Compartmental Ligands. Part 3.[1] Homo- and Hetero-binuclear Transition-metal Complexes of Acyclic Schiff Bases derived from 1,3,5-Triketones

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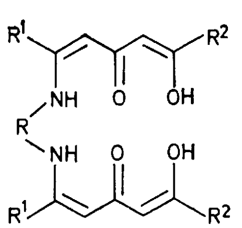
Acyclic Schiff bases derived from 1,3,5-triketones and α,ω-alkanediamines have two ligand compartments for metal co-ordination, one based on N_2O_2 and the other on O_2O_2 donor sets. Homo- and hetero-binuclear metal complexes of such ligands have been prepared and the nature of the site occupancy investigated. The mononuclear complexes [6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(2−)-$N^7N^{10}O^4O^{13}$]copper(II) (5a; M = Cu) and 5,10-dimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-$N^6N^9O^3O^{12}$]copper(II) (5m; M = Cu) have been treated with various metal(II) acetates to give Cu_2, Ni_2, $CuUO_2$, CuVO, CuZn, NiCu, $NiUO_2$, NiVO, and NiZn derivatives. The first named metal is retained in the N_2O_2 compartment of the ligand, whilst the second occupies the O_2O_2 compartment. The pattern of incorporation, and the purity of the binuclear species, have been established by i.r., diffuse-reflectance, and mass spectra and room-temperature magnetic-moment studies. Several dicopper(II) complexes of a range of aliphatic and phenyl-substituted acyclic Schiff bases have also been prepared.

Acyclic Schiff bases (1) derived from the reaction of symmetrical or unsymmetrical 1,3,5-triketones with α,ω-alkanediamines were reported in Part 2,[1] together with the syntheses and properties of their mononuclear transition-metal complexes. These ligands have available two adjacent, and dissimilar, co-ordination compartments, the donor sets of which resemble either 1,3-diketones (O_2O_2) or Schiff bases of 1,3-diketones (N_2O_2).



	R	R¹	R²
(1a)	$[CH_2]_2$	Me	Me
(1l)	$[CH_2]_2$	Me	Bu^t
(1m)	$[CH_2]_2$	Me	Ph
(1n)	$[CH_2]_2$	Me	C_6H_4OMe-*p*
(1o)	$[CH_2]_2$	Me	C_6H_4Me-*p*
(1p)	$[CH_2]_2$	Me	C_6H_4Br-*p*

The pattern of co-ordination selectivity of these ligands was established as $Ni(N_2O_2)$, $VO(O_2O_2)$, and $UO_2(O_2O_2)$ regardless of the nature of the substituent group (*i.e.* $R^1 = R^2 =$ alkyl; $R^1 =$ alkyl, $R^2 =$ Ph). Copper(II) displayed a more ambivalent character; when $R^1 =$ alkyl, $R^2 =$ Ph, the O_2O_2 compartment was occupied, yet when $R^1 = R^2 =$ alkyl the N_2O_2 compartment was filled. For the case $R^1 = R^2 =$ Me, it was also possible to isolate the N_2O_2 and O_2O_2 positional isomers of Cu.

The isolation of pure isomers of these mononuclear complexes provides a basis for the synthesis of hetero-binuclear complexes, as, in the absence of metal-exchange reactions, a second metal may be incorporated into the vacant compartment. The availability of ligand compartments of different donor properties also permits the synthesis of homobinuclear complexes in which it is possible to have two ions of the same metal present in different geometries, spin states, or oxidation numbers. This provides an opportunity to study the spectral and chemical properties of metals in such juxtaposition. The magnetic properties of the binuclear cluster may also give information concerning exchange parameters.

This paper reports the synthesis and properties of homo- and hetero-binuclear complexes of acyclic Schiff-base ligands. Preliminary communication of this work has been made.[2,3]

RESULTS AND DISCUSSION

Investigation of the reactions of metal Schiff-base complexes with metal 1,3-diketonates to yield binuclear complexes such as [Cu(salen)Mg(hfpd)$_2$] and [Cu(salen)-Co(hfpd)$_2$] [4] [salen = *NN'*-ethylenebis(salicylideneiminate), hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dione] led us to conclude that the fusion of a 1,3-diketone, with its O_2O_2 donor set, and a Schiff base, with its N_2O_2

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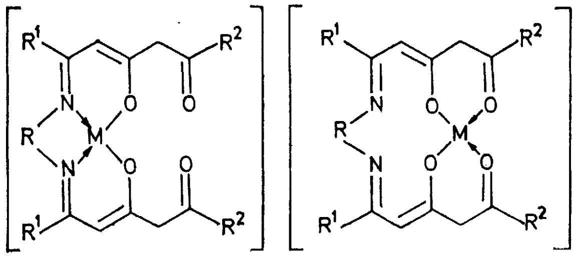
[1] Part 2; D. E. Fenton and S. E. Gayda, preceding paper.

