

Transition metal polymeric chelates: Spectral, magnetic, thermal behaviour of polymeric chelates of poly(resacetophenone diyl ethylene)s with Ni(II), Cu(II), Mn(II), Zn(II) and Co(II)

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Abstract. Polymeric chelates of the type $[ML_2]_n$, where M = Ni(II), Cu(II), Zn(II) or Co(II), L = poly(resacetophenone diyl ethylene)s, and n = degree of polymerization, have been synthesized. Their structures have been elucidated on the basis of analytical, magnetic, electronic and IR spectral studies. Electronic spectra in conjunction with magnetic moments are in accord with an octahedral environment around the central metal ion in all polymeric chelates except Cu(II) and Zn(II) polymeric chelates which have been shown to possess square planar and tetrahedral geometries, respectively. IR spectral studies further suggest that the metal ions are coordinated through the oxygens of the carbonyl and the phenolic hydroxyl groups. All the chelates are paramagnetic except Zn(II), which is found to be diamagnetic.

Keywords. Resacetophenone; ethylene glycol; polyphosphoric acid; resacetophenone-ethylene glycol resin.

1. Introduction

Coordination polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials from both polymeric and monomeric ligands. It was only a few decades ago that polychelates derived from polymeric ligands and transition metal ions attracted the attention of many investigators (Flaska and Barnard 1967). An efficient method for synthesizing such polymers consists of the introduction of the inorganic component either chemically bound or as a filler into the polymer. Depending on their structures, metal chelates of polymers can be used as catalysts (Davydov *et al* 1968), high temperature and flame resistance fibres (Van Krevelen 1972), semiconductors (Patel and Patil 1983), ion-exchanging resins (Patel and Patel 1981) and for agricultural purposes (Dentini *et al* 1974). Resacetophenone has been condensed with formaldehyde in the presence of acidic catalyst (Parmer *et al* 1981) as well as basic catalyst (Pennington and Williams 1959) to obtain polymeric ligand. No previous work on transition metal polychelates of poly(resacetophenone diyl ethylene)s is reported. In this work we report the preparation and characterization of Ni(II), Cu(II), Zn(II) and Co(II) polychelates with this resin.

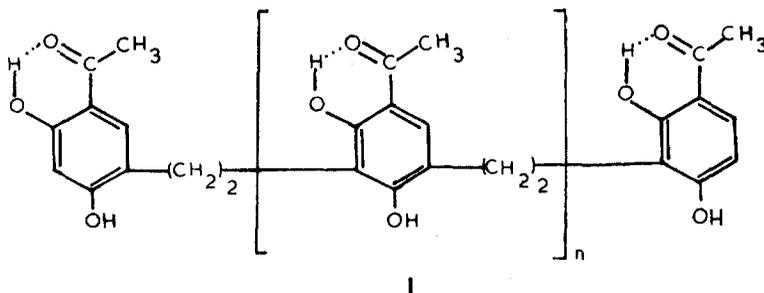
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2. Experimental

All the chemicals used were of AR or equivalent grade. DMSO was used after distillation.

2.1 Preparation of resin

A typical procedure to prepare the ligand is given below. Resacetophenone (RAP) (4.56 g, 0.03 mol) and ethylene glycol (1.3 ml, 0.03 mol) were mixed and refluxed at 120°C for 11 h in the presence of 40 g of polyphosphoric acid catalyst (PPA). The reaction mass was poured into crushed ice and left overnight. The separated product was filtered, washed with water and Soxhlet-extracted with methanol to purify it. Finally it was washed with acetone and dried at 60°C for 24 h. The proposed structure of the resin is given below (Patel and Patel 1981).



2.2 Preparation of polymeric chelates

Resacetophenone-ethylene glycol (1.78 g, 0.01 mol) was dissolved in DMSO (50 ml). Copper acetate (0.995 g, 0.005 mol) was also dissolved in DMSO (20 ml), and the hot solution of metal was added slowly to the hot solution of ligand with stirring. A reddish brown solid precipitated out. The product was digested for two hours on a water bath. It was filtered, washed with DMSO, and then a large amount of hot water and acetone. The product was dried at 60°C for 24 h. The yield was quantitative. The remaining chelates were prepared following a similar procedure with the corresponding metal acetates.

