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Mononuclear Ni(II) and Zn(II) Complexes of Some Potentially Binucleating Schiff Base Ligands

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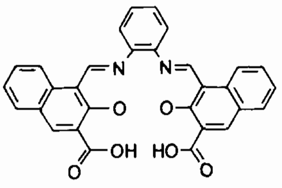
Abstract

Mononuclear Zn(II) and Ni(II) complexes have been prepared from two new Schiff base ligands in which two alternative co-ordination sites (N_2O_2 or O_2O_2) occur. The first ligand is the Schiff base derived from 1,2-diaminobenzene and 2-hydroxy-3-carboxy-1-napthaldehyde (bopaH_4). The complexes of this ligand contain the metal ions in the N_2O_2 coordination site as a result of the steric requirements of the co-ordinated ligand. The second ligand series are derivatives of X-substituted 1,2-diaminobenzenes, 2-hydroxy-3-carboxy-1-naphthaldehyde and 2-hydroxy-5-methyl isophthaldehyde (X-bolaH_3). In this case Ni(II) occupies the N_2O_2 site in its complexes with the X-bolaH_3 ligands, whereas the Zn(II) complexes are co-ordinated through the O_2O_2 site since the steric restrictions are less severe.

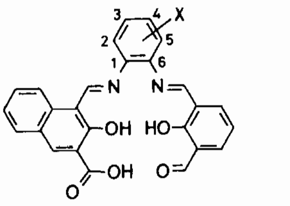
Introduction

There has been recent interest in polydentate ligands which are capable of co-ordinating metals in more than one site [1] and in their mononuclear [2, 3] and binuclear [2, 4, 5] metal complexes. In some cases the provision of dissimilar co-ordination sites (*e.g.* N_2O_2 and O_2O_2) within the same molecule has led, in the mononuclear series, to different site occupancies by different metal ions [6]. This 'co-ordination-selectivity' [7] is generally explicable in terms of the known ligand preferences of the metal ions. Thus Ni^{2+} tends to prefer N_2O_2 sites and UO_2^{2+} prefers O_2O_2. Cu^{2+} on the other hand has been found to form both Cu–N_2O_2 and Cu–O_2O_2 mononuclear complexes with the same ligand [6, 7].

The mononuclear Ni(II) and Zn(II) complexes of some new binucleating ligands are now reported. The complexes were derivatives of two related types of ligand, both containing N_2O_2 and O_2O_2 metal ion sites but which one was potentially tetra-basic and the other potentially tri-basic. It was of interest to compare the behaviour of the two types of ligand and to assess to what extent the requirements of accommodating either one or two acidic protons within a mononuclear derivative might effect the site preference of a metal ion. Mononuclear Ni(II) and Zn(II) complexes of the Schiff base ligands, bopaH_4, (*1*) and X-bolaH_3 (*2*) were obtained by template reactions and the free ligands were not isolated.



bopaH_4 (1)

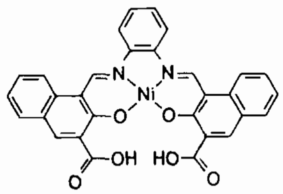


X-bolaH_3 (2) X = H, PhO, NO_2

In each case the site of the metal ion has been assigned by infra-red spectroscopy.

Results and Discussion

The bright red complex (bopaH_2)Ni was prepared by treating 1,2-diaminobenzene with a mixture of 2-hydroxy-3-carboxy-1-napthaldehyde and nickel acetate in 2-ethoxyethanol. An intense band at 1728 cm^{-1} in its infra-red spectrum indicated the presence of carboxylic acid groups and the complex was therefore assigned the structure (*3*). This is consistent with



(3) (BopaH_2)Ni

reports on related systems [8].

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TABLE I. Elemental Analyses of Compounds Prepared.

Compound	Carbon %		Hydrogen %		Nitrogen %	
	Calc.	Found	Calc.	Found	Calc.	Found
(bopaH_2)Ni	64.17	64.57	3.20	3.43	4.99	4.69
(bopaH_2)Zn·H_2O	61.53	61.70	3.41	3.64	4.78	4.26
(bopaH_2)Zn·py	65.01	64.78	3.56	3.64	6.50	6.78
(bopaH_2)Zn·$(DMSO)_2$[a]	56.43	55.82	4.14	4.23	3.87	4.25
(H-bolaH-N_2O_2)Ni·½H_2O	62.54	62.45	3.66	3.56	5.41	5.58
(3-NO_2-bolaH-N_2O_2)Ni·1½H_2O	55.86	55.76	3.44	3.25	7.23	7.37
(4-PhO-bolaH-N_2O_2)Ni·H_2O	64.08	63.94	3.72	3.96	4.53	4.61
(H-bolaH-O_2O_2)Zn	58.75	58.59	3.26	3.34	5.08	4.77
(3-NO_2-bolaH-O_2O_2)Zn·1½H_2O	51.96	51.90	3.21	3.20	6.74	6.72

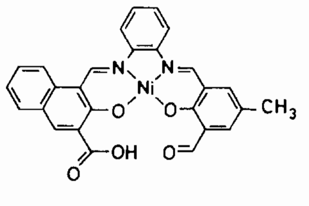
[a] Also S analysis for this compound. Calc. S = 8.85%, Found S = 8.74%.

