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The Preparation and Reactivity of New Binucleating Ligands Derived from 2-Acetyl-1,8-dihydroxy-3,6-dimethyl Naphthalene

P. A. VIGATO, U. CASELLATO

Laboratorio di Chimica e Tecnologia dei Radioelementi CNR, Area della Ricerca, Corso Stati Uniti, 35100 Padua, Italy

M. VIDALI, R. GRAZIANI

Istituto di Chimica Generale, Università di Padova, Via Loredan, 35100 Padua, Italy

D. E. FENTON and C. M. REGAN

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

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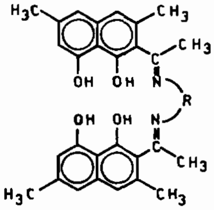
It is well known that metal complexes containing two similar or different metal ions are of interest in connection with spin exchange, charge transfer, in the domain of metalloenzymes and in homogeneous catalysis. Although a great many studies on homobinuclear chelates containing binucleating ligands have been carried out, relatively little is known about heterobinuclear systems.

One method for obtaining pure heterobinuclear chelates is to use a step-wise reaction of two different metal ions with coordinatively selective ligands, in which the two coordinating sets differ in the ligand field strength or in the stereochemistry of coordination.

In our previous paper the preparation of Cu(II)–M(II) and Ni(II)–M(II) heterobinuclear complexes (M = Cu(II), Ni(II), Mn(II), Co(II) and UO_2^{2+}) have been reported using Schiff bases derived from 3-formylsalicylic acid and diamines [1], 2,4,6-heptanetrione and ethylenediamine [2, 3] and *o*-acetoacetylphenol and ethylenediamine [4]. These complexes have coordination sites with different donor atoms, thus associating coordination selectivity with each site.

Other workers have prepared heterobinuclear complexes derived from related ligands [5, 6].

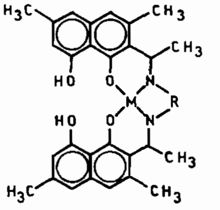
We now report the preparation of a series of ligands derived from the reaction of 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene (H_2addn) with diamines (Table). The ligands



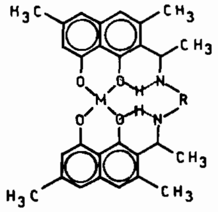
R	
CH_2–CH_2	H_4addn-en
CH_2–CH_2–CH_2	H_4addn-pn
CH_2–CH_2–NH–CH_2–CH_2	H_4addn-dien

were prepared by reacting H_2addn with the appropriate diamine in boiling ethanol (molar ratio 2:1). After cooling the yellow product was filtered off and washed with ethanol. The ligands have one coordination site with two or three nitrogen and two oxygen atoms (N_2O_2 or N_3O_2) and a second with four oxygen atoms (O_2O_2).

A number of mononuclear chelates of H_4addn-diam ligands were prepared by allowing a 1:1 molar ratio of metal acetate and the ligand to react in hot ethanol or in $CHCl_3$–ethanol solution. In each case, two positional isomers may result:



Isomer I (N_2O_2)



Isomer II (O_2O_2)

The mononuclear Ni(II) chelates are an example of Isomer I. These complexes are readily isolated from the reaction mixture as crystalline powders, which are soluble in some organic solvents and insoluble in water. On the basis of spectral and magnetic data it was established that isomers of type I are produced. Ni(H_2addn-en) and Ni(H_2addn-pn) are diamagnetic and have visible spectra corresponding to those of Ni(salen) and Ni(salpn) [7, 8]. It is therefore proposed that the Ni(II) chelates are square planar in coordination geometry as are Ni(salen) and Ni(salpn).

The mononuclear Cu(H_2addn-en) and Cu(H_2addn-pn) chelates are also designated as isomer I, the spectral and magnetic data being diagnostic of a N_2O_2 square planar geometry around the copper(II) ion. Their ir spectra are similar to those of Cu(salen) [11].

