Compartmental Ligands: Routes to Homo- and Hetero-dinuclear Complexes

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1 Introduction

A decade ago Robson initiated a series of studies concerned with a rational synthetic approach to cluster compounds.[1,2] In this work he introduced the concept of a macrocyclic dinucleating ligand, *i.e.* 'a ligand capable of securing two metal ions in close proximity'. This definition may be extended to include acyclic ligands having similar properties.[3]

The area of homodinuclear complexation has seen extensive growth, stimulated by interest in areas such as metalloenzymes, homogeneous catalysis, electrical conductance, and magnetic exchange processes, and has been comprehensively reviewed.[4,5] Examples of heterodinuclear complexes are less evident. Although an isolated reference appeared in 1936,[6] systematic approaches were not revealed until 1974—75.[7–11]

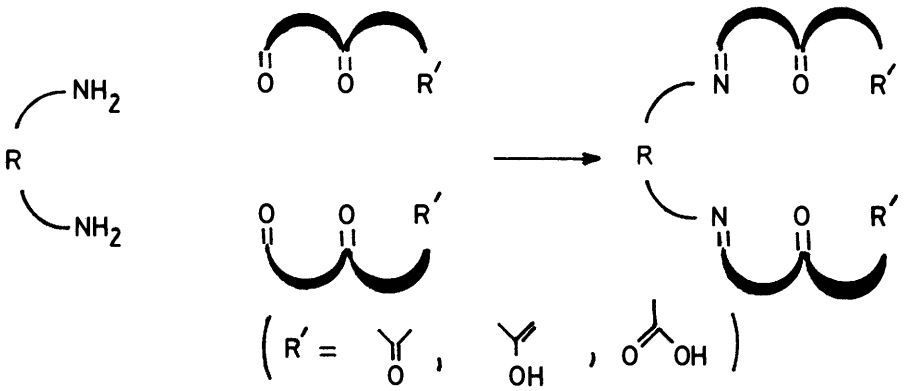
This account is concerned with dinucleating ligands derived from β-triketones, and related keto-phenols and keto-carboxylic acids, and their application to homo- and heterodinuclear complexation.

[1] R. Robson, *Austral. J. Chem.*, 1970, **23**, 2217.
[2] N. H. Pilkington and R. Robson, *Austral. J. Chem.*, 1970, **23**, 2225.
[3] The use of metal complexes of quinquedentate Schiff bases, such as the salicylidimines, as bidentate chelating agents to form dinuclear and trinuclear centres has been well documented (E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 1969, **4**, 391). Such complexes are not considered to fall into the framework described above.
[4] U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, 1977, **23**, 31.
[5] S. E. Groh, *Israel J. Chem.*, 1976—7, **15**, 277.
[6] S. N. Poddar, *Z. anorg. Chem.*, 1963, **322**, 326.
[7] U. Casellato, M. Vidali, and P. A. Vigato, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 437.
[8] M. Vidali, P. A. Vigato, U. Casellato, E. Tondello, and O. Traverso, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1715.
[9] H. Okawa, M. Tanaka, and S. Kida, *Chem. Letters*, 1974, 987.
[10] B. Tomlonovic, R. L. Hough, M. D. Glick, and R. L. Lintvedt, *J. Amer. Chem. Soc.*, 1975, **97**, 2925.
[11] D. E. Fenton and S. E. Gayda, *Inorg. Chim. Acta.*, 1975, **14**, L11.

2 Concept and strategy

Observations on the formation of bimetallic complexes derived using transition-metal Schiff-base complexes as ligands for metal β-diketonates[12–14] led to the realization that fusion of a β-diketone, with oxygen donors, and a Schiff base, with oxygen and nitrogen donor atoms, could in principle provide a single ligand capable of bimetallic complexation.

It was envisaged that the reaction of an α,ω-diamine with one terminal keto-function of a β-triketone, keto-phenol or keto-carboxylic acid, would lead to the formation of a Schiff base having available adjacent, dissimilar co-ordination compartments (Scheme 1). One of the compartments, (A), would resemble a Schiff base and is therefore designated —N_2O_2; the other compartment, (B), may be compared with a β-diketone, keto-phenol, or keto-carboxylic acid, and so is designated —O_2O_2.

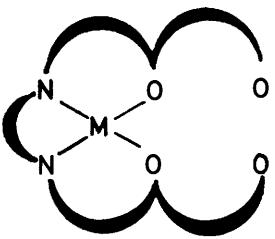


Scheme 1 *Synthesis of compartmental ligands*

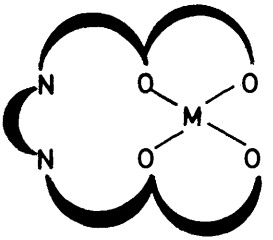
In a metal complexation reaction with such a ligand the metal is presented with a choice of compartments, leading to the availability of mononuclear positional isomers. In order to determine the donor set preferences a series of metal ions may be allowed to react with a given ligand, and the compartmental occupancy established using magnetic and spectroscopic techniques. Mass spectrometry is then used, where possible, to confirm that only a mononuclear complex is present. The pure mononuclear complex can then be treated with a second metal to yield a dinuclear complex.

If the same metal is used a homodinuclear complex results, whereas if a different metal is used a heterodinuclear complex is formed. For the latter, a stepwise incorporation of metals is preferred, as this avoids the statistical distribution of

[12] D. E. Fenton and S. E. Gayda, *J.C.S. Dalton*, 1977, 2095.
[13] D. E. Fenton, N. Bresciani-Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Chem. Comm.*, 1979, 39.
[14] N. B. O'Bryan, T. O. Maier, I. C. Paul, and R. S. Drago, *J. Amer. Chem. Soc.*, 1973, **95**, 6640.

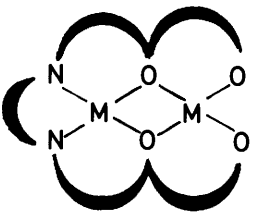


$M_{N_2O_2}$

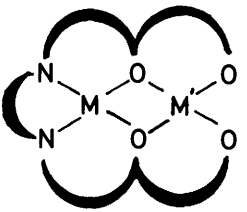


$M_{O_2O_2}$

Mononuclear positional isomers



Homodinuclear complex

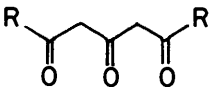


Heterodinuclear complex

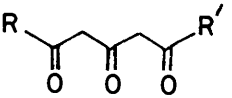
products that could arise if a mixture of metals were added to the free ligand. Metal exchange processes could also complicate the procedure leading to positional isomers, or a preferential precipitation of homodinuclear, or mononuclear species. Such an exchange has been seen in the reaction of bis(hexafluoroacetylacetonato) copper(II), $Cu(hfac)_2$, with *NN'*-ethylenebis-(salicylideneiminato)-cobalt(II), Co(salen), in which the metal ions exchange primary co-ordination spheres to yield $Cu(salen),Co(hfac)_2$.[14] In the absence of metal exchange pure heterodinuclear products can be recovered.[15–17]

3 Compartmental Ligands

A Ligands derived from Triketones.—1,3,5-Triketones may be divided into symmetric (1a) and asymmetric (1b) species.



