

NOTE

Chelate Polymers of Alkaline-Earth Metals with Bis(8-hydroxy-5-quinolyl)-methane

DHARAM PRAKASH* and ASHOK KUMAR YADAV†

*Department of Chemistry
Patna University, Patna-800 005, India*

Four chelate polymers of alkaline-earth metals with bis(8-hydroxy-5-quinolyl)-methane having the general formula $[ML'_n]$ where M = Mg, Ca, Sr or Ba and L' = deprotonated bis(8-hydroxy-5-quinolyl)-methane, have been synthesized and characterized. Their FTIR spectra suggest the coordination of the alkaline-earth metal through oxygen atom of hydroxy group as well as nitrogen atom of quinoline ring.

In order to understand and unfold the mechanism of transportation and storage of metal cations in animals and plants with the assumption that a knowledge of coordination chemistry of the alkaline-earth metals would facilitate full understanding of the mechanism, our attention has been drawn towards the ligand bis(8-hydroxy-5-quinolyl)-methane. Evidently, this ligand behaves as a bidentate double-faced ligand and has been shown to form stable complexes with a number of transition¹⁻⁴ and alkali metals⁵⁻⁷. However, it appears from the literature survey that no attempt has yet been made to examine its chelating ability with alkaline-earth metals. The present work is an attempt in this direction.

We have synthesized and characterized four chelate polymers of alkaline-earth metals with this ligand having the general formula $[ML'_n]$ where M = Mg, Ca, Sr or Ba and L' = deprotonated bis(8-hydroxy-5-quinolyl)-methane, henceforth designated as bis8HQ or H_2L' .

The ligand bis(8-hydroxy-5-quinolyl)-methane was prepared by the method as described in literature¹.

The chelate polymers were synthesized by taking equimolecular ratio of the alkaline-earth metal hydroxide and the ligand (H_2L') in dimethylformamide with the ligand in slight excess. First the ligand was dissolved in dimethylformamide (DMF). A clear solution was obtained. Now alkaline-earth metal hydroxide was added and refluxed with continuous stirring for about more than 2 h when the precipitate finally attains yellowish green colour. It was filtered, washed with DMF and dried in an electric oven at 80°C and kept in a desiccator over anhydrous $CaCl_2$.

All the four polymers are coloured and stable under dry condition. They are considerably resistant to temperature. They show no change upto 300°C, a temperature more than the melting point of the corresponding ligand, which

†Department of Chemistry, P.Sc. College, Kirtinagar, Madhepura, B.N. Mandal University, Laloonagar, Madhepura-852 113, India.

indicates the greater thermal stability of chelate polymers. The colours, decomposition/transition temperatures and the analytical data of these polymers are listed in Table-1. The polymers are either insoluble or very little soluble in solvents like benzene, carbon tetrachloride, ether, acetone, methanol, absolute alcohol, chloroform, nitrobenzene, N-methyl-2-pyrrolidone, dimethyl-sulphoxide (DMSO) but are soluble in hot N,N-dimethylformamide (DMF).

TABLE-1
ANALYTICAL DATA OF ALKALINE-EARTH METAL COMPLEXES

Compound	Colour	m.p./decomp. temp./trans. temp. (°C)	% Analysis, found/(calcd.)			
			C	H	N	M
Bis 8HQ (H ₂ L')	white	280	75.70 (75.50)	4.60 (4.64)	9.25 (9.26)	— —
[MgL'] _n	yellowish green	> 300	68.12 (70.37)	3.56 (3.70)	8.52 (8.64)	7.00 (7.40)
[CaL'] _n	light green (pista)	> 300	65.21 (67.06)	3.34 (3.53)	7.79 (8.24)	11.04 (11.76)
[SrL'] _n	deep green	> 300	56.89 (58.76)	3.00 (3.09)	6.65 (7.22)	22.25 (22.68)
[BaL'] _n	geeen	> 300	50.69 (52.17)	2.69 (2.75)	6.40 (6.41)	30.27 (31.35)

FTIR measurements of the title ligand and the newly prepared chelate polymers of the type [ML']_n where M = Mg, Ca, Sr or Ba and L' = deprotonated bis(8-hydroxy-5-quinolyl)-methane were recorded in the region 4000–400 cm⁻¹ in KBr phase with the help of FTIR spectrophotometer. Pertinent FTIR data for these compounds are recorded in Table-2.

