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Synthesis of Poly-Schiff Bases and some Copper(II) and Manganese(II) Polychelates

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Abstract

Four poly-Schiff bases derived from hydroxyketones and aromatic diamines have been synthesized, and their copper and manganese complexes were prepared and characterized by elemental analyses, spectral, magnetic and thermal data. The polychelates are of 1:1 (metal–poly-Schiff base) stoichiometry and exhibit four and six-coordination for copper and manganese respectively. The chelation is through the nitrogen of the azomethine group and oxygen of hydroxy group in the poly-Schiff bases.

Introduction

Schiff bases and related azomethines have attracted the attention of the investigators as very useful catenating ligands. Coordination polymers derived from polymeric Schiff bases have been extensitvely studied [1, 2]. Polymeric reagents have developed over the past decade from a somewhat exotic and esoteric research activity into a fast-growing field in applied and specific separations [3, 4].

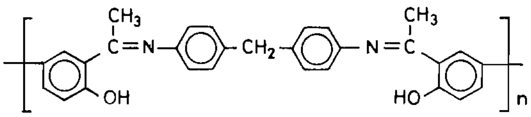
It is known that reaction of metal ions with organic ligands produces coordination systems having enhanced thermal stability and often improved chemical resistance [5]. We have synthesized and characterized several new poly-Schiff bases and have selected two transition metal ions, manganese(II) from the middle (d^5) and copper(II) from the end of the series (d^9) for chelate formation. The coordination geometry around metal ions has been assigned on the basis of analytical and magnetic measurements along with infrared and reflectance spectroscopy. We have obtained selected thermal data to compare the stability of polychelates complexes to the free polymeric ligands.

Experimental

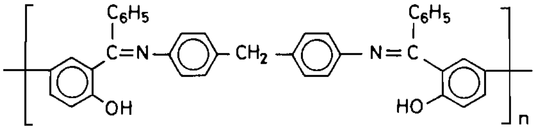
All the chemicals used in this work were of reagent grade. *o*-Dianisidine was received from Loba Chemie. 4,4′-Diaminodiphenylmethane, purchased from Aldrich Chemical Company, was purified by vacuum sublimation. The poly-Schiff bases (PSB) were prepared from the hydroxyketones and diamines by standard procedure [6].

Preparation of 4,4′-Dihydroxy-3,3′-diacetylbiphenyldiaminodiphenylmethane

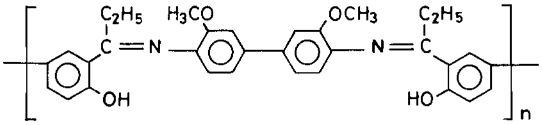
The synthesis of 4,4′-dihydroxy-3,3′-diacetylbiphenyldiaminodiphenyl methane represents a typical procedure. 4,4′-Dihydroxy-3,3′-diacetylbiphenyl (5.4 g) was dissolved in hot ethanol (15 ml). Diaminodiphenylmethane (1.8 g) in ethanol (10 ml) was added; the reaction mixture was heated at reflux for ten hours. On cooling, crystals of dark yellow PSB formed. It was filtered, washed with ethanol and dried. The following PSBs were prepared in this manner.



4,4′-dihydroxy-3,3′-diacetylbiphenyldiaminodiphenylmethane (A)



4,4′-dihydroxy-3,3′-dibenzylbiphenyldiaminodiphenylmethane (B)



4,4′-dihydroxy-3,3′-dipropylbiphenyl-*o*-dianisidine (C)

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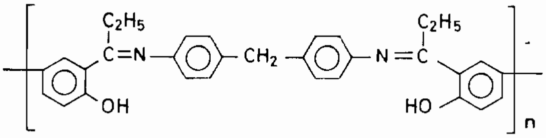
TABLE I. Analytical, Magnetic and Electronic Spectral Data for Polychelates

