

Studies in Coordination Polymers of Bis(8-hydroxy-5-quinolyl)methane with Group III Metals

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Bis(8-hydroxy-5-quinolyl)methane forms coordination polymers with Group III metals. These coordination polymers have been characterized by their elemental analyses, IR and reflectance spectral data, conductance and DTA measurements.

Coordination polymers of bis(8-hydroxy-5-quinolyl)methane (abbreviated as BHQM) have been reported earlier^{1,2}. However, coordination polymers of BHQM with Group III metals have not been studied in detail. The synthesis and characterization of coordination polymers of BHQM with Al(III), Ga(III), In(III), Tl(III), Sc(III), Y(III) and La(III) form the subject of this note.

The ligand was prepared according to the literature method¹⁻³ and recrystallized from dimethylformamide (DMF); m.p. 283° (lit. m.p. 283°).

The coordination polymers were prepared by reacting equimolar solutions of metal nitrate/chloride/oxinate/acetylacetonate and BHQM in DMF. In the case of Tl(III), DMF-ethanol (3:2, v/v) was used as a solvent. Metal nitrates were used for the coordination polymers of Al(III) and Y(III) and metal chloride for Sc(III). Other coordination polymers were prepared by the reaction of appropriate metal oxinates/acetylacetonates (0.005 mol) and BHQM (0.005 mol). In synthesizing Al(III)-BHQM, Al(III)-acac-BHQM, Al(III)-oxine-BHQM, Y(III) and La(III)-acac-BHQM polymers, the solutions of the reactants were mixed and refluxed while in the case of Ga(III)-oxine-BHQM, In(III)-oxine-BHQM, Tl(III)-oxine-BHQM and Sc(III)-BHQM the solutions of the reactants were mixed and then digested on a water-bath. Sc(III)-acac-BHQM polymer was synthesized by first refluxing and then digesting the mixture on a water-bath. All the coordination polymers are coloured, amorphous solids (Table 1), insoluble in common organic solvents. Analytical data of BHQM polymers are given in Table 1. The unsatisfactory nitrogen analyses may be due to incomplete digestion even when heated for a long time.

The IR spectra of polymers exhibited a broad band around 3500 cm⁻¹, assignable to νOH of water of

Table 1—Characterization Data of Coordination Polymers of BHQM(L) with Group III Metal Ions

Sr. No.	Polymer	Found (Calc.) %				Decomp. temp. (°C)	Specific conductance (mhos)	Colour
		C	H	N	M			
1.	{[Al-L-NO ₃ (H ₂ O)].4H ₂ O} _n	46.10 (47.61)	4.07 (4.59)	8.69 (8.77)	5.84 (5.61)	280	7.4 × 10 ⁻⁷	Dark green
2.	[Al ₂ L ₃ (acac) ₂].6H ₂ O	61.55 (63.77)	4.66 (6.07)	4.77 (6.66)	4.86 (4.26)	280	1.6 × 10 ⁻⁸	Bright yellow
3.	{[Al-L-oxine].3H ₂ O} _n	62.5 (64.01)	4.94 (4.57)	6.93 (8.00)	5.23 (5.12)	260	2.4 × 10 ⁻⁸	-Do-
4.	{[Ga-L-oxine].3H ₂ O} _n	57.40 (59.27)	4.68 (4.22)	5.51 (7.39)	11.63 (12.27)	255	1.6 × 10 ⁻⁹	-Do-
5.	{[In-L-oxine].3H ₂ O} _n	55.05 (54.81)	4.22 (3.91)	6.39 (6.85)	17.70 (18.47)	255	1.3 × 10 ⁻⁹	-Do-
6.	†[Tl-L-oxine] _n	50.10 (51.82)	2.90 (2.77)	5.85 (6.47)	—	230	5.0 × 10 ⁻⁸	Yellow brown
7.	{[Sc-L-Cl(H ₂ O)].3H ₂ O} _n	50.55 (50.44)	4.60 (4.41)	4.71 (4.92)	9.48 (9.93)	240	3.1 × 10 ⁻⁷	Yellow
8.	Sc ₂ L ₃ (acac) ₂	66.60 (67.30)	4.90 (4.54)	6.68 (7.06)	6.27 (7.56)	235	4.4 × 10 ⁻⁷	-Do-
9.	[Y ₂ L ₃ (NO ₃) ₂ (H ₂ O) ₂].8H ₂ O	49.10 (49.45)	4.71 (4.19)	6.50 (8.09)	12.48 (12.85)	270	1.9 × 10 ⁻⁷	Dirty green
10.	{[Y-L-acac].3H ₂ O} _n	52.30 (53.15)	4.38 (4.61)	4.31 (5.16)	15.12 (16.14)	265	1.3 × 10 ⁻⁸	Yellow
11.	{[La-L-acac].3H ₂ O} _n	53.20 (54.54)	3.47 (4.73)	3.87 (5.30)	24.56 (23.45)	235	1.7 × 10 ⁻⁸	-Do-