TABLE-2
KEY IR BANDS (cm⁻¹) OF METAL CHELATE POLYMERS

Compounds	v(—OH)	v(C=C)/(C=N)	v(—OH)	v(C—O)
Bis 8HQ(H ₂ L')	3340 s	1625 sh	1580 m	1420 s 1120 m
[MgL'] _n	3440 br	1660 m	1575 m	1425 m 1090 m
[CaL'] _n	3370 br	1660 w	1575 m	1440 br 1090 m
[SrL'] _n	3440 br	1610 w	1575 m	1460 m 1080 m
[BaL'] _n	3500 br	—	1575 br	1425 br 1090 m

The FTIR spectra of ligand, bis(8-hydroxy-5-quinolyl)-methane, and its coordination compounds with various divalent transition metal have been reported by Horowitz and Perros¹. They observed that these complexes are polymeric in nature. Although qualitatively the peaks of many of the absorption bands in the spectra of these polymers differ somewhat, examination of these spectra indicates that their peak frequencies are actually very similar.

The absorption bands of principal interest in the FTIR spectra of bis(8-hydroxy-5-quinolyl) methane are 3340, 1625, 1580, 1420 and 1120 cm⁻¹.

The moderately strong band at 3340 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 frequency¹. The absorption bands at 1625 cm^{-1} and 1580 cm^{-1} have been assigned to C=C/C=N groups while the absorption band at 1120 cm^{-1} is assigned to C—O group frequency.

It is evident that the spectrum of the ligand contains a moderately strong band at 3340 cm^{-1} ; this band has virtually disappeared or appeared with the shift of 30 to 160 cm^{-1} in the polymers, 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 polymers, shifting by 5 – 35 cm^{-1} 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 shifting in the bending —OH frequency of 1420 cm^{-1} from 5 to 40 cm^{-1} indicates the chelation through oxygen atom of —OH group.

The C—O band frequency shift by 25 – 40 cm^{-1} 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 chelate polymers of alkaline-earth metals with bis(8-hydroxy-5-quinolyl)-methane is found to be $[\text{ML}']_n$, where $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}$ or Ba ; $\text{L}' =$ deprotonated bis(8-hydroxy-5-quinolyl)-methane. The FTIR-data suggests that the alkaline-earth metal is bonded to oxygen atom of hydroxy group by replacing the hydrogen atom and also to the nitrogen atom of the quinoline ring. Probable structure of the chelate polymer is shown in Fig. 1.

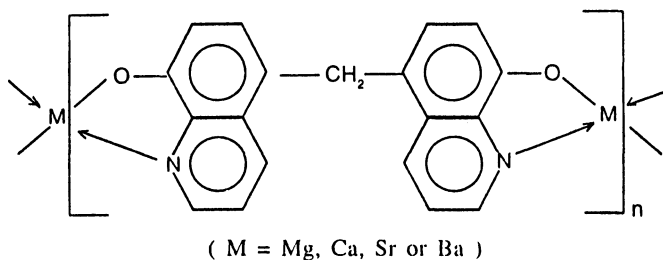


Fig. 1

REFERENCES

1. E. Horowitz and T.P. Perros, *J. Inorg. Nucl. Chem.*, **26**, 139 (1964).
2. V.V. Korsak, S.V. Vinogradova and T.M. Babchinister, *Polymer Science (USSR)*, **2**, 344 (1960).
3. D.N. Sen and P. Umapathy, *Indian J. Chem.*, **5**, 209 (1967).
4. R.C. Poller and D.L.B. Toley, *J. Inorg. Nucl. Chem.*, **31**, 2973 (1969).
5. D. Prakash and S.P. Singh, *J. Indian Chem. Soc.*, **58**, 1143 (1981).
6. _____, *J. Indian Chem. Soc.*, **61**, 471 (1984).
7. D. Prakash, A.P. Roy and O.P. Gupta, *Asian J. Chem.*, **6**, 956 (1994).

(Received: 9 November 1998; Accepted: 1 June 1999)

AJC-1740