R = Me, Et, Pr^n
(1a)

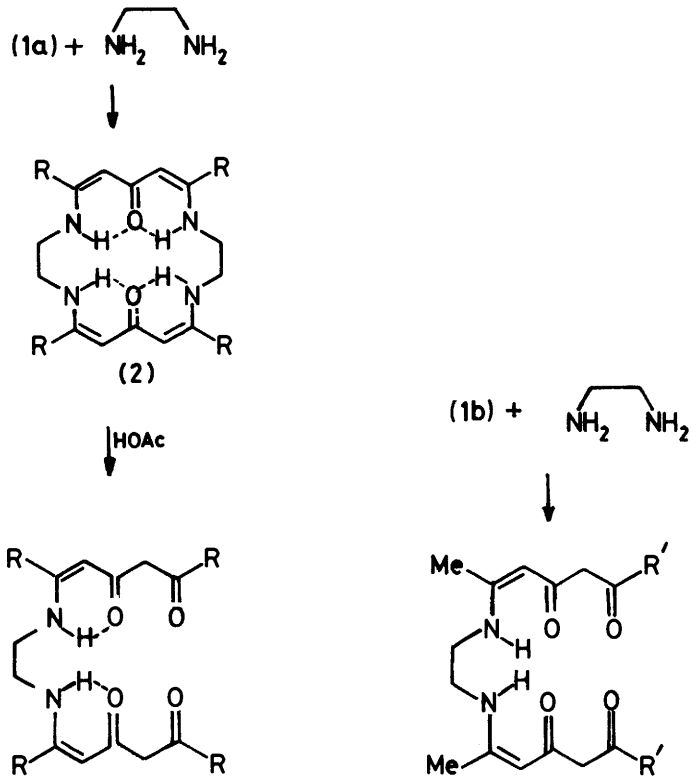


R = Me; R' = Ph, *p*-X-C_6H_4—,Bu^t
(1b)

[15] R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, and D. P. Gavel, *Inorg. Chem.*, 1976, **15**, 1646.
[16] D. E. Fenton and S. E. Gayda, *J.C.S. Dalton*, 1977, 2109.
[17] H. Okawa, Y. Nishida, M. Tanaka, and S. Kida, *Bull. Chem. Soc. Japan*, 1977, **50**, 127.

Their division is mirrored in their behaviour towards diamines in the absence of metal ions. Whereas it is possible to prepare the acyclic Schiff bases, (3), directly from the asymmetric triketones,[10,11,15,18] a macrocyclic product, (2), is recovered from reactions using the symmetric triketones.[12,18–20] Ring opening of the macrocycle using acetic acid must then be effected in order to prepare the acyclic species from the free ligand.[18,21]

Similar behaviour patterns have been seen in the formation of Schiff bases from



(3a, R = Me; 3b, R = Et; 3c, R= Pr^n) (3d, R = Ph; 3e, R= *p*-X-C_6H_4—; 3f, R = Bu^t)

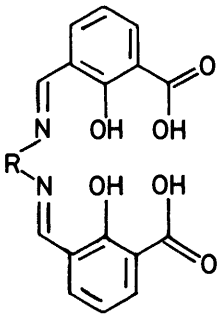
Scheme 2 *Schiff bases derived from 1,3,5-triketones*

[18] D. E. Fenton and S. E. Gayda, *J.C.S. Dalton*, 1977, 2101.
[19] T. Yano, T. Ushijama, M. Sasaki, H. Kobayashi, and K. Ueno, *Bull. Chem. Soc. Japan*, 1972, **45**, 2452.
[20] M. Vidali, U. Casellato, P. A. Vigato, and R. Graziani, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1455.
[21] D. E. Fenton, S. E. Gayda, and R. S. Z. Kowalski, *Transition Metal Chem.*, 1976, **1**, 95.

1,3-diketones and may arise from steric and electronic controls.[22,23] The relative ease of formation of the macrocycle, (2), may be facilitated by a small loss of internal entropy on cyclization.[24] A relatively rigid precursor unit, together with the presence of -imino double bonds to restrict rotations in the open-chain intermediates could be important in this context.

The bridging group provided by the diamine may be varied to give a wider range of ligands [*e.g.*, —$CH_2CH(Me)$—,—$(CH_2)_3$—, and —C_6H_4—].[19] Metal complexes derived from the macrocyclic ligands, (2), have been restricted so far to mononuclear derivatives.[12,20]

B Ligands derived from Keto-acids and Keto-phenols.—A second class of ligands, (4), capable of offering dissimilar, adjacent co-ordination compartments is derived from the reaction of α,ω-diamines with 3-formylsalicyclic acid.[6,9,17,25–27]



(4)

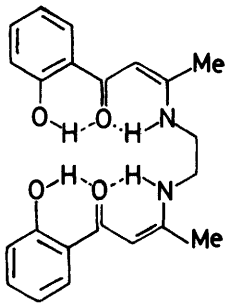
a; R = —CH_2CH_2—
b; R = —$CH_2CH(Me)$—
c; R = —$(CH_2)_3$—
d; R = —CH_2CH_2 NH CH_2CH_2—
e; R = Me CH-CH Me
f; R = — C_6H_{10}—
g; R = —C_6H_4— , *ortho*
h; R = —CH_2 $C(Me)_2$—

a; R = —CH_2CH_2—
b; R = —$(CH_2)_3$—
c; R = —$CH_2CH_2NHCH_2CH_2$—

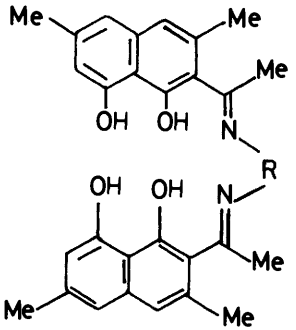
The free ligands (4a),[25,27] (4c),[28] (4e),[28] (4f),[28] and (4g)[6] have been isolated and characterized, the remaining ligands have been formed using metal template procedures, and isolated as their metal complexes.

The third group of ligands discussed here are derived from the reaction of keto-phenols with α,ω-diamines. *o*-Acetoacetylphenol reacts with 1,2-diaminoethane to yield the acyclic Schiff base, (5),[29] and 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene similarly reacts to yield the ligands (6).[30]

[22] L. F. Lindoy and W. E. Moody, *J. Amer. Chem. Soc.*, 1975, **97**, 2275.
[23] P. J. McCarthy, R. J. Horey, K. Ueno, and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.
[24] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856.
[25] M. Tanaka, M. Kitaoka, H. Okawa, and S. Kida, *Bull. Chem. Soc. Japan*, 1976, **49**, 2469.
[26] N. S. Rawat, *Indian J. Chem.*, 1976, **14A**, 440.
[27] M. Vidali, U. Casellato, P. A. Vigato, L. Doretti, and F. Madalosso, *J. Inorg. Nuclear Chem.*, 1977, **39**, 1985.
[28] N. Torihara, H. Okawa, and S. Kida. *Bull. Chem. Soc. Japan*, 1978, **51**, 3236.
[29] D. E. Fenton, S. E. Gayda, U. Casellato, P. A. Vigato, and M. Vidali, *Inorg. Chim. Acta.*, 1978, **27**, 9.
[30] P. A. Vigato, U. Casellato, M. Vidali, R. Graziani, D. E. Fenton, and C. M. Regan, *Inorg. Chim. Acta.*, 1979, **32**, L27 and in the press.



(5)



(6)

For all three classes, the free ligands, where isolable, have been fully characterized using i.r., ^{1}H and ^{13}C n.m.r., and mass spectrometry.

4 Mononuclear Complexes

Pure mononuclear complexes of compartmental ligands (Table 1) have been prepared by application of the following methods:

(i) the reaction of the free acyclic Schiff base with a metal salt (usually the hydroxide or acetate) in a suitable solvent;

(ii) the reaction of the corresponding macrocyclic Schiff base with a metal salt in a mixed solvent system using water as one phase;

(iii) a metal template procedure using the keto-precursor, the diamine, and a metal salt.

It has been suggested[19,20] that in method (ii) the addition of a metal ion to the macrocycle facilitates hydrolysis of the ligand by enhancing the electropositive nature of the azomethane carbon atom. It is not certain that this is the definitive mode of reaction as acid-catalysed hydrolysis of the macrocycle occurs readily in the absence of metal ions, and acetic acid would be generated in complexation reactions based on metal acetates.

