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Alkaline-Earth Metal Complexes: Mixed Ligand Complexes of Alkaline-Earth Metal Salts of Some Organic Acids with Bis(8-hydroxy-5-quinolyl)-methane

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Eight mixed ligand complexes of alkaline-earth metal salts of organic acids like 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP) and salicylaldehyde (Sal.H) with bis(8-hydroxy-5-quinolyl)-methane having the general formula $[ML_2]_2H_2L'$, where M = Mg or Ca; L = deprotonated organic acids and H_2L' = bis(8-hydroxy-5-quinolyl)-methane, have been synthesized and characterized by elemental analysis and FTIR-spectral studies.

Key words: Mixed complexes, Alkaline-earth metals, Bis(8-hydroxy-5-quinolyl)-methane.

INTRODUCTION

In continuation to our previous work[1–4] we have synthesized and characterized some more complexes of alkaline-earth metal salts of some organic acids with bis(8-hydroxy-5-quinolyl)-methane. This ligand behaves as a bidentate double-faced ligand and has been shown to form stable complexes with a number of transition[5–8] and alkali metals[9–11]. However, it appears from the literature survey that no attempt has yet been made to examine the complexing ability of this ligand with alkaline-earth metal salts of some organic acids like 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP) and salicylaldehyde (Sal.H).

We have synthesized and characterized eight mixed ligand complexes having the general formula $[ML_2]_2H_2L'$, where M = Mg, Ca; L = deprotonated organic acids, *i.e.*, 1-nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP) and salicylaldehyde (Sal.H) etc. and H_2L' = bis(8-hydroxy-5-quinolyl)-methane.

EXPERIMENTAL

The ligand bis(8-hydroxy-5-quinolyl)-methane was prepared by the method described in literature[5]. 1-Nitroso-2-naphthol (1N2N), *o*-nitrophenol (ONP), 2,4-dinitrophenol (DNP) and salicylaldehyde (Sal.H) of AnalaR grade were used.

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Alkaline-earth metal salts of the organic acids were prepared by the method described earlier[4].

Preparation of Complexes: Alkaline-earth metal salt and ligand were taken in 2 : 1 molar ratio. At first the ligand (slight excess than the calculated amount) was dissolved in N-N-dimethyl formamide in a conical flask. A clear solution was obtained. Now alkaline-earth metal salt of organic acid was added and refluxed with constant stirring for about 4–6 h. In the course of refluxion appreciable change in colour of the suspension took place which finally attained a particular colour. The content was then cooled, filtered, washed with absolute ethanol, dried in electric oven at 100°C, collected in a sample tube and finally kept in a desiccator over anhydrous $CaCl_2$.

RESULTS AND DISCUSSION

The physical properties and analytical data of the ligand bis(8-hydroxy-5-quinolyl)-methane and its newly prepared mixed ligand complexes are listed in Table-1. All these complexes are coloured and stable in dry condition, *e.g.*, over anhydrous calcium chloride in a desiccator for reasonably long period of time. They are highly resistant to temperature and all of them show no change up to 300°C. This indicates their greater thermal stability.

TABLE-1

ANALYTICAL DATA OF COMPLEXES OF ALKALINE-EARTH METAL SALTS OF SOME ORGANIC ACIDS WITH BIS(8-HYDROXY-5-QUINOLYL)-METHANE

Compound (Colour)	m.p./d.t./t.t. temp. (°C)	% analysis, found (calcd.)			
		C	H	N	M
Bis8HQ (white)	280 m	75.70 (75.50)	4.60 (4.64)	9.25 (9.26)	—
$[Mg(1N2N)_2]_2$.Bis8HQ (deep brown)	> 300	65.52 (68.21)	3.51 (3.66)	7.95 (8.09)	4.40 (4.62)
$[Ca(1N2N)_2]_2$.Bis8HQ (blackish green)	> 300	63.25 (66.17)	3.45 (3.55)	7.00 (7.85)	7.22 (7.48)
$[Mg(ONP)_2]_2$.Bis8HQ (greyish green)	> 300	54.52 (57.21)	3.30 (3.33)	9.00 (9.31)	5.00 (5.32)
$[Ca(ONP)_2]_2$.Bis8HQ (deep green)	> 300	52.74 (55.25)	3.15 (3.21)	8.46 (8.99)	8.22 (8.57)
$[Mg(DNP)_2]_2$.Bis8HQ (greyish green)	> 300	45.12 (47.69)	2.32 (2.40)	12.24 (12.94)	4.25 (4.44)
$[Ca(DNP)_2]_2$.Bis8HQ (green)	> 300	43.75 (46.32)	2.28 (2.33)	12.02 (12.56)	7.00 (7.18)
$[Mg(Sal.H)_2]_2$.Bis8HQ (blackish green)	> 300	62.24 (65.13)	3.82 (3.93)	3.20 (3.23)	8.98 (9.24)
$[Ca(Sal.H)_2]_2$.Bis8HQ (green)	> 300	56.25 (58.69)	3.44 (3.54)	2.78 (2.91)	17.95 (18.21)

