

Magnetic, spectral and thermal properties of some new coordination polymers

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Abstract. A tetradentate poly Schiff base ligand has been prepared from 4,4'-dihydroxy-3,3'-diacetyl biphenyl with *o*-dianisidine. Polychelates of this ligand have been prepared from metal acetates of the first transition series. The stereochemistry of these polychelates has been discussed in terms of their magnetic behaviour, IR and diffuse reflectance spectra, and thermal and elemental analyses. All the polychelates are dark in colour and are insoluble in common organic solvents.

Keywords. 4,4'-Dihydroxy-3,3'-diacetyl biphenyl; *o*-dianisidine; polychelates; DMF.

1. Introduction

The importance of coordination polymers of Schiff-base ligands in inorganic chemistry is seen by the large number of publications (Horowitz *et al* 1965; Chakravarty and Drinkard 1960). Some of the polymers containing metal ions linked by chelate rings from organic groups show exceptional thermal stability.

We intend in this present survey to reconsider some of the properties of a restricted number of the polychelates, especially their stereochemistry and thermal stability. An attempt has been made to characterize these compounds by elemental analysis, magnetic behaviour, diffuse reflectance spectra, IR spectra and thermal analysis.

2. Experimental

2.1 Preparation of ligand

The hydroxy ketone 4,4'-dihydroxy-3,3'-diacetyl biphenyl (DABP), and the aromatic diamine *o*-dianisidine (DA), were dissolved separately in hot ethanol in a 1:2 stoichiometric ratio and mixed. The reaction mixture was refluxed for 10 hr. On cooling, dark yellow coloured PSB (poly schiff base) separated out, which was filtered, washed with ethanol and dried. It was insoluble in common organic solvents but was soluble in DMF, DMSO and H₂SO₄. The polymeric Schiff base so prepared may act as a quadridentate ligand.

2.2 Preparation of the polychelates

The polychelates of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) were prepared by dissolving equimolar quantities of metal acetate and polymeric ligand in DMF separately

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and mixing. The reaction mixture was refluxed for 6 hr. The hot solution was poured into crushed ice. The precipitates were allowed to settle down, then were filtered, washed with hot water and dried. The polychelates were insoluble in common organic solvents and were purified by soxhlet extraction in methanol to remove impurities and dried.

2.3 Elemental analyses

Carbon, hydrogen and nitrogen were analysed by a Coleman C-H-N analyzer.

2.4 Metal content in the complexes

The metal content was determined by the EDTA titration technique after decomposition of the polychelates.

2.5 Physical measurements

The magnetic susceptibility of the polychelates was determined by the Gouy method at room temperature using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. IR spectra were scanned in KBr on a Carl Zeiss Jena UR-10 spectrophotometer. Electronic spectra were obtained from a Beckman DU spectrophotometer using MgO as reference. Thermogravimetric (TG) analysis was carried out on a 'Linseis thermogravimetric analyzer' in air at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and discussion

In a system like this it is likely that extensive cross linking of the macromolecules exists, which makes polychelates insoluble. Due to 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 are summarized in table 1 and support the formulae assigned to them.

Table 1. Analytical and magnetic moment data.

Compound	Colour		Elemental analysis				μ_{eff} (BM)
			M%	C%	H%	N%	
DABP DA	Dark yellow	Calc.	—	70.00	5.83	5.44	—
		Found		70.85	5.40	6.00	
$\text{Cu}[\text{DABP DA}]$	Brick red	Calc.	11.03	62.57	4.86	4.86	1.87
		Found	10.75	62.10	4.55	5.12	
$\text{Ni}[\text{DABP DA} \cdot 2\text{H}_2\text{O}]$	Brown	Calc.	9.67	59.36	5.27	4.61	2.82
		Found	9.25	59.72	5.42	4.22	
$\text{Co}[\text{DABP DA}]$	Brown	Calc.	10.31	63.08	4.90	4.90	4.10
		Found	10.72	63.62	4.40	4.61	
$\text{Mn}[\text{DABP DA} \cdot 2\text{H}_2\text{O}]$	Dark brown	Calc.	9.10	59.73	5.30	4.64	5.90
		Found	8.88	59.20	5.65	4.00	
$\text{Zn}[\text{DABP DA}]$	Brick red	Calc.	11.01	62.59	4.86	4.86	Diamagnetic
		Found	11.25	62.10	4.42	4.12	