Mononuclear complexes of Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, VO^{2+} and UO_2^{2+} have been synthesized using the above methods. For complexes derived from β-triketones a selectivity pattern emerges and it is seen that Ni^{II} is exclusively preferred by the $—N_2O_2$ compartment,[15,18,20] and that Co^{II},[21] VO^{2+},[15,18] and UO_2^{2+}[18,20] occupy the $—O_2O_2$ compartment. Copper(II) is ambivalent, occupying either set depending upon the ligand and reaction conditions used. With (3d) the $—O_2O_2$ isomer is formed whereas with (3a) both isomers may be isolated.[18] This selectivity has been viewed as a manifestation of the 'hard' and 'soft' compatabilities of the metal and donor compartments.[20] There is a paucity of information concerning stability constants for related Schiff base systems, and concerning

Table 1 *Mononuclear complexes of acyclic Schiff bases*

$Cu_{(N_2O_2)}$	:	3a;[18,19,20] 3b;[18] 3f;[18,34]
		4a;[26,27] 4a,$\frac{1}{2}H_2O$;[25] 4a,py;[27] 4b,$\frac{1}{2}H_2O$;[25] 4e;[33] 4f,$\frac{1}{2}H_2O$;[33]
		4g;[33] 4h[26]
		5[29]
		6a;[30] 6b[30]
$Cu_{(O_2O_2)}$	:	3a,H_2O;[18] 3d;[15] 3d,H_2O;[18] 5,$CHCl_3$;[29] 3e,$CHCl_3$ (X=CCH_3);
		3e,2H_2O (X = Br);[18] 3e (X = CH_3)[18]
$Ni_{(N_2O_2)}$	:	3a;[18,20] 3d[15,18]
		4a,$\frac{1}{2}H_2O$;[25] 4a;[27] 4b,$\frac{1}{2}H_2O$;[25] 4h[26]
		5[29]
		6a;[30] 6b[30]
$UO_{2(O_2O_2)}$	:	3a,L (L = H_2O, MeOH,dmso, Ph_3PO, Ph_3AsO);[18,20]
		3d, EtOH;[18]
		4g[6]
		5,H_2O[29]
		6a,H_2O;[30] 6b,H_2O[30]
$VO_{(O_2O_2)}$	:	3a;[18,19] 3d, Me_2CO[15,18]
$VO_{(N_2O_2)}$	:	4a,2H_2O[32]
$Zn_{(N_2O_2)}$	:	4a,2H_2O[31]
$Co_{(O_2O_2)}$	:	3a,2H_2O[21]

oxovanadium(IV) and dioxouranium(VI) with pentane-2,4-dione, but the pattern Cu > Ni is characterized for the diketone.[35]

In contrast, all mononuclear complexes derived from (4) have been shown to contain the metal in the inner, —N_2O_2 compartment.[25,27] The complexes derived from (5) and (6) parallel the trends observed for (3), and similarly provide positional isomers for the Cu^{II} derivatives of (5).[29,30]

The co-ordination selectivity of the compartments is established using physicochemical techniques. The spectral and magnetic properties for the metals in the —N_2O_2 and —O_2O_2 compartments correspond to those for the metals in the 'precursor' Schiff-bases, β-diketonates, keto-acids, or keto-phenols. In addition the i.r. spectra give assistance in assignment by indicating, for example, the presence of or absence of free carbonyl bands, depending upon occupancy, in species derived from (3) or (4).

This process is exemplified by the identification of the positional isomers of (3a)-Cu.[18] The reaction of (3a) with $Cu(OAc)_2$ gave three products, green and purple mononuclear complexes, and a green homodinuclear complex (see below). The purple complex has i.r. absorptions at 1721 and 1705 cm^{-1} indicative of

[31] P. Tola, O. Kahn, C. Chauvel, and H. Coudanne, *Nouveau. Journal de Chimie*, 1977, **1**, 467.
[32] O. Kahn, P. Tola, and H. Coudanne, *Inorg. Chim. Acta.*, 1978, **31**, L405.
[33] N. Torihara, H. Okawa, and S. Kida, *Inorg. Chim. Acta.*, 1976, **26**, 97.
[34] R. L. Lintvedt, B. Tomlonovic, D. E. Fenton, and M. D. Glick, *Adv. Chem. Ser.*, No. 150, 1976, 407.
[35] G. Gutnikov and H. Freiser, *Analyt. Chem.*, 1968, **40**, 39.

non-co-ordinated keto-groups, and the electronic spectrum, in $CHCl_3$, has a strong band *ca.* 550 nm which compares directly with the spectrum of *NN'*-ethylenebis(acetylacetoneiminato)copper(II),[Cu(acen)].[36] The latter molecule has a square planar Cu^{II} atom in an —N_2O_2 environment, and so the purple isomer is assigned such an occupancy. The green isomer has no free keto-bands in the infra-red, and the electronic spectrum has bands at 671 and 558 nm which compare with those in the spectrum of bis(pentane-2,4-dionato)copper(II), $[Cu(acac)_2]$,[36] where there is an —O_2O_2 occupancy. A similar methodology is used to assign the positional isomers, (5)-Cu.[29]

A further refinement to the above technique is made by adding the use of magnetic moment measurements.[15,18] The spectral results for (3d)-Ni indicate an —N_2O_2 occupancy[15] [i.r., 1675 and 1628 cm^{-1}, characteristic of free enol and keto-carbonyl groups; electronic spectrum ($CHCl_3$), 565 nm, essentially identical to that of Ni(acen)[37]]. The magnetic moment confirms this assignment since the molecule is rigorously diamagnetic as expected for square planar nickel(II). The isomer with Ni^{II} in the —O_2O_2 compartment would be expected to produce paramagnetic, octahedral Ni^{II} through oligomerization, or solvent addition. Similarly (4a)-Ni can be shown to have the metal present in the —N_2O_2 compartment.[25] (3a)-Ni, however, exhibits a residual paramagnetism even though the electronic and i.r. spectra indicate —N_2O_2 occupancy.[18] The mass spectrum shows the presence of a trace of the homobinuclear complex (3a)-NiNi, and so provides an excellent method for screening the purity of the mononuclear complexes.

It is usually possible to assign the compartmental occupancy by the above methods. However when the spectroscopic and magnetic properties are such that unequivocal assignment is not possible, as with (3d)-VO, Me_2CO,[15] then *X*-ray crystal structure analysis serves as the final arbiter. Crystal and molecular structures have been solved for (3a)-$Cu_{(N_2O_2)}$;[38] (3a)-$UO_{2(O_2O_2)}$,MeOH;[40] (3a)-$VO_{(O_2O_2)}$;[38] (3d)-$VO_{(O_2O_2)}$, Me_2CO;[15] and (3d)-$Cu_{(O_2O_2)}$,[39] and have provided some interesting features.

The structure of (3d)-$Cu_{(O_2O_2)}$ has the Cu^{II} atom co-ordinated to the four oxygen atoms of the ligand leaving the —N_2O_2 compartment free.

The species is a mononuclear dimer in which the Cu^{II} atoms are raised to five co-ordination *via* an axial interaction with the central oxygen atom from an adjacent molecule (Figure 1).[39] The magnetic moment of the complex is normal down to 10 K indicating little, or no, exchange. The structure of (3d)-$VO_{(O_2O_2)}$, Me_2CO is composed of discrete monomeric molecules in which the oxovanadium (IV) is located within the —O_2O_2 compartment but displaced by 0.5 Å from the mean plane of the ligand oxygens.[15] The vanadium is therefore square pyramidal in geometry as it is in (3a)-$VO_{(O_2O_2)}$.[38] The acetone molecules are not co-

[36] S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, 1961, **35**, 105.
[37] R. H. Holm, *J. Amer. Chem. Soc.*, 1960. **82**, 5632.
[38] N. A. Bailey and C. A. Phillips, to be published.
[39] R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, 1976, **15**, 1633.
[40] R. Graziani, M. Vidali, U. Casellato, and P. A. Vigato, *Acta. Cryst.*, 1976, **B32**, 1681.

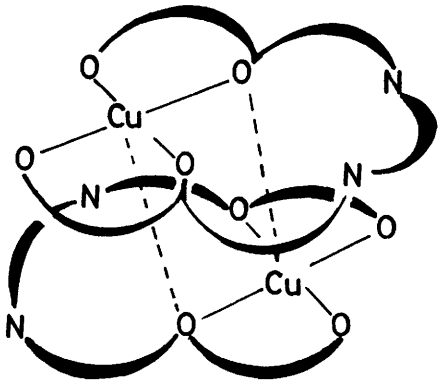


Figure 1 *Schematic diagram of the* (3d)-$Cu_{(O_2O_2)}$ *dimer*

ordinated. In both structures the NCCN bridge is aliphatic in character and joins the two fragments having π-delocalization.