†Satisfactory results could not be obtained for (Tl-L-oxine)_n metal content.

crystallization. In a few of these polymers this band was absent. The free ligand band at 3400 cm^{-1} due to νOH (phenolic OH) disappeared in the coordination polymers indicating coordination to the metal ion after deprotonation of phenolic OH. In the case of polymers prepared using metal acetylacetonates, the $\nu\text{C}=\text{O}$ of free acetylacetonate at 1709 cm^{-1} shifted to lower wavenumber and appeared in the region $1650\text{--}1575\text{ cm}^{-1}$, suggesting coordination of acetylacetonate also to the central metal ion.

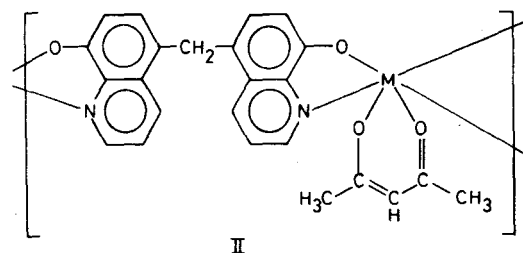
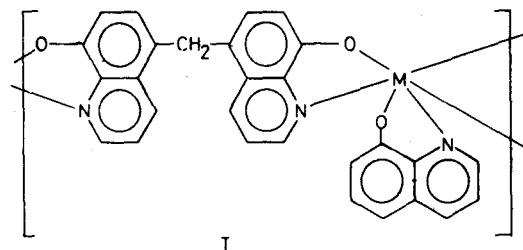
The free ligands BHQM and oxine exhibit IR absorptions around 1580 and 1577 cm^{-1} , respectively assignable to $\nu\text{C}=\text{N}$. These bands appear in the region $1575\text{--}1565\text{ cm}^{-1}$ in the coordination polymers indicating bonding through lone pair of ring nitrogen atoms. BHQM also shows a strong band around 1420 cm^{-1} due to OH deformation which appears as a less intense band in all polymers in the region $1400\text{--}1410\text{ cm}^{-1}$. Such a shift in OH-deformation was also observed by earlier workers^{1,4}. Moreover, in the coordination polymers if the chain ends with a bis-ligand the complete disappearance of this band is also not possible. The band around 1100 cm^{-1} in the coordination polymers has been assigned to $\nu\text{C}-\text{O}$ (phenolic).

It is difficult to show the presence of anions in the infrared spectra as the spectra obtained are of mixed nature.

The reflectance spectrum of BHQM exhibits a band at 335 nm , which appears at $390\text{--}440\text{ nm}$ in the spectra of the coordination polymers. This may be due to charge transfer. All the coordination polymers of BHQM are diamagnetic.

Decomposition temperatures of BHQM polymers reported in Table 1 are on the basis of DTA. The exothermic peak being very large, temperature corresponding to the starting point of exothermic peak is taken as decomposition temperature. It is observed that metal-BHQM polymers are more stable than the metal-acac-BHQM polymers. In the case of Al(III) no such stability difference is noted. However, in the case of metal-oxine-BHQM coordination polymers the thermal stability decreases from Al(III) to Ti(III) . Ga(III) -oxine-BHQM and In(III) -oxine-BHQM have, however, the same thermal stability.

Amongst the Sc(III) , Y(III) and La(III) -acac-BHQM polymers, Y(III) -acac-BHQM polymer is thermally



the most stable. Sc(III) -acac-BHQM polymer appears to be more conducting.

Conductances of BHQM polymers show that in Al(III) , Ga(III) and In(III) -oxine-BHQM series, the electrical resistivity increases from Al(III) to In(III) analogous to the increase in their atomic number.

The unambiguous characterization of the compounds prepared in the present investigations is no doubt difficult because of their insolubility and intractability. Their assignment as polymers from steric considerations and on the basis of elemental analyses is, therefore, tentative. The following tentative structures (I and II) can be proposed on the basis of infrared spectral data.

While proposing these structures, not only the complexing behaviour of central metal ion but several other factors like the nature of primary ligand and bis-ligands, ionic size of the metal, the subsequent replacement of primary ligand by bis-ligands and its role in replacing the ligands of the same nature and different in nature have been considered.

References

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