Ligand	Metal	Empirical formula	% M[a]	% N[a]	μ_{eff} (B.M.)	Electronic spectral data (cm^{-1})		
A	Copper	$C_{29}H_{22}O_2N_2 \cdot Cu$	12.86 (12.52)	5.67 (5.58)	1.87	14600	18350	24190
A	Manganese	$C_{29}H_{22}O_2N_2 \cdot 2H_2OMn$	10.55 (9.93)	5.37 (5.30)	5.90	15270	18690	21500
B	Copper	$C_{39}H_{26}O_2N_2Cu$	10.28 (10.10)	4.53 (4.43)	1.94	14800	18350	24500
B	Manganese	$C_{39}H_{26}O_2N_2 \cdot 2H_2OMn$	8.52 (8.30)	4.34 (4.30)	5.80	15000	18600	21400
C	Copper	$C_{32}H_{28}O_4N_2 \cdot Cu$	11.18 (11.03)	4.93 (4.82)	1.84	14610	18400	24450
C	Manganese	$C_{32}H_{28}O_4N_2 \cdot 2H_2OMn$	9.24 (9.00)	4.70 (4.54)	5.92	15410	18680	21000
D	Copper	$C_{31}H_{26}O_2N_2 \cdot Cu$	12.17 (11.89)	5.36 (4.94)	1.90	14800	18200	24630
D	Manganese	$C_{31}H_{26}O_2N_2 \cdot 2H_2O \cdot Mn$	10.10 (10.00)	5.10 (5.03)	5.86	15400	18640	21280

[a]Figures in parentheses are experimental values.



4,4′-dihydroxy-3,3′-dipropylbiphenyldiaminodiphenylmethane (**D**)

These PsBs may act as quadridentate ligands.

Preparation of Metal Polychelates

In a typical reaction, compound **A** (4.2 g, 0.01 mol) in dimethylformamide (20 ml) was added to copper acetate (2 g, 0.01 mol) in absolute ethanol (25 ml). It immediately gave a dark-brown coloured compound which was shaken mechanically for six days to complete chelation. The polychelates were found to be insoluble in common organic solvents. All other polychelates were prepared by the above general procedure.

Analytical Methods and Physical Measurements

The metal percentage was determined by titrating with standard EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric, perchloric, nitric and sulphuric acid. The method of Kjeldahl was used to determine the nitrogen content.

The infrared (IR) spectra were recorded from KBr pellets on a Perkin-Elmer 683 spectrophotometer. Electronic spectra were recorded on a Beckman DU spectrophotometer using MgO as reference material. Thermogravimetric measurements were made on DuPont 9900 Thermal Analyzer. Decomposition temperatures were determined by extrapolating the break in the TGA curve. Magnetic measurements were made on a Sortorius semimicro Gouy balance.

Results and Discussion

Analytical and Magnetic Data

The analytical data (Table I) suggest that all the polychelates have 1:1 metal to ligand stoichiometry with the general formula $[ML]_n$. The magnetic moments of the copper chelates are in the range 1.84–1.94 B.M. which is slightly higher than the spin only value of one unpaired electron for planar environment [7]. The room temperature magnetic moments of the manganese chelates are in the range 5.80–5.92 B.M. which compare well with the spin only moment expected for octahedral stereochemistry [8].

Thermal and Electronic Spectral Properties

The synthesis of thermally stable polychelates is now a promising area in the chemistry of heat resistant polymers. Some of the polymers containing metal ion linked by chelate rings derived from organic groups show exceptional thermal stability. Aromatic backbone units are much more stable than aliphatic ones and they have significant higher melting temperatures. Because all the ligands and polychelates are structurally similar, we collected TGA data only for compound A and its copper and manganese chelates. The decomposition temperatures are 225, 250 and 300 °C for compound **A**, the copper and the manganese chelate respectively. The order of increasing thermal stability is therefore **A** < Cu chelate < Mn chelate.

Although the thermal data indicate higher stability for the manganese chelate, such a comparison is not perfect since coordination around copper and manganese is different in the two compounds. The coordinated water molecules for manganese chelate of compound **A** were calculated by taking the amount of residue at 200 °C.