Cu(II) polychelate shows a magnetic moment 1.87 BM which is slightly higher than the spin only value of a one unpaired electron (1.73 BM) for a square planar environment (Mahapatra and Rama Rao 1972). The excess of the magnetic moment over the spin only value may be due to orbital contribution (Baker *et al* 1966). The magnetic moment of Ni(II) polychelate is 2.82 BM which is in the range expected for the spin only value for two unpaired electrons in an octahedral or distorted octahedral geometry (Nyholm 1953). Cobalt (II) polychelate exhibits a magnetic moment of 4.10 BM. The low value could be indicative of the presence of a mixture of high spin tetrahedral and low spin planar forms (Calvin and Barkelew 1946). The room temperature magnetic moment of manganese(II) polychelate is 5.90 BM which conforms well with the spin only moment for an octahedral stereochemistry (Siddiqi *et al* 1982). Zinc (II) polychelate is diamagnetic as it has no unpaired electron.

The electronic spectrum of copper (II) complex shows three bands at 24 390, 18 350 and 14 600 cm^{-1} . The band at 24 390 cm^{-1} may be assigned to charge transfer or intraligand transition (Sacconi and Ciampolini 1964). The other two bands are *d-d* transitions for which a planar structure is proposed (Patel and Patil 1981). Nickel (II) polychelate exhibits bands at 22 000, 16 130, 9050 and 8660 cm^{-1} . The position of these transitions is consistent with those of an octahedral, essentially distorted structure (Rastogi and Sharma 1974). The γ_1 transition is found to split into two bands (9050 and 8660 cm^{-1}) which can be assigned to the transition arising from the splitting of the ${}^3T_{2g}(F)$. The Racah parameter, B_{35} , is calculated using the method suggested by Konig (1971). Transition energies γ_2 and γ_3 are calculated using the Racah parameter (table 2). In nickel (II) polychelate having octahedral geometry, the value of γ_1 corresponds to $10 D_q$ which is calculated using the Konig (1971) equation (table 2). An attempt has been made to compute the repulsion parameter using the splitting values γ_1 and γ_2 by known methods (Rastogi and Sharma 1971; Lever 1968).

Table 2. Spectral data of the polychelates.

Compound	Energies (cm^{-1})		Assignment
	Observed	Calculated	
Cu[DAMP DA]	14 600	—	${}^2B_{1g} \rightarrow {}^2A_{1g}$
	18 350	—	$\rightarrow {}^2E_g$
	24 390	—	charge transfer
Ni[DABP DA · 2H ₂ O]	8660	8660	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	9050	—	—
	16 130	14 160	$\rightarrow {}^3T_{1g}(F)$
	22 000	23 970	$\rightarrow {}^3T_{1g}(P)$
Co[DABP DA]	—	4115	${}^4A_2 \rightarrow {}^4T_2(F)$
	8930	9665	$\rightarrow {}^4T_1(F)$
	16 100	15 335	$\rightarrow {}^4T_1(P)$
	25 000	—	charge transfer
Mn[DABP DA · 2H ₂ O]	15 270	—	${}^6A_1(S) \rightarrow {}^4T_{1g}(G)$
	18 690	—	$\rightarrow {}^4T_{2g}(G)$
	21 500	—	$\rightarrow {}^4T_{1g} \cdot {}^4E_g(G)$

$$B_{35} = 810 \text{ cm}^{-1}, \quad \beta_{35} = 0.75, \quad D_t = 44.57 \text{ cm}^{-1},$$

$$D_q = 866.00 \text{ cm}^{-1}, \quad D_{q(\text{av})} = 827.00 \text{ cm}^{-1},$$

$$\gamma_2/\gamma_1 = 1.86 \text{ and LFSE (ligand field splitting energy) = } 29.70 \text{ kcal/mol.}$$

The reflectance spectrum of cobalt (II) complex under study shows bands at 16 100 and 8930 cm^{-1} which may be assigned to tetrahedral geometry (Patel and Patil 1982). The band at 25 000 cm^{-1} may arise due to charge transfer or internal ligand transitions (Sacconi *et al* 1962). The transition energies $\gamma_1, \gamma_2, \gamma_3$ have been calculated using the equation applied for nickel (II) polychelate (table 2). The value of B_{35} is calculated by the Konig (1971) relation. The calculated values of B_{35}, β_{35} and LFSE are found to be 877.9 $\text{cm}^{-1}, 0.78$ and 14.39 kcal/mol respectively. The electronic spectrum of manganese (II) polychelate exhibits three weak bands at the expected positions for an octahedral environment (Bates *et al* 1966). The zinc (II) complex is diamagnetic and may have tetrahedral geometry.

