

Synthesis and characterization of polychelates of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), oxovanadium(IV) and dioxouranium(VI) with 2,4-dihydroxybenzaldehyde-urea-formaldehyde polymer

G C Patel, H B Pancholi & M M Patel*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanaagar 388 120

Received 30 August 1990; revised 28 December 1990; accepted 28 January 1991

Polychelates of Cu(II), Ni(II), Co(II), Mn(II), Zn(II), oxovanadium(IV) and dioxouranium(VI) with 2,4-dihydroxybenzaldehyde (2,4-DB)-urea(U)-formaldehyde(F) polymer (2,4-DBUF) have been prepared. Elemental analyses of the polychelates indicate a metal:ligand ratio of 1:2. The structures of the polychelates have been assigned on the basis of their elemental analyses, IR, reflectance spectra, magnetic moment, thermal data and their electrical conductivity behaviour.

In continuation of our earlier studies¹⁻³ on polymeric ligands, we report here the synthesis and characterization of 2,4-dihydroxybenzaldehyde-urea-formaldehyde (2,4-DBUF) polymer and its polychelates.

Experimental

All the chemicals were either of AR or CP grade. 2,4-Dihydroxybenzaldehyde was prepared following a known method⁴. Elemental analyses, determination of Mn, electronic and IR spectra, magnetic and electrical conductivity measurements were carried out as described earlier^{1,3}.

Preparation of the polymer

2,4-Dihydroxybenzaldehyde (13.6 g, 0.1 mol), formaldehyde (37%, 16.2 ml, 0.2 mol) and HCl (2M, 50.0 ml) were mixed and refluxed while stirring at 60°C; urea (6.0 g, 0.1 mol in water) was added dropwise and then the reaction mixture was refluxed at 110°C for 5 hr on an oil-bath. The yellow solid product obtained was purified as described earlier⁵. It is soluble in DMF, pyridine and aq. NaOH.

Preparation of the polychelates

2, 4-Dihydroxybenzaldehyde-urea-formaldehyde (2.2g, 0.01 mol) was dissolved in DMF (50 ml). To this

solution was added the respective metal nitrate (0.005 mol) in DMF (50 ml) dropwise with constant stirring. The polychelate separated out on addition of saturated solution of sodium acetate. The polychelate was digested for 30 min on a water-bath, filtered, washed with DMF and hot distilled water and dried at 60°C for 24 hr. In case of oxovanadium(IV) chelate, vanadyl sulphate was used as the starting material.

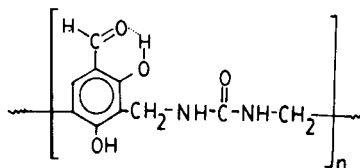
Results and discussion

All the polychelates are coloured and amorphous in nature. They are insoluble in all common organic solvents. The elemental analyses shown in Table 1 agree with a 1:2 (metal:ligand) stoichiometry.

The molecular weight of 2,4-DBUF polymer was found to be 1552 g/mol by conductometric titration and 1490 g/mol by vapour pressure osmometry. IR spectral study of polymer shows a broad band in the region 3100-3600 cm⁻¹ due to νOH and νNH mode. A sharp but weak band at 2720 cm⁻¹ indicates intra-molecular hydrogen bonding⁶. The band appearing at 1640 cm⁻¹ is attributed to νC=O of -NHCONH group and νC=O of -CHO group.

On the basis of elemental analyses, molecular weight determination and IR spectral study, the polymer is suggested to have the following structure (I).

A comparison of the IR spectra of polymer and its polychelates shows that a broad band in the region 3100-3600 cm⁻¹ due to νOH and νNH remains unchanged, while the weaker band at 2720 cm⁻¹ disappears from the spectra of polychelates. This indicates the replacement of hydrogen of the phenolic OH group by metal ions. The lowering of ketonic νC=O band by 10-20 cm⁻¹ in the polychelate suggests coordination of metal ions through oxygen of -CHO group. In oxovanadium(IV) and dioxouranium(VI) polychelates, sharp bands at 960 and 920 cm⁻¹ are assigned to the νV=O and νU=O modes respectively^{7,8}. The bands around 565 and 475 cm⁻¹ correspond to the νM-O vibrations⁶.



(I)

Table 1—Analytical and electrical data of the polychelates

Polychelates	Found (Calc.), %				-log σ_0	E_a (eV)
	C	H	N	Metal		
L	53.60 (54.05)	4.47 (4.50)	12.28 (12.61)	—	19.80	1.13
[CuL ₂] _n	47.01 (47.47)	3.51 (3.56)	10.81 (11.08)	12.39 (12.57)	14.57	1.42
[NiL ₂ .X ₂] _n	44.37 (44.72)	4.02 (4.10)	10.27 (10.43)	10.85 (10.94)	6.92	0.99
[CoL ₂] _n	47.61 (47.91)	3.51 (3.59)	10.82 (11.18)	11.36 (11.76)	1.18	0.60
[MnL ₂ .X ₂] _n	44.70 (45.03)	4.11 (4.13)	10.25 (10.51)	10.14 (10.31)	-1.62	0.51
[ZnL ₂ .X ₂] _n	43.61 (44.17)	4.00 (4.05)	10.16 (10.31)	11.62 (12.03)	-4.76	0.29
[VO ₂ L ₂ .X] _n	45.01 (45.55)	3.71 (3.80)	10.41 (10.63)	12.51 (12.70)	-6.38	0.26
[UO ₂ L ₂] _n	33.21 (33.71)	2.45 (2.53)	7.42 (7.86)	37.41 (37.92)	7.52	0.95