This last feature may be contrasted with (3a)-$UO_{2(O_2O_2)}$, MeOH.[40] A structural study of this complex reveals two independent molecules having substantially similar molecular conformation, but chemically inequivalent ligands (Figure 2). In one species the NCCN bridge is aliphatic whereas in the other species an NC=CN chain is observed.

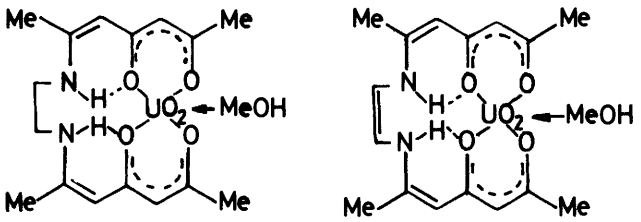


Figure 2 *Formulae units for* (3*a*)-$UO_{2(O_2O_2)}$,MeOH

It has not been established why such a dehydrogenation occurs: the synthesis is the reaction of the macrocycle (2; R = Me) with dioxouranium(VI) nitrate in methanol, neutralized with a methanol–water solution of lithium hydroxide. In both species the uranium occupies the —O_2O_2 compartment and achieves seven co-ordination through further equatorial co-ordination with a methanol molecule.

The i.r. spectrum of (3a)-$Cu_{(N_2O_2)}$ showed two free keto-stretches suggesting the presence of two dissimilar keto-groups in the solid state; only one band is seen in solution.[18] This is indicated in the crystal structure of this complex where the Cu^{II} atom occupies the —N_2O_2 chamber and the free keto-groups are non-symmetrically disposed.[38]

5 Homodinuclear Complexes

Homodinuclear complexes of copper(II), nickel(II), and cobalt(II) (Table 2) have been synthesized using the following techniques:

(i) a template procedure involving reaction of the parent keto-derivative, the diamine and the metal acetate;

(ii) stoicheiometric reaction of the acyclic Schiff base with metal acetate;

(iii) reaction of a pure, mononuclear isomer with the corresponding metal salt.

Table 2 *Homodinuclear complexes of acyclic Schiff bases*

CuCu	:	3a;[16,20] 3a,pyr;[16] 3a,4-Me-py;[16] 3c;[16] 3d;[16] 3e (X = Me, Me, Br);[16] 3f [16,34] 4a,$2H_2O$;[25,27,41] 4b,$2H_2O$;[25] 4b,$2.5H_2O$;[48] 4c,H_2O;[41] 4c,$2H_2O$;[25,27] 4f,$2H_2O$;[25] 4g,$2H_2O$[25] 5[29] 6a;[30] 6b;[30] 6c[30]
NiNi	:	3a,$2H_2O$;[16] 3a,2py;[16] 3d,3py;[15] 3d,MeOH[15] 4a;[27] 4a,$3H_2O$;[25] 4b,$3H_2O$;[34] 4c,$5H_2O$;[25] 4f,$3H_2O$;[25] 4g,$5H_2O$[25] 5[29] 6a,$2H_2O$;[30] 6b,$2H_2O$;[30] 6c,$2H_2O$[30]
CoCo	:	4a,3pyr;[28] 4a,MeOH,$\frac{1}{2}H_2O$;[28] 4c,3py;[28] 4c,$(MeOH)_2O_2$,$\frac{1}{2}H_2O$;[28] 4e,3py;[28] 4e,$(MeOH)_2O_2$,$\frac{1}{2}H_2O$;[28] 4f,3py;[28] 4f,MeOH,$\frac{1}{2}H_2O$;[28] 4g,3py;[28] 4gMeOH,$\frac{1}{2}H_2O$[28]

[Complexes of (3) in which R = R′ = Me and the bridging unit is —$CH_2CH(Me)$— and —$(CH_2)_3$— have yielded CuCu species, as has R = Me, R^1 = Ph with a —$(CH_2)_3$ bridge[16]]

The homodinuclear complexes of Ni^{II} and Co^{II} feature a class of compounds with two similar metals in juxtaposition but having different spin states and geometries. This is evidenced by the magnetic moments observed for the compounds of nickel in which values for isolated d^8 octahedral ions are recorded.[15,18,25,30] *X*-ray crystal structure analysis of (3d)-NiNi, 3py shows that one Ni^{II} atom is square planar and bonded in the —N_2O_2 compartment and that the second Ni^{II} atom is octahedral and in the —O_2O_2 compartment (Figure 3).[42] The co-ordinative saturation of this Ni^{II} atom is achieved through *trans*-axial addition of two pyridine molecules, whilst the third pyridine molecule remains non-co-ordinated. It is not unreasonable to assume that such a structure persists throughout the group of homodinuclear nickel complexes.

The magnetic moment of (3d)-NiNi, MeOH, 3.17 BM, indicates an octahedral environment which cannot be achieved from the formula unit unless some oligomerization occurs.[15]

[41] K. Dey and R. K. Maiti, *Indian J. Chem.*, 1976, **14A**, 602.
[42] M. D. Glick, R. L. Lintvedt, T. J. Anderson, and J. L. Mack, *Inorg. Chem.*, 1976, **15**, 2258.

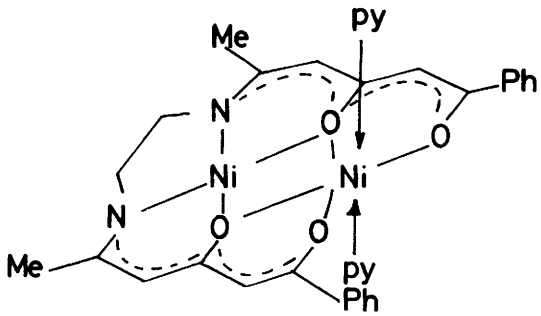
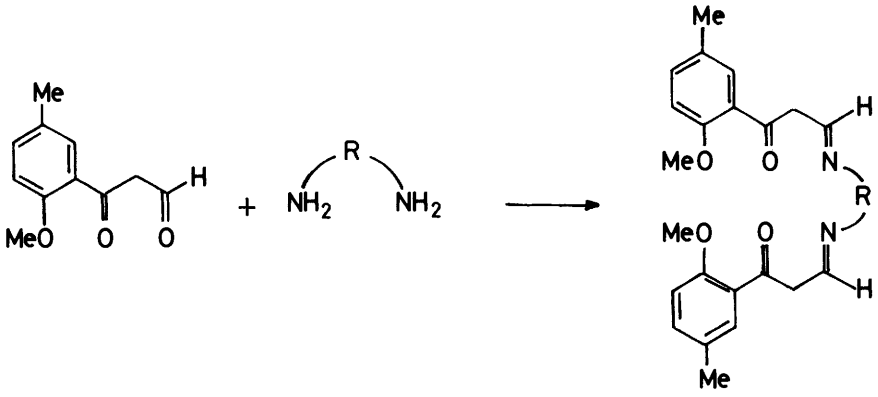


Figure 3 *Schematic view of* (3*d*)-NiNi,3py

The complexes (4)-CoCo,3py are proposed to have a dinuclear structure in which there are low-spin tetragonal-pyramidal and spin-free pseudo-octahedral cobalt(II) atoms present. This is supported by the reflectance spectra and magnetic moments of the complexes.[28] The compounds (4)-CoCo(MeOH)$_2$,O$_2$,$\frac{1}{2}$H$_2$O are tentatively assigned as dioxygen carriers as the colour changes from red to black on exposure to the atmosphere. The dioxygen is believed to be co-ordinated to the inner, N$_2$O$_2$, cobalt(II), by analogy with corresponding Schiff base complexes.