A similar method was used to prepare a zinc derivative of bopaH_4. In this case the analysis of the isolated complex identified it as the monohydrate (bopaH_2)Zn·H_2O. The compound was recrystallised from pyridine (Py) to give (bopaH_2)Zn·Py and from dimethylsulphoxide (DMSO) to give (bopaH_2)Zn·$(DMSO)_2$. Each of these solvates had a strong band at *ca.* 1700 cm^{-1} in its IR spectrum which is attributable to the carbonyl frequency of a carboxylic acid. The zinc is likely to be five co-ordinate in the solvated species with a molecule of solvent occupying the fifth (apical) position of a square pyramid in which the metal atom is situated just above the N_2O_2 plane [9].

In (bopaH_2)Ni and (bopaH_2)Zn·L (L = H_2O, Py, DMSO) therefore, the spectroscopic evidence suggests that in each case the metal ion is in the N_2O_2 co-ordination site. In fact the possibility of forming an O_2O_2 isomer, even if this were more consistent with the ligand preferences of the metal ion, is unlikely on steric grounds. The strain imposed by attempting to accommodate the two acidic protons on the azomethine nitrogen atoms will clearly be unacceptable for a molecule in which most other factors favour strict planarity. It is significant that the reaction between UO_2^{2+} (which strongly favours oxygen donors) and a ligand closely related to bopaH_4 failed to yield a characterisable product [3]. Neutral uranyl(VI) complexes of potentially tetra-ionic N_2O_2/O_2O_2 binucleating ligands have been isolated only where flexibility of the invironment around the nitrogen atoms is possible [6, 7].

In contrast, a potentially tri-basic ligand such as X-bolaH_3 should be capable of accommodating a divalent metal ion in its O_2O_2 site without introducing intolerable strain. The single acidic proton of the resultant complex could reside on one of the azomethine nitrogen atoms and the molecule retain its essentially planar structure. Steric interactions, which probably play an important part in determining the behaviour of bopaH_4 towards divalent metal ions, will therefore not influence the 'co-ordination selectivity' of X-bolaH_3 to the same extent. The choice of site can be expected to reflect the donor atom preferences of the metal ion more accurately in the case of X-bolaH_3.

The nickel derivatives of X-bolaH_3 (X = H, OPh, NO_2) were each prepared by treating 2-hydroxy-5-methyl isophthalaldehyde with 2-hydroxy-3-carboxy-1-napthaldehyde, nickel acetate and the appropriate substituted 1,2-diaminobenzene in 2-ethoxyethanol. All three compounds show a pair of strong bands just above 1650 cm^{-1} in their infra-red spectra which were assigned to the carbonyl frequencies of carboxylic acid and aldehyde groups. Variations in the positions of the bands between complexes (Table II) probably reflect hydrogen bonding effects. The occurrence of these bands indicates very strongly that in each complex the nickel atom occupies an N_2O_2 co-ordination site as in (*4*). This is in agreement with its behaviour towards other N_2O_2/O_2O_2 binucleating ligands [6].



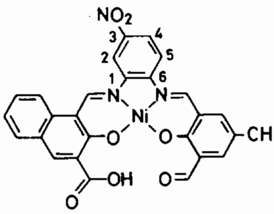
(4) (H-bola H-N_2O_2)Ni

The use of substituted 1,2-diaminobenzenes in the preparation of the nickel complexes of X-bolaH_3 (X = NO_2, OPh) offered the possibility of a pair of isomers in each case. However the method of preparation was expected to yield a predominance of one isomer. By first mixing the diamine with 2-hydroxy-

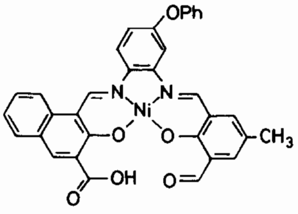
TABLE II. Principal Infra-red Bands (cm^{-1}), (Nujol mulls) for the Compounds Prepared.