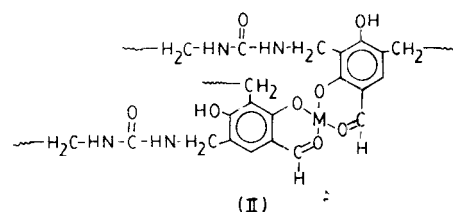
Where L = 2,4-dihydroxybenzaldehyde-urea-formaldehyde; X = H₂O

The magnetic moment of Cu(II) polychelate is 1.92 BM. The reflectance spectrum shows two bands at 14,600 and 24,681 cm⁻¹ which may be assigned to the transition ²B_{1g} → ²A_{1g} in a square planar geometry⁹ and charge-transfer transition respectively. The magnetic moment of Ni(II) polychelate is 3.07 BM which is close to the range observed for octahedral stereochemistry¹⁰. The reflectance spectrum of Ni(II) chelate exhibits three bands at, 9,852, 16,650 and 24,691 cm⁻¹ which may be assigned to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{1g}(P) transitions respectively considering an octahedral geometry¹¹. The Co(II) polychelate has a magnetic moment of 3.87 BM which is consistent with the spin-only value for three unpaired electrons in tetrahedral environment¹². Its reflectance spectrum shows three bands at 8,969, 15,384 and 25,641 cm⁻¹ which may be assigned to ⁴A₂ → ⁴T₁(F), ⁴A₂ → ⁴T₁(P) and charge-transfer transitions respectively¹³. The Mn(II) polychelate has magnetic moment of 5.23 BM which is lower than spin-only value (5.95 BM) which may be due to partial aerial oxidation of Mn(II) to Mn(III) during synthesis suggesting an octahedral structure¹⁴. The electronic spectrum of Mn(II) polychelate exhibits three absorption bands at 13,900, 16,120 and 23,500 cm⁻¹. The magnetic moment of oxovanadium(IV) polychelate is 1.76 BM which is normally observed for octahedral symmetry¹⁵. The reflectance spectrum of oxovanadium(IV) polychelate exhibits three bands at 12,810, 15,600 and 24,300 cm⁻¹ which may

correspond to ²B₂ → ²E, ²B₂ → ²B₁ and ²B₂ → ²A₁ transitions, respectively for an octahedral geometry¹⁶. The Zn(II) and dioxouranium(VI) polychelates are found to be diamagnetic as expected.

From the above data, the following structure(II) has been proposed for the polychelates.

The thermal stability data of the ligand and the polychelate showed the order as: 2,4-DBUF > Co(II) > Ni(II) > dioxouranium(VI) > Cu(II) > Mn(II) > oxovanadium(IV) > Zn(II). The removal of water above 150°C in polychelates indicates the presence of coordinated water molecules¹⁷. The negative logarithm of conductivity for the polymer is found to be a linear function of reciprocal of temperature in the range of study. The activation energy (E_a) and specific conductivity (σ_0) of the polychelates were evaluated using the relation $\sigma = \sigma_0 \exp(-E_a/kT)$, where σ is the conductivity at TK and k is the Boltzman constant. The electrical conductivity at room temperature decreases in the order 2,4-DBUF > Cu > UO₂ > Ni > Co > Mn > Zn > VO; while the activation energy declines as Cu >



2,4-DBUF > Ni > UO₂ > Co > Mn > Zn > VO¹⁸.

Acknowledgement

One of us (GCP) is thankful to the Gujarat Government for the award of a research fellowship.

References

- 1 Patel B K & Patel M M, *Angew makromol Chem*, 165 (1989) 47.
- 2 Patel B K & Patel M M, *J Indian chem Soc*, 67 (1990) 186.
- 3 Patel M M & Manavalan R, *J macromol Sci Chem*, A20 (1983) 487.
- 4 Mangoni L, *Ann Chem*, 48 (1958) 930.
- 5 Patel G C & Patel M M, *Indian J Technol*, 28 (1990) 567.
- 6 Nakanishi K, *Infrared absorption spectroscopy* (Nankodo Company, Tokyo), 1964, 20, 30, 50.
- 7 Madan S K & Donohue A M, *J inorg nucl Chem*, 28 (1966) 1303.
- 8 Ahuja I S & Singh R, *J inorg nucl Chem*, 35 (1973) 561.
- 9 Syamal A & Kale K S, *Indian J. Chem*, 16 (1978) 46.
- 10 Utseno S, *J inorg nucl Chem*, 32 (1970) 1631.
- 11 Walton R A, *J inorg nucl Chem*, 28 (1966) 2229.
- 12 Figgis B N & Nyholm R S, *J chem Soc*, (1959) 338.
- 13 Patel M N & Patil S H, *J macromol Sci Chem*, 17 (1982) 675.
- 14 Dey K, *J Indian chem Soc*, 48 (1971) 641.
- 15 Bovey D M H & Clark E R, *J inorg nucl Chem*, 29 (1967) 755.
- 16 Selbin J, *Coord chem Rev*, 1 (1966) 293.
- 17 Nakolaev M A, Logvinenko V A & Myachina L I, *Thermal analysis*, Vol 2 (Academic Press, New York) 1969, 779.
- 18 D'Sa J T, Rao V J, Patel K C & Patel R D, *Angew makromol Chem*, 79 (1970) 133.