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Studies on Complexes of 1,2-Bis-(8-quinoxy) Ethane with Some Bivalent Metal Ions

S. ANNAPOORANI and V.R. PARAMESWARAN*
Department of Chemsitry, Annamalai University
Annamalainagar-608 002, India

1,2-Bis-(8-quinoxy) ethane was prepared by refluxing 8-hydroxy quinoline with 1,2-dibromoethane for 22 h. Some complexes were synthesised using this ligand with some bivalent metal ions. The complexes were characterised by elemental analysis, infrared, UV-visible spectra and conductivity measurements.

INTRODUCTION

Complexes of 8-hydroxy quinoline, which is a bidentate ligand are well known in analytical chemistry. Its coordination was reviewed by Phillips[1] while Schulma and Dwyer[2] reviewed their microbiological activity. Their use in analytical chemistry for extraction and colorimetric estimation of metal ions was discussed by Stray[3]. An unusual bridged bonding made by oxide has been reported. In the present work synthesis and characterisation of some complexes with the above ligand are discussed.

EXPERIMENTAL

Preparation of 1,2-*bis*-(8-*quinoxy*) *ethane*[4]: Mixture of 8-hydroxy quinoline and potassium hydroxide (0.2 mole) in the molar ratio 1 : 1 was dissolved in ethanol. 1,2-Dibromoethane (0.095 mole) was added to the clear solution and then refluxed for 22 h on a water bath. The reaction mixture was cooled and then poured into cold water. Dark brown solid was separated, which was filtered and washed with distilled water. It was recystallised from ethanol. Yield 98%; m.p. 96°C.

Preparation of complexes: Metal ions (Co^{2+}, Mn^{2+} and Zn^{2+}) (2 mmol) and the ligand (2 mmol) in 100 mL of ethanol was refluxed on a water bath for 10 h. The contents were cooled and then poured into distilled water. The separated solid was filtered and washed with hot water and ethanol.

The elemental analysis was done using Heraeus-CHN Rapid Analyser at IIT Chennai. Molar conductances were determined in DMF. IR spectra were recorded on JASCO-IR-700 IR spectrophotometer. UV spectra were recorded on JASCD-UVIDEC-340 double beam spectrophotometer.

RESULTS AND DISCUSSION

The ligand 1,2-bis-(8-quinoxy) ethane contains two nitrogen donor atoms and two oxygen donor atoms. It is assumed that the coordination to the metal can take place through these donor atoms. It may act as either a bidentate or a tetradentate ligand.

If we assume that the ligand is to be bidentate, then three structures (Figures I, II and III) are assumed for the complex. In structure I, the coordination of the ligand to the metal takes place through two nitrogen atoms. In structure II, the coordination takes place through two oxygen atoms and in structure III, the coordination occurs through one nitrogen and one oxygen atoms. The structure I in which the coordination occurs through two nitrogen atoms is ruled out based on the fact that the chelae is expected to be a ten membered ring which is less stable than five or six membered ring. Fig. IV is also proposed for the structure of the complex in which the ligand is a tetradentate one. In the tetradentate structure, two nitrogen atoms and two oxygen atoms are involved in coordination to the metals.