[2] D. E. Fenton and S. E. Gayda, *Inorg. Chim. Acta*, 1975, **14**, L11.

[3] D. E. Fenton, S. E. Gayda, and R. S. Z. Kowalski, *Transition Metal Chem.*, 1976, **1**, 95.

[4] D. E. Fenton and S. E. Gayda, unpublished work.

donor set, could give a ligand capable of heterobinuclear complex formation. In reactions of the above species the process of metal exchange, such that specific site preferences could be accommodated, was demonstrated in the reaction of [Cu(hfpd)$_2$] with [Co(salen)].[5] The single-crystal *X*-ray structure of the product showed that the metal atoms exchanged primary co-ordination spheres to give [Cu(salen)Co(hfpd)$_2$].[5] Thus it appeared that in the proposed ligands a predictive approach could be made to the synthesis of heterobinuclear complexes if the co-ordination selectivity of the metal atoms for a given site in the ligand was first established.



	R	R¹	R²	
(5a)	[CH$_2$]$_2$	Me	Me	(6a)
(5b)	CH(Me)CH$_2$	Me	Me	
(5m)	[CH$_2$]$_2$	Me	Ph	(6m)

The potentially binucleating acyclic Schiff bases (1) were synthesised and the pattern of co-ordination selectivity established in mononuclear complexes in order that pure positional isomers arising from specific co-ordination could be used as precursors for heterobinuclear complexes.[1] This approach was chosen as if a mixture of both metals to be co-ordinated and the ligand were allowed to react a statistical distribution of homobinuclear, heterobinuclear, and mononuclear complexes could arise. The characterised mononuclear complexes were used as ligands to co-ordinate a second metal, and, in the absence of metal-exchange reactions, pure heterobinuclear chelates were obtained. These products were characterised by several physical methods. Of the available range of acyclic Schiff bases, 6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone (1a) and 5,10-dimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1m) were chosen for study. For these ligands it was established that the pure mononuclear chelates (5a) and (5m) (M = Ni), (6a) and (6m)·Me$_2$CO (M = VO), and (6a)·MeOH and (6m)·EtOH (M = UO$_2$) were readily isolated, establishing a selectivity pattern for the ligands. The behaviour of Cu^{II} with these ligands however is ambivalent; only (6m)·H$_2$O is isolated but both positional isomers, (5a) and (6a)·H$_2$O (M = Cu) may be recovered from the reaction of Cu[O$_2$CMe]$_2$ with (1a).

The pure complexes (5) having the first metal co-ordinated to the N$_2$O$_2$ donor set were investigated further. These were chosen as it was expected that their open jaws would act more readily as a donor site than would the empty N$_2$O$_2$ compartment in (6). Furthermore, square-planar d^8 Ni^{II} is diamagnetic and so any magnetic moment of the heterobinuclear species should arise from occupation of the O$_2$O$_2$ compartment. It would be expected that Ni^{II}, if it had migrated to the O$_2$O$_2$ compartment, would be paramagnetic because of the achievement of co-ordinative saturation through oligomerisation, or solvation, as occurs in nickel(II) diketonates.[6]

Heterobinuclear complexes, (9), were prepared by using the pure mononuclear metal complex as a donor ligand in its reaction with an equimolar amount of the acetate of the second metal in a suitable solvent [*e.g.* equations (1)—(3)]. Complexes of UO$_2$ have a molecule

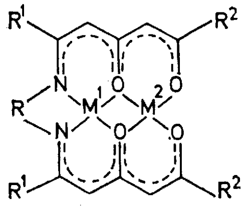
$$(5a;\ M = Ni) + Cu[O_2CMe]_2 \longrightarrow (9a;\ M^1 = Ni, M^2 = Cu) \quad (1)$$

$$(5a;\ M = Ni) + [VO][O_2CMe]_2 \longrightarrow (9a;\ M^1 = Ni, M^2 = VO) \quad (2)$$

$$(5a;\ M = Cu) + [UO_2][O_2CMe]_2 \longrightarrow (9a;\ M^1 = Cu, M^2 = UO_2)\cdot EtOH \quad (3)$$

of solvation to complete the preferred seven-co-ordination of uranium.