The Schiff bases, (8), may be prepared by the reaction of (7) with an α,ω-diamine (Scheme 3).[43] The mononuclear complexes formed by reaction of (8) with nickel(II) acetate are neutral and diamagnetic and so are likely to have the metal in the —N$_2$O$_2$ compartment. On adding an excess of nickel(II) acetate, the homodinuclear chelate, (8b)-NiNi(OAc)$_2$, has been obtained. It is paramagnetic with an effective magnetic moment of 2.57 BM per Ni^{II} atom; this



(8) a; R = —CH$_2$—CH$_2$—
b; R = —C$_6$H$_4$—, *para*

Scheme 3

[43] L. A. Khulkhachieva, G. A. Osipov, V. A. Kurbatov, and T. K. Dentsova, *Zhur. obschei Khim.*, 1976, **46**, 2703.

value is associated with an antiferromagnetic exchange between the metal atoms. The structure of this molecule is proposed to contain bridging acetate groups (Figure 4). The complex (4c)-NiNi,5H_2O has also been shown to have two paramagnetic nickel atoms present.[25]

The homodinuclear copper complexes provide an interesting class of compounds as they exhibit reduced magnetic moments for copper(II) at room temperature, quite strong antiferromagnetic exchange being observed (Table 3). This property parallels that found in dinuclear complexes of the parent triketones,[44] and is exemplified by (3f)-CuCu which is essentially diamagnetic at room temperature, has no e.p.r. signal, and gives a high resolution ^{1}H n.m.r. signal in chloroform.[16,34] (3f)-CuCu has also been shown to undergo reversible reduction in a one-step two-electron process per molecule; a colour change from green to yellow was discovered on electrolysis and it is believed that a stable copper(I) species is formed.[34] The *X*-ray crystal structure of (3f)-CuCu has been solved[38] and shows that the Cu—Cu distance, 2.98Å, is comparable to those found in β-triketonate complexes, 3.05—3.06Å.[44]

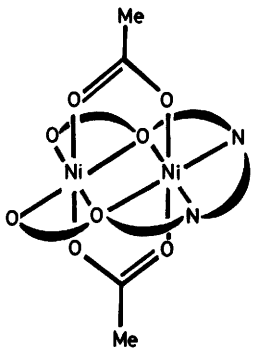


Figure 4 *Proposed structure of* (8*b*), NiNi$(OAc)_2$

Such molecules are of potential importance as models for the study of the so-called Type III copper sites in copper oxidases. This site has been shown to consist of pairs of copper atoms and is characterized by the lack of e.p.r. signal and the large antiferromagnetic coupling present.[45] The electronic spectra of the oxidases shows an absorption band near 330 nm, as do the binuclear complexes.

The binuclear copper complexes with (4a), (4b), (4c), (4f), and (4g) have similar geometric features at the binding sites, but the nature of the connecting bridge is changed.[25] The three alkyl linked species have similar $-2J$ values (650—660 cm^{-1}) whereas the other two complexes lie outside this range [720 cm^{-1} (4g) and 550 cm^{-1} (4f)]. [The spin–spin interaction from the coupling of unpaired electron spins on adjacent metals may be given by $H = -2J.\vec{S_1}\vec{S_2}$, where J is the

[44] M. D. Glick and R. L. Lintvedt, *Progress in Inorg. Chem.*, 1976, **21**, 233.
[45] J. A. Fee, *Struct. and Bonding*, 1975, **23**, 1.

Table 3 *Magnetic moments of dicopper complexes*

Complex	μ_{eff}	T/K	*ref.*
(4a)-CuCu,2H_2O	0.76	295.4	25
(4b)-CuCu,2H_2O	0.85	299.0	25
(4c)-CuCu,2H_2O	0.68	295.4	25
(4f)-CuCu,2H_2O	1.03	298.4	25
(4g)-CuCu,2H_2O	0.89	296.7	25
(3a)-CuCu	0.62	293	16
(3a)-CuCu,py	0.54	296	16
(3a)-CuCu,4-Me-py	0.57	295	16
(3d)-CuCu	0.37	293	16
(3f)-CuCu	0.39	300	16
(5)-CuCu	0.92		29
(6a)-CuCu	0.85	295	30
(6b)-CuCu	0.79	295	30
(6c)-CuCu	0.85	295	30

exchange integral and $|2J|$ is the energy separation between the singlet and triplet states. Negative J values indicate ground-state spin-pairing and antiferromagnetic behaviour. In the complexes described here, the mechanism of antiferromagnetic exchange is believed to be a superexchange operating *via* the bridging atoms present.] Given the changes in $-2J$ it is conceivable that by changing either the nature of the bridge, or the side-chain substituents, that a series of ligands could be constructed to provide varying degrees of magnetic interaction.

As with the dinickel complexes it is possible to juxtapose two copper atoms with different co-ordination geometries. *X*-ray crystal structure analysis of (5)-CuCu,H_2O shows that one Cu^{II} is square planar —N_2O_2 and the second is five-co-ordinate being bound to the —O_2O_2 site and to an axial water.[46] The Cu^{II} atom is square pyramidal with the metal lying 0.21Å above the —O_2O_2 plane. The Cu—Cu distance is 2.96Å which compares with that found in (3f)-CuCu. The molecules, related by screw axes, are bridged by hydrogen bonding from the water molecule of one unit to the terminal oxygen atoms of the succeeding unit.

6 Heterodinuclear Complexes

A. Complexes involving only Transition Metals.—A comprehensive range of heterodinuclear complexes derived from ligands (3), (4), (5), and (6) have been prepared by reaction of the pure mononuclear precursor with the required metal salt (Table 4). These reactions are often carried out in the presence of alkali hydroxide, *e.g.*,

[46] R. Graziani, M. Vidali, U. Casellato, and P. A. Vigato, *Transition Metal Chem.*, 1978, 3, 138.

$$(3a)\text{-}Ni_{(N_2O_2)} + UO_2(OAc)_2 \xrightarrow{EtOH} (3a)\text{-}NiUO_2,C_2H_5OH$$

$$(4a)\text{-}VO_{(N_2O_2)} + Ni(OAc)_2 + LiOH \xrightarrow{H_2O} (4a)\text{-}VONi,2H_2O$$

$$(5a)\text{-}Cu_{(N_2O_2)} + Mn(OAc)_2 + LiOH \xrightarrow[EtOH]{pyridine} (5)\text{-}CuMn$$

Table 4 *Heterodinuclear complexes of acyclic Schiff bases**

3a :	$CuVO,H_2O$;[16] CuZn;[16] $CuUO_2,2H_2O$;[20] $CuUO_2,EtOH$;[16] $CuNi,2H_2O$[20] NiCu;[16] NiCu,py;[16] $NiVO,H_2O$;[16] NiZn,EtOH;[16] $NiUO_2,2H_2O$;[20] $NiUO_2,EtOH$[16]
3d :	NiCu[15,16] NiZn;[15] $NiZn,H_2O$;[16] NiZn,py;[15] $NiUO_2,EtOH$;[16] NiVO;[15,16] NiCo,MeOH;[15] NiMn,MeOH;[15] $(NiFe,H_2O)_2\text{-}O$;[15]
4a :	$CuNi,H_2O$[27] $CuNi,2H_2O$;[41] $CuNi,3H_2O$;[17] $CuCo,3H_2O$;[17] $CuFe,2H_2O$;[17] $CuMn,H_2O$;[17] $CuZn,\frac{3}{2}H_2O$;[31] CuVO,MeOH;[47] $CuVO,H_2O$;[41] $CuUO_2,2H_2O$;[27] CuTh/2,H_2O;[27] $CuNa_2,H_2O$;[6] CuBa[6] $NiCu,H_2O$;[17] $NiCo,2H_2O$;[17] $NiFe,2H_2O$;[17] NiCd;[32] $NiMn,2H_2O$;[17] $NiVO,H_2O$;[41] $NiUO_2,2H_2O$;[27] NiTh/2,H_2O;[27] $NiNa_2,H_2O$[6] $VOMn,3H_2O$;[32] $VOZn,3H_2O$;[32] $VONi,2H_2O$;[41] $VOCu,2H_2O$;[41] $VOPd,H_2O$[41]
	$CoNa_2$;[6] CoBa[6]
	$ZnMn,4H_2O$[31]
	UO_2Na_2[6]
4b :	$CuNi,2H_2O$;[33] $CuCo,2H_2O$;[33] $CuLi_2,2H_2O$;[26,48] $CuNa_2,4H_2O$;[26,48] $CuMg,H_2O$;[26,48] $CuCa,5H_2O$;[26,48] $CuSr,3H_2O$;[26,48] $CuBa,2H_2O$[26,48] $NiLi_2,4H_2O$;[26,48] $NiNa_2,4H_2O$;[26,48] $NiMg,2H_2O$;[26,48] $NiSr,3H_2O$;[26,48] $NiBa,5H_2O$;[26,48] $NiCa,3H_2O$[26,48]
4c :	$CuNi,2H_2O$[33]
	$NiCu,2H_2O$;[41] $NiVO,2H_2O$[41]
	$VONi,H_2O$;[41] $VOCu,H_2O$;[41] $VOPd,H_2O$[41]
4e :	$CuCo,2H_2O$[33]
4f :	$CuNi,2H_2O$[33]
4g :	$CuNi,5H_2O$,[33] $CuCo,2H_2O$;[33] $CuVO,4H_2O$;[41] $CuNa_2,H_2O$[6] $NiVO,2H_2O$;[41] $NiNa_2,H_2O$[6] $VONi,5H_2O$;[41] $VOCu,H_2O$;[41] VOPd[41]
	$CoNa_2$;[6] CoBa[6]
4h :	$CuLi_2,1.5H_2O$;[26] $CuNa_2,5H_2O$;[26] CuLiNa,$4H_2O$;[26] $CuMg,4H_2O$;[26] $CuMg,2.5H_2O$;[26] $CuSr,4H_2O$;[26] $CuBa,2H_2O$[26]
5 :	$UO_2Li_2,2H_2O$[29]
6a :	$UO_2Li_2,2H_2O$[30]
6b :	$UO_2Li_2,2H_2O$[30]