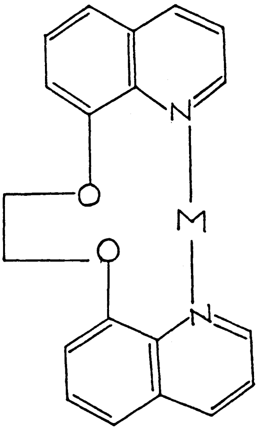

Fig. I

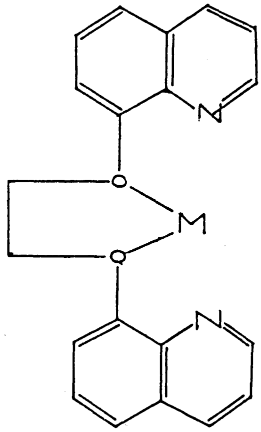

Fig. II

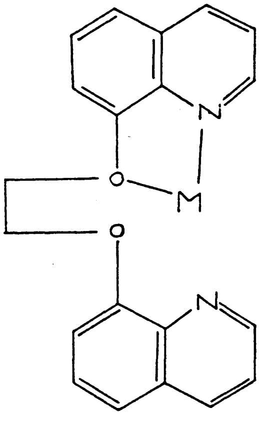

Fig. III

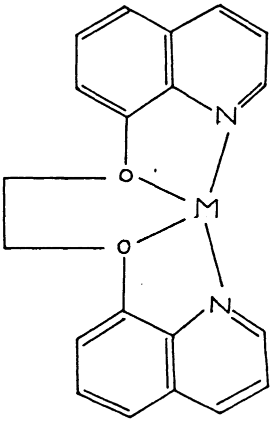

Fig. IV

The analytical data of the complexes are given in Table-1 and correspond to 1 : 1 metal : ligand stoichiometry. The observed conductance values in DMF are very low (Table-2). So the complexes are considered as non-electrolytes[5–7]

TABLE-1
ANALYTICAL DATA OF THE COMPLEXES

Complexes	m.f.	m.w.	% Analysis; Found (Calcd.)		
			C	H	N
Co(BQE)	$C_{20}H_{16}N_2O_2Co$	374.93	63.98 (64.01)	4.18 (4.26)	7.53 (7.47)
Mn(BQE)	$C_{20}H_{16}N_2O_2Mn$	370.94	64.95 (64.70)	4.29 (4.31)	7.64 (7.55)
Zn(BQE)	$C_{20}H_{16}N_2O_2Zn$	381.37	62.62 (62.93)	4.26 (4.19)	7.23 (7.34)

BQE = 1,2-bis-(8-quinoxy)ethane.

TABLE-2
CONDUCTANCE DATA FOR THE COMPLEXES OF 1,2-bis-(8-quinoxy)ethane

Complexes	Solvent	Conductance (Λ_m) ohm^{-1} cm^2 mol^{-1}	Remarks
Co(BQE)	DMF	27.55	Non-electrolyte
Mn(BQE)	DMF	11.04	Non-electrolyte
Zn(BQE)	DMF	19.16	Non-electrolyte

The IR spectra exhibit band at 1460 cm^{-1} corresponding to ν(C═C) stretching frequency. There is also a band at 1019 cm^{-1} which corresponds to ν(C—N) stretching frequency which was shifted in complexes with respect to the ligand. The band due to ν(C═C) was obtained near 1580 cm^{-1} instead of one around 1607 cm^{-1} in both ligand and complexes. The absence of the band in the 3500 cm^{-1} region indicates that the —OH group of the 8-hydroxyquinoline ring was involved in condensation during the formation of the ligand. In the spectrum of the complexes, it was found that the bands assigned to ν(C═N) and ν(C—O) stretching frequencies are shifted to lower frequencies. This shift is an indicative of the involvement of the (C═N) and (C—O) group in binding to the metal. The bands near 1490 cm^{-1} are assigned to ν(C═C).

The IR spectral data (Table-3) indicate the presence of ν(M—N) and ν(M—O) bond formation near 400 cm^{-1} in complexes[8, 9]. From this, structure II of the complex was ruled out. If structure III is proposed for the complexes, then two types of (C—O) stretching frequencies, one complexed with the metal and the other for the uncomplexed C—O—C are to be expected. But the IR spectrum of the complex gives only one C—O stretching frequency. This indicates that both the oxygen atoms are involved in coordination to metal. Moreover, it is also expected that two types of (C═N) stretching frequencies should appear as for (C—O group). But the IR spectrum gives only one ν(C═N) stretching frequency. All of these indicate that both nitrogen atoms and oxygen atoms are involved in coordination. Therefore the structure III is also ruled out and structue IV is proposed for the complexes.

TABLE-3
INFRARED SPECTRAL DATA (cm^{-1}) FOR 1,2-BIS-(8-QUINOXY)ETHANE AND THEIR COMPLEXES

Ligand/ Complex	ν(C=C)	ν(C=N)	ν(C—O)	ν(C—H)	ν(C—N)	ν(M—N)	ν(M—O)
BQE	1460	1578	—	2922	1019	—	—
Co(BQE)	1498 1458	1572	1110 1281	2926 1381 1320	—	—	531
Mn(BQE)	1495 1459	1575	1108 1272	2924 1381 1318	1020	465 407	532
Zn(BQE)	1495 1459	1576	1107 1271	2924 1382 1324	1019	462 410	528

In the electronic spectra, the band above 450 nm in the ligand is shifted to 415 nm in the complex and there is no appreciable change in the band at 255 nm of the ligand. This indicates that the complex formation has taken place.

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