Compound	ν(C=O) (acid)	ν(C=O) (aldehyde)	ν(C=N) (free)	Others
$(bopaH_2)Ni$	1728			
$(bopaH_2)Zn \cdot H_2O$	1700			
$(bopaH_2)Zn \cdot py$	1701			
$(bopaH_2)Zn \cdot (DMSO)_2$	1700			
$(H\text{-}bolaH\text{-}N_2O_2)Ni$	1726	1662		
$(3\text{-}NO_2\text{-}bolaH\text{-}N_2O_2)Ni \cdot 1\frac{1}{2}H_2O$	1721	1700		1532, 1340 $\nu(NO_2)$
$(4\text{-}PhO\text{-}bolaH\text{-}N_2O_2)Ni \cdot H_2O$	1728	1669		
$(H\text{-}bolaH\text{-}O_2O_2)Zn$			1644	3400br ν(N–H)
$(3\text{-}NO_2\text{-}bolaH\text{-}O_2O_2)Zn \cdot 1\frac{1}{2}H_2O$			1642	1523, 1336 $\nu(NO_2)$

3-carboxy-1-naphthaldehyde, the more basic of the amine groups would be expected to condense with the naphthaldehyde. On this basis the $3\text{-}NO_2$ (*5*) and 4-OPh (*6*) nickel derivatives would be expected to be isolated.

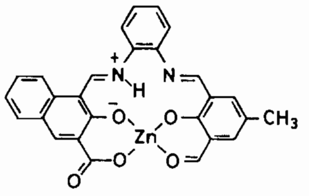


(5)



(6)

A procedure similar to that used for the preparations of the nickel derivatives of $X\text{-}bolaH_3$ was employed to make the zinc complexes. The reaction involving the phenoxy substituted diamine failed to give a complex of $PhO\text{-}bolaH_3$ but in both other cases (X = H, NO_2) solids were isolated which were found by analysis to correspond to 1:1 complexes of zinc(II) and $X\text{-}bolaH_3$. Unlike their nickel analogues the compounds show no bands between 1650 and 1750 cm^{-1} in their IR spectra, suggesting the absence of free carboxylic acid and aldehyde groups. A medium intensity band at *ca.* 1652 cm^{-1} in the spectra of the zinc complexes was attributed to the C=N stretching frequency of an unco-ordinated azomethine [10] and further supported the conclusion that in both the isolated derivatives the zinc(II) ion occupied the O_2O_2 site. A broad, weak band at 3400 cm^{-1} in the spectrum of the anhydrous complex $(H\text{-}bola\ H\text{-}O_2O_2)Zn$ was assigned to the N–H mode(II) of a protonated azomethine group and the complex is therefore concluded to have the structure (*7*). It was assumed that protonation occurred on the nitrogen atom adjacent to the naphthalene system as this is likely to be the more basic. The very low solubility of the complex in suitable solvents precluded the observation of a ^1H NMR spectrum.



(7)

The nitro derivative of (*7*) is suggested to exist as the $3\text{-}NO_2$ isomer for the same reason as the nickel analogue, (*5*).

Experimental

Physical Measurements

Infra-red spectra were recorded as Nujol mulls on a Perkin-Elmer 457 spectrometer, calibrated using a polystyrene film.

Preparations

$(bopaH_2)Ni$

Nickel(II) acetate (0.125 g, 0.05 mol) and 2-hydroxy-3-carboxy-1-naphthaldehyde (0.216 g, 0.001 mol) were mixed together in 2-ethoxyethanol (15 cm^3). The mixture was stirred at about 60 °C on a hotplate until all the nickel acetate had dissolved (15 mins). A solution of 1,2-diaminobenzene (0.054 g, 0.0005 mol) in 2-ethoxyethanol (10 cm^3) was then added and the whole was stirred at about 100 °C on a hotplate for 3 hours. The mixture was then cooled and the red solid filtered off. It was washed with 2-ethoxyethanol and then with ethanol until the washings were colourless. The solid was dried in a vacuum oven at 100 °C for 2 hours. Yield = 87%.

$(bopaH_2)Zn \cdot H_2$

Zinc(II) acetate (0.22 g, 0.001 mol) and 2-hydroxy-3-carboxy-1-napthaldehyde (0.432 g, 0.002 mol) were dissolved together in methanol (100 cm^3) containing a few drops of added water. The temperature of the solution was maintained at 40 ℃ and it was stirred magnetically. A solution of 1,2-diaminobenzene (0.108 g, 0.001 mol) in methanol (50 cm^3) was added dropwise at 40 ℃. After cooling to room temperature yellow crystals of the complex were filtered off and dried over silica gel under vacuum. Yield = 84%.

(bopaH$_2$)Zn·py, (bopaH$_2$)Zn·(DMSO)$_2$

These two complexes were prepared by recrystallising the hydrate, prepared by the above method, from the appropriate solvent.

(H-bola H-N_2O_2)Ni·½H_2O, (3-NO_2-bolaH-N_2O_2)-Ni·1½H_2O, (4-PhO-bola H-N_2O)Ni·H_2O

These three complexes were prepared by similar methods using the appropriate substituted 1,2-diaminobenzene. The preparation of (4-PhO-bolaH-N_2O_2)-Ni·H_2O is illustrated.

