Inorganica Chimica Acta, 120 (1986) L9–L10

Manganese(II), Nickel(II) and Copper(II) Complexes with Schiff Bases Containing Sulphonic or Phosphonic Groups

P. GUERRIERO, D. AJÒ, P. A. VIGATO, U. CASELLATO and S. TAMBURINI

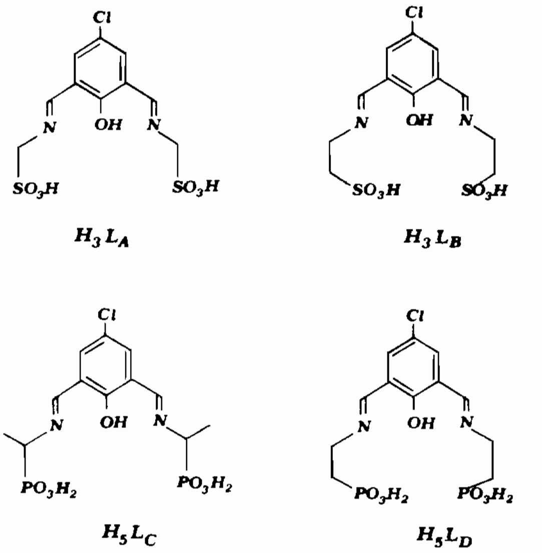
Istituto di Chimica e Tecnologia dei Radioelementi del C.N.R., Area della Ricerca, C.so Stati Uniti 4, Padua, Italy

(Received May 29, 1986)

Metal complexes with 'end-off' compartmental Schiff bases have been known for quite some time [1–3]. These ligands have been obtained by condensation of diformyl- or diacetylphenols with substituted amines or aminoacids [1, 2].

Comparative little attention has been devoted to systems derived from 2,6-diformyl-4-chlorophenol and α- or β-aminosulphonic or the analogous phosphonic acids, which can give rise, in principle, to complexes comparable with those obtained by α- and β-aminoacids. A recent paper [4], however, reported a non compartmental behaviour of the very similar Schiff base *N,N*-(2-hydroxy-5-methyl-1,3-dibenzylidene)-bis(4-methyl-2-sulphonic acid-aniline).

In order to elucidate the compartmental behaviour of these systems and to obtain also water-soluble complexes of high paramagnetic ions for their possible use for biological tests we have synthesized and characterized manganese(II), nickel(II) and copper(II) complexes with the Schiff bases shown in Scheme 1. These ligands have been prepared as trisodium (for sulphonates) and pentasodium (for phosphonates) salts by reaction of 2,6-diformyl-4-chlorophenol with the appropriate amino acids (aminomethanesulphonic acid, 2-aminoethanesulphonic acid, (±)1-aminoethanephosphonic acid and 2-aminoethanephosphonic acid) in alcoholic solution and in presence of NaOH.

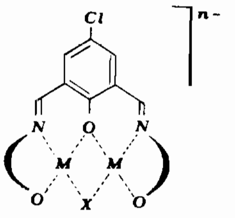


Scheme 1.

The complexes, green for copper(II) and nickel(II) and brown–yellow for manganese(II), have been synthesized by reaction of the sodium salt of the preformed ligands and the appropriate metal acetate or chloride*.

For copper(II) and manganese(II) a template synthesis (without the addition of NaOH) can also be used. The same sulphonate derivatives have been obtained by both procedures, while the phosphonate complex, obtained by template synthesis, contains hydrogen instead of sodium.

The physico-chemical data suggest for copper(II) and manganese(II) a binuclear structure of the type where the exogenous X group is –OH or –Cl according to the type of metal salt used**.



n = 0 for sulphonate derivatives, *n* = 2 for phosphonate derivatives.

Physico-chemical data suggest that nickel(II) gives, by template procedure, the complexes $NiL_E\cdot 2H_2O$ and $NiL_F\cdot 2.5H_2O$ and by reaction with the preformed ligand, $Na_5L_C\cdot 3H_2O\cdot 2CH_3OH$, the complex $Na_2Ni_2L_COH\cdot 3H_2O\cdot 2CH_3OH$ (Scheme 2).

By integration of back-scattered X-ray using a scanning electron microprobe, the metal, chlorine, sulphur or phosphorous) ratios and the sample homogeneity was confirmed [5].

