO^-), indicates that COOH group deprotonated and links to the metal during coordination. On similar grounds such conclusions of —COOH deprotonation and its linkage to the metal have also been reported by earlier workers.[8, 9]

The ligand H·(COOH-Phan) contains two types of OH groups, *viz.*, OH of COOH and phenolic OH. A high order of hydrogen bonding in the molecule is also likely. The ν(OH) shows as a broad band of medium intensity at *ca.* 3400 cm^{-1} in the spectra of H·(COOH-Phan). In the spectra of complexes, this ν(OH) band decreases in its broadness and appears as two bands at *ca.* 3380 and *ca.* 3160 cm^{-1}. This split of ν(OH), most likely, suggests that the phenolic OH coordinates with the metal; all the more so because COOH group deprotonates during complexation.

Spectra of H (NO_2-Phan) shows a weak band at 1555 cm^{-1}. This may be assigned to —N=N— stretching vibration. In the spectra of magnesium and calcium complexes of H(NO_2-Phan), the 1555 cm^{-1} band splits at 1550 and 1535 cm^{-1} further suggests a coordination of —N=N— to the metal in the complexes.

The ν(NO_2) appears as a medium band at 1570 cm^{-1} in the spectra of H(NO_2-Phan). In case of complexes, this band shifts to lower frequency at *ca.* 1565 cm^{-1} suggesting a poor coordination of NO_2 group[7–10].

ν(OH) in the H·(NO_2-Phan) shows as weak and broad bands at 3340, 3160 and 2400 cm^{-1} indicating association of OH group in hydrogen bonding. In the spectra of complexes, however, these bands disappear, indicating deprotonation of phenolic OH group during complexation.

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