The IR spectra are complicated and difficult to interpret. However, only those peaks that could be assigned with reasonable certainty are listed. The spectra indicate strong C=N stretch in the ligand at 1620 cm^{-1} which shows either a positive shift (Busch and Bailar 1956) or a negative shift (Lal *et al* 1978) on complexation. However, in some cases there is no shift at all (Sharma and Bailar 1955). In Co(II), Mn(II) and Zn(II) polychelates the C=N stretch is shifted to higher frequency while in the case of Ni(II) polychelate it is slightly shifted to lower frequency. In Cu(II) polychelate it is not shifted at all. The medium band observed at 1280 cm^{-1} which may be phenolic C-N stretch vibration in the ligand shifted to a higher wavenumber, indicating that oxygen is involved in bonding (Biradar and Kulkarni 1971). Ni(II) and Mn(II) polychelates exhibit bands in the region 790–830 cm^{-1} and 1590–1600 cm^{-1} . These bands are attributed to coordinated water (Nakamoto 1963) and confirmed from TG analysis.

Thermal decomposition data are summarized in table 3. Goodwin and Bailar (1961) observed the given thermal stability order for the polychelates as Ni > Cu > Co which is in agreement with the observation reported by Marvel and Tarkoy (1958). We have observed the change in thermal stability order at 300°C as Co > Ni > Mn > Cu. The magnitude of water molecule was calculated by taking the residue of decomposition at ~ 200°C. The thermal activation energy was calculated by employing the Broido (1969) method.

Table 3. Thermal data of the polychelates.

Compound	Decomposition Temperature (°C)	% Weight loss at temperature						Ea (kcal/mol)
		100	200	300	400	500	600	
DABP DA	250–335 425–510	0.0	1.0	27.00	43.5	83.00	90.00	30.66, 19.1
Cu[DABP DA]	235	0.0	0.5	42.00	82.5	87.5	91.00	29.05
Ni[DABP DA · 2H ₂ O]	270	0.0	6.00	20.5	77.0	88.0	91.00	19.55
Co[DABP DA]	245	0.0	0.00	14.5	69.0	80.0	84.00	27.14
Mn[DABP DA · 2H ₂ O]	265	0.0	6.5	31.5	84.5	89.5	90.0	20.82

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References

- Baker E N, Hall D and Waters T N 1966 *J. Chem. Soc.* 680
Bates C H, White W B and Roy R 1966 *J. Inorg. Nucl. Chem.* **28** 397
Biradar N S and Kulkarni V H 1971 *Z. Anorg. Allg. Chem.* **B318** 312
Broido A 1969 *J. Polym. Sci.* **A277** 1761
Bush D H and Bailar J C Jr. 1956 *J. Polym. Sci.* **78** 1137
Calvin M and Barkelew C H 1946 *J. Am. Chem. Soc.* **68** 2267
Chakravarty D N and Drinkard W C 1960 *J. Indian Chem. Soc.* **80** 517
Goodwin H A and Bailar J C Jr. 1961 *J. Indian Chem. Soc.* **83** 2467
Horowitz E *et al* 1965 *J. Appl. Polym. Sci.* **9(7)** 2321
Konig B 1971 *Structure and bonding* (Springer: Berlin) Vol. 9, p. 175
Lal K, Singh J and Gupta S P 1978 *J. Inorg. Nucl. Chem.* **40** 359
Lever A B P 1968 *Coord. Chem. Rev.* **3** 119
Mahapatra B K and Rama Rao D V 1972 *J. Inorg. Nucl. Chem.* **49** 1065
Marvel C S and Tarkoy N 1958 *J. Am. Chem. Soc.* **80** 832
Nakamoto K 1963 *Infrared spectra of inorganic and coordination compounds* (Wiley: New York)
Nyholm R S 1953 *Chem. Rev.* **53** 263
Patel M N and Patil S H 1981 *Angew. Makromol. Chemie* **97** 69
Patel M N and Patil S H 1982 *J. Macromol. Sci. Chem.* **A17** 4 675
Rastogi D K and Sharma K C 1974 *J. Inorg. Nucl. Chem.* **36** 2219
Sacconi L and Ciampolini M 1964 *J. Chem. Soc.* 276
Sacconi L, Ciampolini M, Magio F and Cavasino F P 1962 *J. Am. Chem. Soc.* **84** 3246
Sharma B D and Bailar J C Jr. 1955 *J. Am. Chem. Soc.* **77** 5476
Siddiqi K S, Siddiqi M R H, Khan P, Khan S and Zaidi S A A 1982 *Synth. React. Inorg. Met.-Org. Chem.* **12** 521