2.3 Elemental analyses

Carbon and hydrogen were analysed with a Coleman C-H-N analyzer.

2.4 Metal content in polymeric chelates

The chelates were analysed for their metal contents by the EDTA titration technique after destroying the organic matter first with a mixture of nitric and sulphuric acid and then with perchloric acid and sodium perchlorate.

2.5 Physical measurements

The magnetic susceptibility of the polymeric chelates was determined by the Gouy

method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant and μ_{eff} values were calculated after applying diamagnetic corrections. Electronic spectra of the polychelates were recorded on a Beckman DK 2A spectrophotometer using MgO as reference. The IR spectra of the ligand and the polychelates were taken as KBr pellets on a Perkin-Elmer-983 spectrophotometer. Thermogravimetric (TG) analysis was carried out on a Du Pont thermal analyser.

3. Results and discussion

All polychelates are reddish-brown coloured amorphous powders in nature. In a system like this, it is likely that extensive cross-linking of the macromolecules exists, which makes polychelates insoluble. Due to the insolubility of the polychelates in common organic solvents it was not possible to characterize them by conventional techniques such as viscosity, osmometry etc. The analytical data summarized in table 1 indicate a 1:2 (metal:ligand) composition. Cu(II) polychelate shows a magnetic moment of 1.87 BM which is slightly higher than the spin only value of one unpaired electron (1.73 BM) for square planar environments (Mahapatra and Ram Rao 1972). The excess of magnetic moment over the spin only value may be due to orbital contribution (Baker *et al* 1966). The magnetic moment of Ni(II) polychelates is 2.77 BM which is in the range of the value expected for two unpaired electrons in an octahedral or distorted octahedral geometry (Nyholm 1953). Co(II) polychelate exhibits a magnetic moment of 4.79 BM which satisfactorily lies in the range for octahedral geometry (Joshi and Patel 1983). Zn(II) polychelate is diamagnetic as it has a $3d^{10}$ configuration. Table 2 presents spectral data. In most cases, Cu(II) complexes possess a single broad band, making the assignment of individual transitions difficult. We have observed two bands at 24,690 and 15,625 cm^{-1} . The band at 24,690 cm^{-1} is due to the symmetry forbidden ligand-metal charge transfer transition (Syamal and Kale 1978). Ni(II) polychelate exhibits three bands at 24,390, 16,393 and 9,345 cm^{-1} . The positions of these three transitions are consistent with those of a compound with

Table 1. Analytical and magnetic moment data for the ligand and chelates.

Compound	Colour	Mol. wt. of repeating unit	Elemental analysis (%)			μ_{eff}
			M	C	H	
RAP-EG*	Reddish brown	178.18	—	67.74 (67.40) [†]	5.70 (5.65)	—
$[\text{Cu}(\text{RAP-EG})_2]_n$	Reddish brown	417.89	15.10 (15.20)	57.32 (57.48)	4.60 (4.34)	1.87
$[\text{Ni}(\text{RAP-EG})_2 \cdot 2\text{H}_2\text{O}]_n$	Reddish brown	449.07	13.20 (13.06)	53.61 (53.49)	4.10 (4.93)	2.77
$[\text{Zn}(\text{RAP-EG})_2]_n$	Reddish brown	419.73	15.42 (15.57)	57.30 (57.23)	4.40 (4.32)	Diamagnetic
$[\text{Co}(\text{RAP-EG})_2 \cdot 2\text{H}_2\text{O}]_n$	Reddish brown	449.32	13.01 (13.11)	53.71 (53.46)	4.11 (4.03)	4.79

* Resacetophenone-ethylene glycol; [†] Numbers shown are experimental values, while those in parentheses are calculated values.

Table 2. Spectral data of polymeric chelates.