We were able to isolate only the binuclear chelates M_2(addn-dien) (M = Ni(II) or Cu(II)) by reaction of the ligand H_4addn-dien with M(II) acetate. Varying the reaction conditions and the metal to ligand ratio did not lead to isolation of the mononuclear species. The room temperature magnetic moment for Cu_2(addn-dien) (1.70 BM) is lower than the spin-only value and this suggests that a spin exchange interaction is operating. Also for Ni_2(H_2addn-dien)·$2H_2O$ the magnetic moment is lower than that expected for spin-only value (2.53 BM).

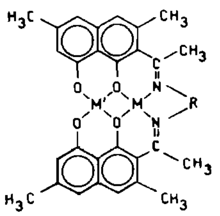
O_2O_2 isomers have been obtained with uranyl(VI) ion, by reaction of uranyl(VI) acetate with the ligands in $CHCl_3$/ethanol solution; they are diamagnetic of the type UO_2(H_2addn-diam)$(H_2O)_n$ (n = 1 or 2). Analytical and spectral data agree with the proposed formulation. The water molecules can be substituted by pyridine to give the complex UO_2(H_2addn-diam)(py).

TABLE. Physicochemical Data of the Prepared Complexes.

Complex	Electronic Data (nm)[a]	Infrared Data (cm^{-1})			μ_{BM} (293.4 K)
		$\nu C{=}N$	$\nu C{-}O$(phenolic)	$\nu_3 O{-}U{-}O$	
Ni(H_2addn-en)	582(sh)	1630	1335		diam
Cu(H_2addn-en)	552(sh)	1640	1330		1.36
UO_2(H_2addn-en)·$2H_2O$	440	1600	1335	885	diam
Ni(H_2addn-pn)	570(sh)	1635	1335		diam
Cu(H_2addn-pn)	560(sh)	1635	1340		1.60
UO_2(H_2addn-pn)·EtOH	444	1625		890	diam
Ni_2(addn-dien)·H_2O	538	1625	1330		2.53
Cu_2(addn-dien)	530(sh)[b]	1601	1330		1.70
UO_2(H_2addn-dien)·H_2O	435(sh)[b]	1605	1335	885	diam

[a] Electronic spectra were recorded in the 250–800 nm range in $CHCl_3$ solution. [b] In dimethylsulphoxide solution.

Synthesis of binuclear chelates was attempted using the mononuclear M(H_2addn-pn) (M = Ni(II) or Cu(II)) as ligands for a second metal to be coordinated to the O_2O_2 site. The M(H_2addn-pn) was dissolved in warm pyridine followed by slow addition of a stoichiometric amount of a metal acetate dissolved in a minimum amount of ethanol. The pyridine was removed under reduced pressure and the residue treated with hot ethanol. The precipitate was filtered off and washed with ethanol to give the binuclear chelates:



These are insoluble in ethanol and non polar solvents and quite soluble in coordinating solvents such as pyridine or dimethylsulphoxide. Preliminary spectral and magnetic data for these complexes are consistent with the proposed formulation.

References

1 M. Vidali, U. Casellato, P. A. Vigato, L. Doretti and F. Madalosso, *J. Inorg. Nucl. Chem., 38,* 1985 (1977).
2 M. Vidali, U. Casellato, P. A. Vigato and R. Graziani, *J. Inorg. Nucl. Chem., 38,* 1455 (1976).
3 D. E. Fenton and S. E. Gayda, *J. Chem. Soc. Dalton,* 2109 (1977).
4 D. E. Fenton, S. E. Gayda, U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta, 27,* 9 (1978).
5 R. L. Lintvedt, M. O. Glick, N. K. Tomlonovic and D. P. Patel, *Inorg. Chem., 15,* 1646 (1976).
6 H. Okawa, Y. Nishida, M. Tanaka and S. Kida, *Bull. Chem. Soc. Japan, 50,* 127 (1977).
7 E. Sinn and C. M. Harris, *Coord. Chem. Rev., 4,* 391 (1969).
8 N. B. Bryan, T. O. Maier, I. C. Paul and R. S. Draco, *J. Am. Chem. Soc., 95,* 6640 (1973).
9 R. H. Holm, *J. Am. Chem. Soc., 82,* 5632 (1960).
10 K. Ueno and A. E. Martell, *J. Phys. Chem., 61,* 257 (1957).
11 C. S. Marvel, S. A. Aspey and E. A. Dudley, *J. Am. Chem. Soc., 78,* 4905 (1956).