* N_2O_2 occupancy precedes O_2O_2 occupancy.

N.B. The alkali metal derivatives are included since, although there are three metals present, the precise nature of the species could allow for an anionic bimetallic species.

[47] O. Kahn, P. Tola, J. Galy, and H. Coudanne, *J. Amer. Chem. Soc.*, 1978, **100**, 3931.
[48] D. J. Phillips, N. S. Rawat, and S. K. Tiwari, *J. Inorg. Nuclear Chem.*, 1977, **39**, 797.

The formula unit is written out with the metal occupying the —N_2O_2 compartment preceding that occupying the —O_2O_2 compartment. In general the precursor has the inner compartment filled as this would provide a more accessible site for the incoming metal. It is, however, possible to use either occupancy in the precursor provided that the metal affinity for the occupied site is strong enough to inhibit metal exchange processes, *e.g.*,

$$(3a)\text{-}UO_{2(O_2O_2)},H_2O + Cu(OAc)_2 \xrightarrow{EtOH} (3a)\text{-}CuUO_2,EtOH$$

$$(3a)\text{-}Cu_{(N_2O_2)} + UO_2(OAc)_2 \xrightarrow{EtOH} (3a)\text{-}CuUO_2,EtOH$$

The occupancy of the complexes may be deduced by reference to electronic spectra, magnetic moments, and *X*-ray analysis.

Nickel(II) complexes have been used extensively as the starting point for heterodinuclear species. The exclusive preference of Ni^{II} for the —N_2O_2 site makes metal exchange processes unlikely, and as this Ni^{II} is diamagnetic any contribution to the magnetic moment comes from the —O_2O_2 occupancy. This is illustrated by the moments for (3d)-NiCu, (1.89 BM),[15] 3d-NiVO, (1.71 BM),[15] (4a)-NiCo,$2H_2O$, (5.15 BM),[17] and 4a-NiMn,$2H_2O$, (5.71 BM),[17] where the recorded values are those for isolated d^9, d^1, high spin d^7, and high spin d^5 ions respectively. Complexes such as (3a)-NiZn are diamagnetic, and some magnetic moments are not so straightforward to explain. Those recorded for (3d)-NiCo, CH_3OH, (4.92 BM),[15] and (3d)-NiMn, MeOH, (5.81 BM)[15] all indicate octahedral occupancy of the —O_2O_2 chamber which cannot be realized unless oligomerization has occurred. One possible explanation is depicted in Figure 5, but as yet there is no crystallographic confirmation. The i.r. spectrum of [(3d)-NiFe, $H_2O]_2O$[15] shows a band at 840 cm^{-1} corresponding to the value indicative of an Fe^{III}—O—Fe^{III} bridge,[49] and this is supported by the Mössbauer spectrum. The magnetic properties show a room temperature moment of 2.0 BM

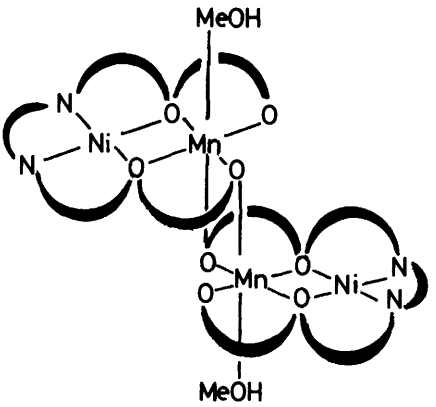
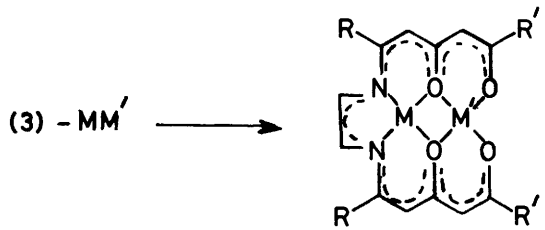


Figure 5 *Proposed structure of* (3d)-NiMn,MeOH

[49] K. S. Murray, *Coord Chem. Rev.*, 1974, **12**, 1.

which decreases to 1.0 BM at 77 K due to strong antiferromagnetic coupling between the iron atoms. Each iron is therefore co-ordinated to four ketonic oxygens, one water molecule and a bridging O^{2-} ion.

The crystal structures of (3d)-NiZn, pyridine, and (3d)-NiVO have been determined[50] and confirm the $—N_2O_2$ occupancy of Ni^{II}. The zinc atom is five-co-ordinated to the four outer oxygen atoms and to an axial pyridine molecule. The environments of the metals are quite typical of metals co-ordinated to β-diketonates or Schiff bases. There is a decrease in the C—C bond length in the ethylenediamine bridge on metal incorporation; in the mononuclear chelates (3d)-$Cu_{(O_2O_2)}$ and (3d)-$VO_{(O_2O_2)}$ the distance is 1.53 Å whereas when the nickel is co-ordinated in the inner site the distance is 1.46 Å. This bond shortening has been seen to favour a dehydrogenation reaction observed to take place in the mass spectrometer,[15,16] The mass spectra of all the binuclear chelates of (3) contain intense peaks due to the loss of two protons from the ethylenediamine bridge to give a product having a conjugated π-system extended throughout the molecule.



It is of interest to recall at this point the crystal structure of (3a)-UO_2,MeOH, in which such a dehydrogenation was detected.

The heterodinuclear complexes, (3)-CuM are believed to follow similar patterns of behaviour as a consequence of the established co-ordination patterns. As Cu^{II} is a d^9 system it is not possible to make unambiguous assignment on the grounds of magnetism alone. The complex (3a)-CuVO gave a moment of 0.88 BM per metal atom suggesting that a fairly strong antiferromagnetic exchange occurs in this molecule.[16] The *X*-ray structure of this complex confirms the site occupancy with square planar, $—N_2O_2$, Cu^{II} adjacent to square pyramidal vanadium in the $—O_2O_2$ compartment.[38]

Chemical evidence for the preference of Ni^{II} for $—N_2O_2$ was seen in the reaction of (3a)-$Cu_{(N_2O_2)}$ with nickel(II) acetate. (3a)-$Ni_{(N_2O_2)}$ was isolated, a straightforward metal exchange reaction having occurred, together with some (3a)-CuCu.[16] The heterodinuclear complex (3a)-CuNi has been reported by a procedure involving the prior formation of (3a)-$CuNi(ClO_4)_2$ and subsequent reaction of the compound with lithium hydroxide to give (3a)-CuNi.[20]

The positional isomers (4a)-CuNi,$3H_2O$ and (4a)-NiCu,H_2O may be readily distinguished by their spectral and magnetic properties.[17] The latter shows in its

[50] M. D. Glick, R. L. Lintvedt, D. P. Gavel, and B. Tomlonovic, *Inorg. Chem.*, 1974, **15**, 1654.

reflectance spectrum bands at 833 and 526 nm assigned to $Cu_{(O_2O_2)}$ and $Ni_{(N_2O_2)}$ respectively. The magnetic moment of 1.87 BM is indicative of an isolated d^9 ion. In contrast the magnetic moment of (4a)-CuNi,$3H_2O$ is 3.05 BM, and can be explained by applying the phenomenological model of Heisenberg–Dirac–Van Vleck for intramolecular exchange, assuming square planar Cu^{II} adjacent to octahedral Ni^{II}. The Ni^{II} would have *trans*-axial water molecules present to effect co-ordinative saturation.