These complexes are either insoluble or very less soluble in solvents like benzene, absolute alcohol, chloroform, nitrobenzene, N-methyl-2-pyrolidone, dimethyl sulphoxide (DMSO), N-N-dimethyl formamide (DMF) in cold condition but are soluble in hot N,N-dimethyl formamide.

Spectral Studies: FTIR spectra of the title ligand and the newly synthesized mixed ligand complexes of the type $[ML_2]_2.H_2L'$ where M = Mg or Ca; L = deprotonated 1-nitroso-2-naphthol, *o*-nitrophenol, 2,4-dinitrophenol and salicylaldehyde and H_2L' = bis(8-hydroxy-5-quinolyl)-methane were recorded in the region 4000–400 cm^{-1} in KBr phase with the help of Testscan Shimadzu FTIR 8000 series spectrophotometer. The pertinent FTIR data for these complexes are recorded in Table-2.

TABLE-2

SELECTED ABSORPTION BANDS (cm^{-1}) OF METAL COMPLEXES

Compound	ν(OH)	ν(C=C)/(C=N)	ν(OH)	ν(C—O)
Bis8HQ	3335 m	1625 sh, 1580 m	1420 s	1120 m
[Mg(1N2N)$_2$]$_2$.Bis8HQ	3336 br	1665 m, 1577 m	1473 m	1090 m
[Ca(1N2N)$_2$]$_2$.Bis8HQ	3368 br	1630 sh, 1577 m	1462 m	1090 w
[Mg(ONP)$_2$]$_2$.Bis8HQ	3395 br	1660 m, 1576 m	1466 m	1090 m
[Ca(ONP)$_2$]$_2$.Bis8HQ	3370 br	1662 m, 1566 m	1462 m	1090 m
[Mg(DNP)$_2$]$_2$.Bis8HQ	3385 br	1661 m, 1574 m	1466 m	1090 s
[Ca(DNP)$_2$]$_2$.Bis8HQ	3393 br	1659 m, —	1458 br	1090 m
[Mg(Sal.H)$_2$]$_2$.Bis8HQ	3367 br	1662 br, 1570 br	1460 br	1090 m
[Ca(Sal.H)$_2$]$_2$.Bis8HQ	3371 br	1770 s, 1661 m	—	1090 m

The absorption bands of principal interest in the FTIR spectra of bis(8-hydroxy-5-quinolyl)-methane are 3335, 1625, 1580, 1420 and 1120 cm^{-1}.

The moderately strong band at 3335 cm^{-1} in the spectrum of bis(8-hydroxy-5-quinolyl)-methane is attributed to the stretching-OH vibration frequency, while the strong band at 1420 cm^{-1} in its spectrum is due to the bending —OH frequency[9–11]. The absorption band at 1625 and 1580 cm^{-1} have been assigned to C=C/C=N group and band at 1120 cm^{-1} and have been assigned to C—O group.

It is evident that the spectrum of the ligand contains a moderately strong band at 3335 cm^{-1}, this band shifted to higher frequency up to 60 cm^{-1} in the newly synthesized mixed ligand complexes indicating that the coordination has taken place through the oxygen atom of the —OH group of the ligand.