Compound	Energies (cm ⁻¹)		Assignment	Calculated ligand field parameters
	Observed	Calculated		
[Cu(RAP-EG) ₂] _n	15,625	—	² B _{1g} → ² A _{1g}	—
	24,690	—	Charge transfer	—
[Ni(RAP-EG) ₂ ·2H ₂ O] _n	9,345	9,346	³ A _{2g} (F) → ³ T _{2g} (F)	D _q = 9,346
	16,393	15,213	→ ³ T _{1g} (F)	B = 849.11
	24,390	25,540	→ ³ T _{1g} (P)	β ₃₅ = 0.785 LFSE* = 32 kcal/mol
[Co(RAP-EG) ₂ ·2H ₂ O] _n	8,850	8,852	⁴ T _{1g} → ⁴ A _{2g}	D _q = 1005.3
	—	18,903	→ ⁴ T _{2g} (F)	B ₃₅ = 878.5
	20,825	20,825	→ ⁴ T _{1g} (P)	β ₃₅ = 0.904 LFSE = 34.48 kcal/mol

*Ligand field stabilization energy

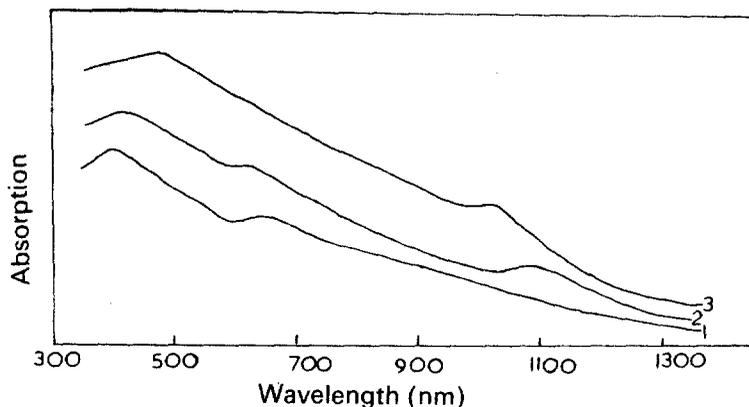


Figure 1. Diffuse reflectance spectra of (1) Cu-chelate (2) Ni-chelate (iii) Co-chelate.

octahedral geometry (Ustuno 1970). v_2/v_1 is 1.74, which is in good agreement with that for a complex with octahedral geometry (Patel and Patil 1981). The diffuse reflectance spectrum of the Co(II) polychelate shows a medium band at 8,850 cm⁻¹ and a broad band at 20,825 cm⁻¹ (figure 1). However, the transition ⁴T_{1g}(F) → ⁴T_{1g}(P)(v_2) could not be observed, because of weakness and proximity to a strong v_3 transition (Beyer *et al* 1977). The value of $v_2(\text{cal})/v_1(\text{obs})$ is 2.13 which is close to the required value for octahedral geometry (Jorgensen 1956). IR spectra of the ligand and polychelates are given in figure 2. Comparing the infrared spectra of the ligand and its polychelates it was inferred that they are virtually identical. The following tentative assignments have been made.

- (i) The broad bands at 3300–3620 cm⁻¹ are due to –OH stretching vibrations.
- (ii) The band observed at 2720 cm⁻¹ in the IR spectra of the ligands is due to intramolecular hydrogen bonding, while this band is not observed in the IR spectra of polychelates strongly suggesting the replacement of the hydrogen of the phenolic group.