Several magnetic studies have been carried out on heterobinuclear complexes of (4)[17,31–33,47,51] and (5).[52] Those complexes having Ni^{II} in the $—N_2O_2$ compartment have given magnetic moments according to the isolated spin system present in the $—O_2O_2$ compartment. For the other complexes magnetic exchange processes have been invoked, usually antiferromagnetic in nature. Representative of these studies are those on (4a) with CuVO, VOMn, CuNi, and CuMn.[31,32,47]

The magnetic behaviour for (4a)-VOMn perfectly obeys the Curie–Weiss law in the range 10—300 K and $|J|$ is less than 5 cm^{-1}.[32] This result may be contrasted with (4a)-CuMn in which $J = -62$ cm^{-1}.[31] It is proposed that it is possible for the antiferromagnetic contribution to be cancelled by a strong ferromagnetic contribution between the a_1 magnetic orbital on the vanadium and the five magnetic orbitals on the manganese. A relatively strong ferromagnetic contribution is found in (4a)-CuVO,MeOH ($J = 118$ cm^{-1}) and in this molecule there is an increase of $\chi_m T$ on cooling to 50 K but below 18 K the dominant contribution is an intermolecular antiferromagnetic coupling.[47]

This latter phenomenon is also observed below 17 K for (4a)-CuNi, and throughout the range 3—300 K for (4a)-CuMn, where it adds itself to the intramolecular coupling.[31] The intermolecular coupling is postulated as arising from the oligomeric structure of the complexes with either water molecules, or the ligand oxygens, bridging the metals in the outer compartments. The (4a)-CuNi complex crystallizes with three water molecules present and the $Ni_{(O_2O_2)}$ would be expected to be six-co-ordinated and each Ni^{II} therefore separated from neighbouring complex molecules by two water molecules. (4a)-CuMn has only one water molecule which likely occupies a bridging position between two Mn^{II} atoms facilitating exchange. In pursuit of the origin of this intermolecular exchange the complexes (4a)-CuZn and (4a)-ZnMn were synthesized.[31] In the former intermolecular exchange between copper atoms is negligible whereas for the latter a non-negligible coupling is detected between the outer Mn^{II} ions. The presence of intermolecular exchange can lessen the accuracy of determination of parameters for the intramolecular process. Therefore it was proposed that adducts yielding single crystals would provide more useful information here. The versatility of $(4a)^{4-}$ is emphasized for magnetic studies as both M_AM_B and M_BM_A complexes may be prepared and studied in order to

[51] N. Torihara, H. Okawa, and S. Kida, *Chem. Letters*, 1978, 185.
[52] M. Vidali, G. Rizzardi, P. A. Vigato, U. Casellato, S. Kida, and H. Okawa, *Inorg. Chim. Acta.*, 1979, **34**, 19.

gain insight into exchange processes. (4a)-NiCd has been prepared and used as a standard for the correction for diamagnetism in magnetic studies.[32]

The crystal structure of (4a)-CuCo,$3H_2O$ has been determined.[53] Spectral and magnetic assignments indicate that the copper is square planar and N_2O_2, and in the crystal structure one metal is in this environment, the other is octahedrally bound to the ligand and two *trans*-axial water molecules. It is concluded that the spectral assignments are confirmed. The bond distances from Co^{II} to the bridging oxygen is slightly longer than to the terminal oxygen, a feature common to other dinuclear complexes of Schiff bases.[50] The third water molecule is not co-ordinated. The terminal carbonyl oxygen (O^3) and the water molecule (O^4) co-ordinated to the cobalt atom of the adjacent molecule are hydrogen-bonded. The absolute configuration of the packing is that of a left-handed helix and each binuclear complex points its —O_2O_2 moiety towards the inside of the helix where the crystal water molecules are held.

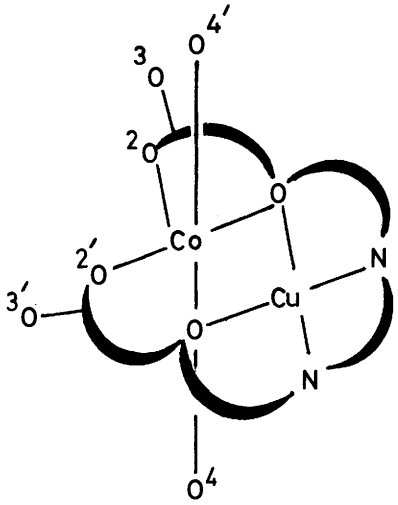


Figure 6 *Schematic view of* (4a)-CuCo,$3H_2O$

In contrast (4a)-CuVO,MeOH has both Cu^{II} and vanadium present in square pyramidal geometry.[47] The unusual feature here is that the Cu^{II} atom in the —N_2O_2 compartment retains a solvent molecule which leads to the suggestion that the metal may have been activated by the adjacent vanadium. It is also possible that the solvent is retained as a packing requirement as no similar feature is noted in (3a)-CuVO.[38]

Retention of solvent by an inner chamber metal is also detected in the *X*-ray crystal structure of (5)-$CuUO_2$,$(dmso)_2$. (Figure 7). The uranium in the —O_2O_2

[53] M. Mikuyira, H. Okawa, S. Kida, and I. Ueda, *Bull. Chem. Soc. Japan*, 1978, **51**, 2920.

compartment achieves its preferred seven co-ordination by adding an equatorial dmso molecule. The Cu^{II} in the inner compartment is slightly distorted from square pyramidal geometry through ligation with dmso.[54] In (5)-CuCu,H_2O the inner Cu^{II} is rigorously square planar and the whole ligand is planar, whereas in the $CuUO_2$ complex a distortion occurs at the dioxouranium(VI) which may in turn modify the requirements of the Cu^{II}.[46]

In (5)-$NiUO_2$, dmso the uranium is again seven co-ordinate and the Ni^{II} is four co-ordinate.[55] Although the electronic spectra, and magnetic moment suggest a square planar environment, a severe distortion occurs such that the Ni^{II} is in a trigonal bipyramidal environment with one equatorial site vacant (Figure 8). Models show that it is impossible to accommodate the dioxouranium-(VI) without severe ligand distortion so inhibiting the achievement of a square

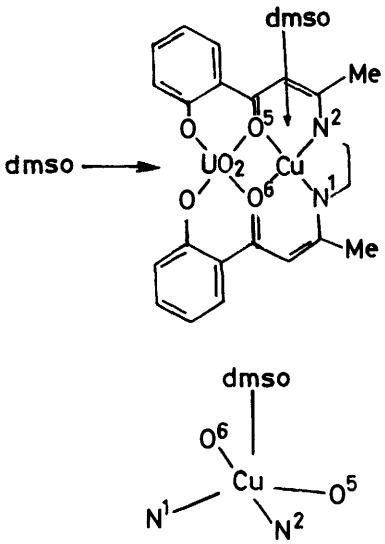


Figure 7 *The* Cu *environment in* (5)-$CuUO_2$,2dmso

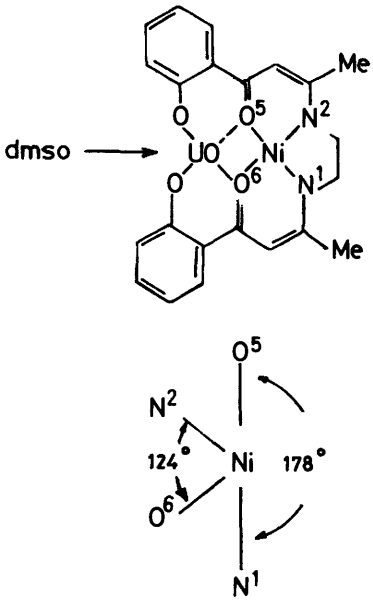


Figure 8 *The* Ni *environment in* (5)-$NiUO_2$,dmso

planar compartment. Why the Ni^{II} is not solvated, as is Cu^{II} in the analogous complex, is not certain. The presence of such a distorted Ni^{II} could be viewed as an entatic situation[56] and a heightened reactivity expected. Crystal packing forces might also be dominant in deciding the degree of distortion.