A solution of 2-hydroxy-3-carboxy-1-napthaldehyde (0.216 g, 0.001 mol) in 2-ethoxyethanol (10 cm^3) was added slowly to a warm stirred solution of 4-phenoxy-1,2-diaminobenzene ((0.02 g, 0.001 mol) in the same solvent (5 cm^3). Nickel(II) acetate (0.25 g, 0.001 mol) in 2-ethoxyethanol (5 cm^3) was then added and the mixture was stirred at 100 ℃ for 30 min to give a yellow/brown suspension. A solution of 2-hydroxy-5-methyl isophthalaldehyde (0.164 g, 0.001 mol) in 2-ethoxyethanol was then added and stirring at 100 ℃ on a stirrer/hotplate was continued for 3 hours. The reaction was then cooled to room temperature and the red complex filtered off, washed with 2-ethoxyethanol and then ethanol and dried in a vacuum oven for 2 hours at 100 ℃.

Yields were between 70 and 90%.

(H-bola H-O_2O_2)Zn

A solution of 2-hydroxy-3-carboxy-1-napthaldehyde (0.108 g, 0.0005 mol) in ethanol (95%) (10 cm^3) was added slowly to a warm solution of 1,2-diaminobenzene (0.054 g, 0.0005 mol) in ethanol (10 cm^3). A yellow suspension developed and to the mixture a solution of zinc(II) acetate (0.11 g, 0.0005 mol) in water (5 cm^3) was added. This mixture was heated on a steam bath for 15 mins and then to it was added a solution of 2-hydroxy-5-methyl isophthalaldehyde (0.100 g, 0.0005 mol) in ethanol (5 cm^3). The whole was then refluxed for 2 days. At the end of this time the flask was cooled to room temperature and the yellow complex was filtered off, washed thoroughly with ethanol and dried over silica gel under vacuum. Yield = 96%.

(3-NO_2-bolaH-O_2O_2)Zn·1½H_2O

A solution of 2-hydroxy-3-carboxy-1-naphthaldehyde (0.108 g, 0.0005 mol) in 2-ethoxyethanol (10 cm^3) was added slowly to a warm, stirred solution of 4-nitro-1,2-diaminobenzene (0.077 g, 0.005 ml) in 2-ethoxyethanol (5 cm^3). A solution of zinc(II) acetate (0.11 g, 0.0005 mol) in 2-ethoxyethanol (5 cm^3) was then added and the mixture was stirred at about 60 ℃ on a hotplate for 15 mins. A solution of 2-hydroxy-5-methyl isophthalaldehyde (0.082 g, 0.0005 mol) in 2-ethoxyethanol (5 cm^3) was added followed by a few cm^3 of water. The mixture was stirred at about 80 ℃ for 5 hours. After cooling to room temperature the orange solid was filtered off, washed with a little 2-ethoxyethanol and then thoroughly with ethanol. The solid was dried over silica gel under vacuum. Yield = 83%.

References

1 U. Casallato, P. A. Vigato and M. Vidali, *Co-ord. Chem. Reviews, 23,* 31 (1977).
2 B. Tomlonovic, R. L. Hough, M. D. Glick and R. L. Lintvedt, *J. Am. Chem. Soc., 97,* 2925 (1975).
3 M. Vidali, P. A. Vigato and U. Casellato, *Inorg. Chim. Acta, 17,* L5 (1976).
4 H. Okawa, Y. Nishida, M.Tanaka and S. Kida, *Bull. Chem. Soc. Japan, 50,* 127 (1977).
5 (a) H. Yokoi and M. Iwaizumi, *Bull. J. Chem. Soc. Japan, 53,* 1489 (1980).
(b) R. R. Gangé, L. M. Henling and T. J. Kistenmacher, *Inorg. Chem., 19,* 1226 (1980).
(c) B. F. Hoskins, M. J. McLeod and H. A. Schaap, *Aust. J. Chem., 29,* 515 (1976).
(d) S. L. Lambert, C. L. Spiro, R. R. Gangé and D. N. Hendrickson, *Inorg. Chem., 21,* 68 (1982).
6 D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.,* 2101 (1977).
7 D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta, 27,* 9 (1978).
8 M. Tanaka, M. Kitaoka, H. Okawa and S. Kida, *Bull. Chem. Soc. Japan, 49,* 2469 (1976).
9 D. Hall and F. H. Moore, *Proc. Chem. Soc.,* 256 (1960).
10 L. J. Bellamy, 'Advances in Infra-red Group Frequencies', Methuen, London (1968).
11 D. E. Fenton and S. E. Gayda, *J. Chem. Soc., Dalton Trans.,* 2095 (1977).