The electronic spectra of the copper chelates show three bands around 24 000, 18 000 and 15 000 cm^{-1}. The band at 24 000 cm^{-1} may be assigned to charge transfer or intraligand transition [9]. The other two bands are d–d bands for which a planar structure is proposed [10]. The electronic spectra of the manganese chelates exhibit three bands at the expected positions for an octahedral environment [11].

IR Spectra

Important IR frequencies and their assignments are available upon request from Dr. M. N. Patel. IR spectra for all poly-Schiff bases and polychelates are recorded. The overall spectra are rather complex, especially for the polychelates and cannot be assigned completely. Again, for PSB they are virtually identical with each other but show important differences with those of polychelates. Although much information is available in the literature concerning the IR spectra of imines, less is known about IR absorption by polymeric azomethines and polychelates.

The C=N stretch in the PSB occurs at 1620 cm^{-1}. The low frequency of the azomethine group is attributed to its conjugation with an aromatic ring [12] and its hydrogen bonding to an adjacent *o*-hydroxy group [13, 14]. The C=N stretch shows either a positive [15] or negative shift [16] on complexation. We have observed a lower shift of about 20 cm^{-1} for polychelates. In addition the medium band observed at 1280 cm^{-1} which may be a phenolic C–O stretching vibration in the ligand shifted to a higher wave numer in the metal complexes, indicating that oxygen is involved in bonding [13]. Manganese polychelates also exhibit bands in the region 790–830 cm^{-1} which may be attributed to coordinated water molecules [17].

Conclusions

Several poly-Schiff bases and their copper and manganese polychelates have been synthesized and characterized. Unfortunately, all the polychelates are amorphous and completely insoluble. The reported data indicate tetra- and hexa-coordinate arrangements around copper and manganese respectively. Two possible structures can be proposed for these polymeric chelates: helical, linear or cross-linked randomly through the metal atoms. The bonding site has been confirmed by considering the IR spectra of the original PSB and those of the polychelates.

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References

1 C. S. Marvel and N. Torkoy, *J. Am. Chem. Soc., 80*, 832 (1958).
2 H. Reitzle and W. Sawodny, *Inorg. Chim. Acta, 103*, 53 (1985).
3 W. Sawodny and M. Riederer, *Angew. Chem., 89*, 897 (1977).
4 W. Sawodny, M. Riederer and E. Urban, *Inorg. Chim. Acta, 29*, 63 (1978).
5 H. A. Goodwin and J. C. Bailar, Jr., *J. Am. Chem. Soc., 83*, 2467 (1961).
6 M. N. Patel and S. H. Patil, *J. Macromol. Sci.-Chem., A18*(4), 521 (1982).
7 B. K. Mahapatra and D. V. Rao, *J. Inorg. Nucl. Chem., 49*, 1065 (1972).
8 K. S. Siddiqi, M. R. Siddiqi, P. Khan, S. Khan and S. A. A. Zaidi, *Synth. React. Inorg. Met.-Org. Chem., 12*, 521 (1982).
9 L. Sacconi, M. Ciapolini, F. Magio and F. P. Cavasioro, *J. Am. Chem. Soc., 84*, 3246 (1962).
10 M. N. Patel and S. H. Patil, *Angew. Makromol. Chem., 97*, 69 (1981).
11 C. H. Bates, W. B. White and R. Roy, *J. Inorg. Nucl. Chem., 28*, 397 (1966).
12 L. E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem., 22*, 462 (1957).
13 N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem., 33*, 2451 (1971).
14 J. E. Kovacic, *Spectrochim. Acta, Part A, 23*, 183 (1967).
15 D. H. Bush and J. C. Bailar, *Z. Anorg. Allg. Chem., 318*, 312 (1971).
16 K. Lal, J. Singh and S. P. Gupta, *J. Inorg. Nucl. Chem., 40*, 359 (1978).
17 I. Gamo, *Bull. Chem. Soc. Jpn., 34*, 760, 1430 (1961).