[54] R. Graziani, M. Vidali, U. Casellato, and P. A. Vigato, *Transition Metal Chem.*, 1978, **3**, 239.

[55] R. Graziani, M. Vidali, U. Casellato, and P. A. Vigato, *Transition Metal Chem.*, 1978, **3**, 99.

[56] B. L. Vallee and R. J. P. Williams, *Proc. Nat. Acad. Sci. U.S.A.*, 1968, **59**, 498.

B. Complexes involving Non-transition Metals.—Heterodinuclear complexes have also been derived from mononuclear transition metal complexes and alkali and alkaline earth metals[6,26,27,29,30,48,57] (Table 4). They are prepared either by reaction of the Schiff base, metal(II) acetate and sodium hydroxide, followed by metatheses to recover the other alkali and alkaline earth metal complexes,[26,48] or be reaction of the mononuclear transition metal complex with metal hydroxide or acetate.[57] Varying degrees of hydration have been observed, depending upon the reaction conditions.

The molar conductivities, in water, show that the (4b), and (4h)-$CuLi_2$ series are uni-univalent electrolytes and so suggest that the species present is Li[(4)-CuLi],nH_2O, (Figure 9a).[26,48] The corresponding complex derived from (4a)-$Cu_{(N_2O_2)}$ has been obtained and the crystal structure shows that the type of structure proposed above exists in the solid state.[58] This complex is also a uni-univalent electrolyte in water.[57] The corresponding disodium complexes are uni-bivalent electrolytes indicating that, in solution, the species present is Na_2[(4)-Cu]. The dipotassium and dicaesium derivatives are also uni-bivalent electrolytes.[57] The nickel analogues follow the same trends and are therefore likewise formulated.

For the alkaline earth metal complexes, only the magnesium complexes were soluble enough to determine the conductivity in methanol. The value indicates a non-electrolyte, and so suggests a dinuclear species with the magnesium in the outer compartment. This is confirmed by the *X*-ray structure of (4a)-CuMg,$3H_2O$. The magnesium is six-co-ordinate and in the outer compartment; two *trans*-axial water molecules help achieve saturation, (Figure 9b).[59]

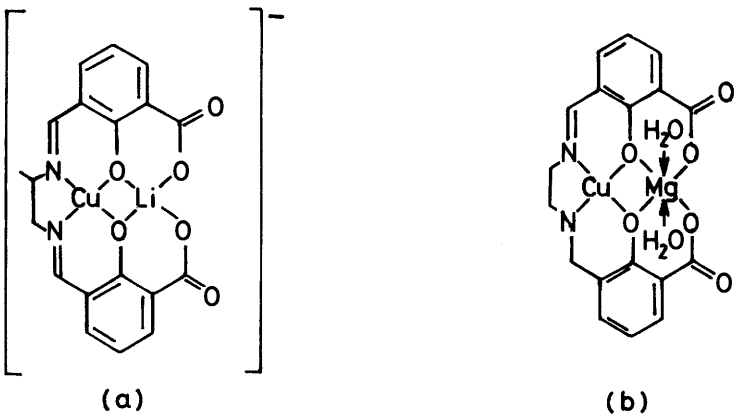


Figure 9 *Proposed structures of* (a), Li [(4b)-CuLi] (b), (4a)-CuMg,$3H_2O$

There is considerable colour change on adding alkali or alkaline earth metals to the copper precursors. CuLi and CuMg complexes are red and as the size of

[57] D. E. Fenton, R. Auty, and A. I. M. Howat, unpublished results.
[58] D. Craig, personal communication reported in reference 51.
[59] D. E. Fenton and L. Randaccio, unpublished results.

the added metal ion increases there is a steady reversion to the violet colour of the Cu complex. A band at *ca.* 515 nm is evident in the CuLi and CuMg dinuclear species and this moves steadily towards *ca.* 560 nm for the parent species and beyond it to 568 nm for the barium complexes. This can be viewed as a steady movement away from occupancy of the outer compartment by the second metal, or as the consequence of gross distortion of the ligand by incorporating the larger metals thus modifying the Cu—N and Cu—O bond lengths. This trend has also been seen in dinuclear complexes derived from Cu(salen) and alkali or alkaline earth metal hexafluoroacetylacetonates.[57] Attempts to prepare the mononuclear dioxouranium(VI) complex of (4a) have so far been unsuccessful, but it has been possible to isolate the well-defined complex $Li_2[(4a)\text{-}UO_2],2H_2O$.[27] On the basis of the known selectivity of uranium, and from i.r. studies in which the carboxylates are shown to be unidentate the co-ordination sphere around this metal is proposed as containing the two carboxylic and two phenolic oxygens, and one water molecule (Figure 10).[27]

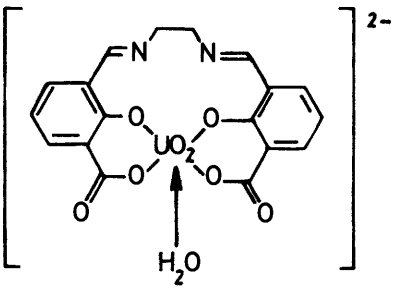


Figure 10 *Proposed formulation of the dianion in* $Li_2[(4a)\text{-}UO_2,H_2O]H_2O$

A dilithium complex, $Li_2[(5)\text{-}UO_2],2H_2O$ has been prepared by the reaction of dioxouranium(VI) nitrate, *o*-hydroxyacetylacetophenol, 1,2-diaminoethane, and lithium hydroxide in a water–methanol mixture.[29] The uranium is proposed as seven-co-ordinate and a similar structure to that shown in Figure 10 is invoked. This complex has been used as a precursor in the synthesis of heterodinuclear complexes containing UO_2^{2+} and Cu^{II} or Ni^{II}.

One synthetic route to heterodinuclear complexes of (5) involves the reaction of the mononuclear precursor with LiOH and metal(II) acetate. It is possible to isolate (5)-$CuLi_2$,[52] and (5)-$NiLi_2$.[57] Attempts to isolate the corresponding disodium complexes has resulted in recovery of the mononuclear complex, and provides further illustration of a cation size effect present in these alkali metal species.

7 Conclusions

It is apparent from the work reported here that this area provides many opportunities for development. The chemical reactivity of these systems is largely unexplored, but the hint that metals may be guided into unusual geometries and

hence reactivity is present. The dinuclear copper(II) complexes lend themselves to study as mimics for the Type III coppers in metalloenzymes, and information on site preference and metal exchange could also be of use in biological areas. The versatility of the ligands also allows a wide range of heterodinuclear complexes to be synthesized. This is of significance in the study of intramolecular magnetic coupling, and it would be possible to employ positional isomers of the type $M_{(N_2O_2)}M'_{(O_2O_2)}$, and $M'_{(N_2O_2)}M_{(O_2O_2)}$ to advantage in this area.

For the future, interest has already developed in encapsulating metals within ligands such as cryptands.[60,61] Two homodinuclear copper complexes have been reported which give an available cavity for substrate inclusion. The development of this area to heterodinuclear complexes is of some interest. Finally 'face to face' porphyrins have been developed, and both homo- and hetero-dinuclear complexes synthesized and it has been proposed that dinuclear iron complexes of these ligands could be capable of catalysing the four-electron reduction of dioxygen to water.[62]

[60] J. M. Lehn, S. H. Pine, E. Watanabe, and A. K. Willard, *J. Amer. Chem. Soc.*, 1977, **99**, 6766.
[61] R. Louis, Y. Agnus, and R. Weiss, *J. Amer. Chem. Soc.*, 1978, **100**, 3604.
[62] J. P. Collman, C. M. Elliott, T. R. Halbert, and B. S. Tourog, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 18.