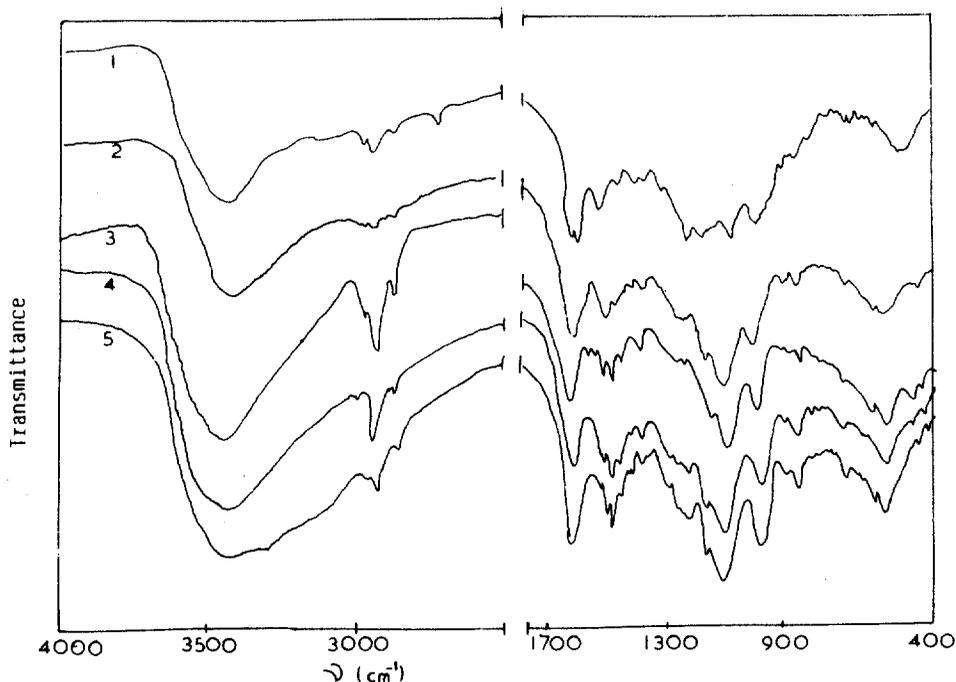


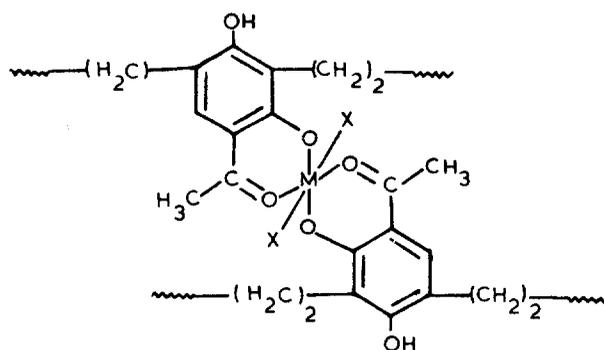
Figure 2. IR spectra of the ligand and its polychelates. (1) RAP-EG (ligand), (2) Cu-chelate, (3) Zn-chelate, (4) Ni-chelate, (5) Co-chelate.

(iii) The band appearing around $1500\text{--}1630\text{ cm}^{-1}$ is attributed to $\nu_{\text{C=O}}$ stretching vibration. This band is observed at lower frequencies as compared to the usual positions indicating the coordination of metal ions through the oxygen of the carbonyl group.

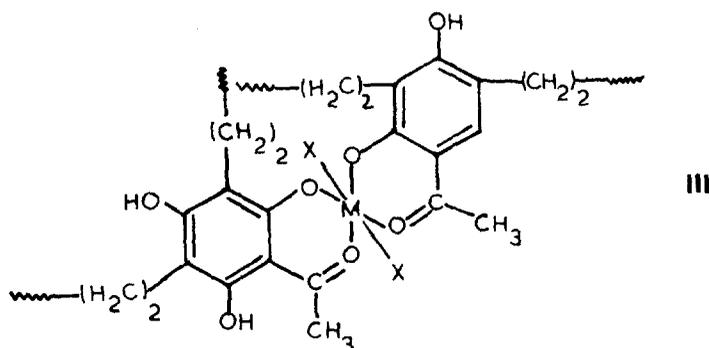
(iv) The band observed around $470\text{--}475\text{ cm}^{-1}$ indicates the M-O bond.

Other bands due to the substitution pattern were found to be similar in polychelates.

The infrared spectral studies, elemental analysis and solubility data of polychelates suggest that chelation might have occurred between two chelating groups from different polymeric chains and not from adjacent groups in the same chain, as shown in structures II and III. The magnitude of absorption by water molecules was calculated



II



Where $M = \text{Cu, Ni, Co}$ and Zn

$X = \text{H}_2\text{O}$ for Ni and Co

by taking the residue of decomposition at 200°C . The thermal activation energy was calculated by employing the Broido (1969) method. The stability order of the ligand and its polychelates was found to be

ligand > $\text{Zn} > \text{Co} > \text{Ni} > \text{Cu}$.

However there is not much variation in the data.

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