The spectra of the ligand also show characteristic absorption of C=C/C=N at 1625 and 1580 cm^{-1}. In the mixed ligand complexes shifting of these bands by 5–40 cm^{-1} towards higher frequency and by 5–15 cm^{-1} towards lower frequency respectively was found. Shifting in this region in the stretching frequency of C=C/C=N suggests the coordination of the ligand with alkaline-earth metal through nitrogen atom of quinoline ring.

The FTIR-spectra of [M(Sal.H)$_2$]$_2$.Bis8HQ (M = Mg or Ca) show a new strong band at 1770 cm^{-1}. The shifting in the bending —OH frequency of 1420 cm^{-1} towards higher frequency up to nearly 55 cm^{-1} indicates the coordination through oxygen atom of —OH group. The lower shift in the C—O band frequency by 30 cm^{-1} in all the mixed ligand complexes is also supporting the coordination of metal through oxygen atom of —OH group.

Structure and Bonding: On the basis of elemental analysis, the molecular formula of the newly synthesized mixed ligand complexes is found to be [ML$_2$]$_2$.HL′ where M = Mg or Ca; L = deprotonated 1N2N, ONP, DNP and Sal.H and HL′ = bis(8-hydroxy-5-quinolyl)-methane.

The FTIR data suggest that the alkaline-earth metal is coordinated with oxygen atom of —OH group and nitrogen atom of the quinoline ring. FTIR also suggests the presence of hydrogen bonding. Probable structure is shown in Fig. 1.

TABLE-2
SELECTED ABSORPTION BANDS OF METAL COMPLEXES (cm^{-1})

Compound	ν(OH)	ν(C=C)/(C=N)	ν(OH)	ν(C—O)
Bis8HQ	3335 m	1625 sh, 1580 m	1420 s	1120 m
[Mg(1N2N)$_2$]$_2$.Bis8HQ	3336 br	1665 m, 1577 m	1473 m	1090 m
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[Ca(ONP)$_2$]$_2$.Bis8HQ	3370 br	1662 m, 1566 m	1462 m	1090 m
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[Mg(Sal.H)$_2$]$_2$.Bis8HQ	3367 br	1662 br, 1570 br	1460 br	1090 m
[Ca(Sal.H)$_2$]$_2$.Bis8HQ	3371 br	1770 s, 1661 m, —	—	1090 m

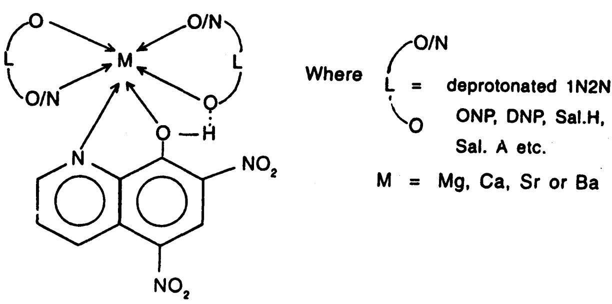

Fig. 1

REFERENCES

1. S.S. Chandra, S.W Imam, A.K. Yadav and S.R. Prasad, *Oriental J. Chem.*, **14**, 413 (1998).
2. D. Prakash and A.K. Yadav, *Asian J. Chem.*, **11**, 1037 (1999).
3. S.S. Chander, A.K. Yadav, S.R. Prasad and S.W Imam, *Vijnana Parishad Anusandhan Patrika*, **43**, 261 (2000).
4. D. Prakash and A.K. Yadav, *Asian J. Chem.*, **13**, 944 (2001).
5. E. Horowitz and T.P. Perros, *J. Inorg. Nucl. Chem.*, **26**, 139 (1964).
6. V.V. Korsak, S.V. Vinogradova and T.M. Babchinister, *Polymer Science (USSR)*, **2**, 344 (1960).
7. D.N. Sen and P. Umapathy, *Indian J. Chem.*, **5**, 209 (1967).
8. R.C. Poller and D.L.B. Toley, *J. Inorg. Nucl. Chem.*, **31**, 2973 (1969).
9. D. Prakash and S.P. Singh, *J. Indian Chem. Soc.*, **58**, 1143 (1981).
10. ———, *J. Indian Chem. Soc.*, **61**, 471 (1984).
11. D. Prakash, A.P. Roy and O.P. Gupta, *Asian J. Chem.*, **6**, 956 (1994).

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