The magnetic susceptibility measurements were carried out by the Faraday method. Diamagnetic corrections were introduced [6].

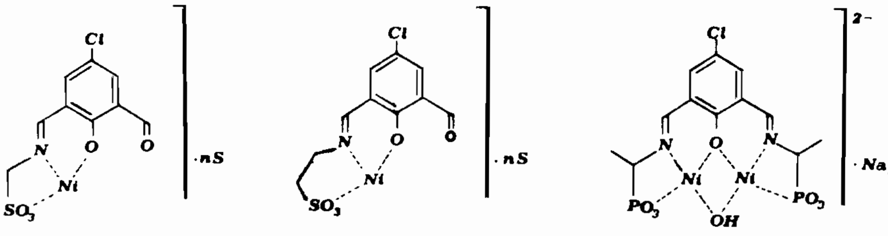
The IR data show for the ligands broad bands in the range 1651–1522 cm^{-1}, for the binuclear complexes sharp bands in the range 1647–1540

---

*It must be noted that the isomeric complexes, derived from (±)1-aminoethanephosphonic acid, have not been separated.

**The exogenous group was –OH when metal acetates were used.

0020-1693/86/$3.50



$NiL_E·nS$ $NiL_F·nS$ $Na_2Ni_2L_COH·2CH_3OH\ 3H_2O$

Scheme 2.

cm^{-1}; for nickel(II) mononuclear complexes there is a band at ≃1665 cm^{-1} attributable to ν(C=O) and a band at 1636 cm^{-1} attributable to ν(C=N). Moreover there are absorptions in the range 1160–1020 cm^{-1} for $\nu(PO_3^{2-})$ and in the range 1212–1037 cm^{-1} for $\nu(SO_3^-)$, respectively.

The room temperature magnetic moments (μ_{eff}) for binuclear complexes are: $Cu_2L_AOH·CH_3OH$ (2.00 BM), Cu_2L_BOH (2.07 BM), $Cu_2L_ACl·2H_2O$ (1.87 BM), $Na_2Cu_2L_DOH·2H_2O·2CH_3OH$ (2.34 BM), $H_2Cu_2L_COH·H_2O·CH_3OH$ (2.50 BM) (the magnetic moment per copper atom is 1.32–1.77, higher values for phosphonate analogues than sulphonate ones), $Mn_2L_AOH·4H_2O$ (7.19 BM), $Mn_2L_BOH·H_2O·CH_3OH$ (7.76 BM), $Na_2Mn_2L_DOH·H_2O·CH_3OH$ (7.70 BM), $Na_2Mn_2L_COH·2CH_3OH$ (7.64 BM) (the magnetic moment per manganese atom is 5.08–5.47 BM).

Preliminary results of the copper(II) derivatives in the 70–290 K range show a decrease of magnetic susceptibility at the lowest temperatures in most cases, but a different behaviour for the phosphonate derivative has been observed.

The magnetic moments for mononuclear nickel(II) complexes show the usual values for isolated nickel(II) ions (μ_{eff} 2.97–3.03 BM). The binuclear complex $Na_2Ni_2L_COH·3H_2O·2CH_3OH$ has a magnetic moment (μ_{eff}) 4.26 BM, 3.01 BM per nickel atom.

Further investigations (X-ray structures, electrochemical and variable temperature susceptibility measurements down to liquid helium) are in progress.

Acknowledgements

The technical assistance of Mr. F. De Zuane, for magnetic data collection, and Mr. E. Bullita, for assistance in the synthesis, is gratefully acknowledged.

References

1 U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev., 23,* 31 (1977).
2 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev., 8,* 199 (1979).
3 D. E. Fenton, in A. G. Spiro (ed.), 'Advanced in Inorganic and Bioinorganic Mechanisms', Vol. 2, Academic Press, New York, 1983, p. 187.
4 J. M. Bellerby, J. H. Morris and W. E. Smith, *Inorg. Chim. Acta, 102,* 121 (1985) and refs. therein.
5 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta,* in press.
6 Ch. J. O'Connor, in S. J. Lippard (ed.), 'Progress in Inorganic Chemistry', Vol. 29, Wiley, New York, 1982, pp. 208–211.