The homobinuclear complexes, (8), were prepared by one of the following routes: (*a*) a template procedure involving reaction of the parent triketone, the diamine, and Cu[O$_2$CMe]$_2$ in hot ethanol; (*b*) reaction of the phenyl-substituted Schiff base (1 mol) with Cu[O$_2$CMe]$_2$ (2 mol) in chloroform–ethanol; (*c*) reaction of the pure mononuclear, positional isomer (1 mol) with the corresponding metal acetate (1 mol); or (*d*) reaction of a macrocyclic Schiff base, dissolved in CHCl$_3$, with Cu[O$_2$CMe]$_2$ dis-



(M¹ = M²)	R	R¹	R²	(M¹ ≠ M²)
(8a)	[CH$_2$]$_2$	Me	Me	(9a)
(8b)	CH(Me)CH$_2$	Me	Me	
(8c)	[CH$_2$]$_3$	Me	Me	
(8g)	[CH$_2$]$_2$	Pr^n	Pr^n	
(8l)	[CH$_2$]$_2$	Me	Bu^t	
(8m)	[CH$_2$]$_2$	Me	Ph	(9m)
(8n)	[CH$_2$]$_2$	Me	C$_6$H$_4$OMe-*p*	
(8o)	[CH$_2$]$_2$	Me	C$_6$H$_4$Me-	
(8p)	[CH$_2$]$_2$	Me	C$_6$H$_4$Br-*p*	
(8r)	[CH$_2$]$_3$	Me	Ph	
(8t)	CH(Me)CH$_2$	Me	C$_6$H$_4$OMe-*p*	
(8u)	[CH$_2$]$_3$	Me	C$_6$H$_4$Me-*p*	

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[5] N. B. O'Bryan, T. O. Maier, I. C. Paul, and R. S. Drago, *J. Amer. Chem. Soc.*, 1973, **95**, 6640.

[6] J. P. Fackler, jun., *Progr. Inorg. Chem.*, 1966, **7**, 361.

solved in water [used only for the preparation of (8c) and (8l) ($M^1 = M^2 =$ Cu)].

The i.r. spectra of the mononuclear complexes (5) show bands at *ca.* 1 700 cm^{-1} which are assigned to the uncoordinated carbonyl functions in the empty O_2O_2 compartment. The spectra of the binuclear complexes (Table 1) do not have these bands but exhibit bands at 1 600 cm^{-1} attributable to the now chelated terminal carbonyls. No bands at *ca.* 3 100 cm^{-1} due to N–H stretches are observed for the binuclear species and so these observations suggest that both compartments are occupied. The complexes of VO and UO_2 have strong bands at *ca.* 990 and 920 cm^{-1} respectively and these are considered diagnostic for the vanadyl[7] and uranyl[8] groups. The general features of the i.r. spectra are very similar, and, due to the complexity of the molecules, frequency assignment has not been made.

TABLE 1

Major i.r. bands (cm^{-1}) for homo- and hetero-binuclear complexes (KBr disc)

Complex	$\nu(C\overset{\cdots}{-}O)$	$\nu(C\overset{\cdots}{-}O) + \nu(C\overset{\cdots}{-}C)$	$\nu(C\overset{\cdots}{-}N)$	Other bands
(*a*) Aliphatic acyclic Schiff bases				
(8a; $M^1 = M^2 =$ Cu)		1 564	1 509	
(8a; $M^1 = M^2 =$ Cu)·py	1 596	1 563	1 525	
(8a; $M^1 = M^2 =$ Cu)·4Me-py	1 601	1 572	1 486	
(9a; $M^1 =$ Cu, $M^2 =$ VO)·H_2O	1 580	1 560	1 480	3 420 H_2O 988 V=O
(9a; $M^1 =$ Cu, $M^2 =$ Zn)	1 630	1 580	1 491	
(9a; $M^1 =$ Cu, $M^2 = UO_2$)·EtOH	1 602	1 560	1 500	3 370 O–H 920 O=U=O (ν_3)
(8a; $M^1 = M^2 =$ Ni)·$2H_2O$		1 575	1 490	3 360 H_2O
(8a; $M^1 = M^2 =$ Ni)·2py	1 601	1 568	1 475	
(9a; $M^1 =$ Ni, $M^2 =$ Cu)		1 586	1 500	
(9a; $M^1 =$ Ni, $M^2 =$ Cu)·py	1 596	1 580	1 480	
(9a; $M^1 =$ Ni, $M^2 =$ VO)·H_2O		1 591	1 500	3 400 H_2O 990 V=O
(9a; $M^1 =$ Ni, $M^2 =$ Zn)·EtOH		1 580	1 495	3 400 O–H
(9a; $M^1 =$ Ni; $M^2 = UO_2$)·EtOH	1 606	1 560	1 511	3 100 O–H 920 O=U=O (ν_3)
(8b; $M^1 = M^2 =$ Cu)		1 565	1 498	
(8c; $M^1 = M^2 =$ Cu)		1 571	1 506	
(8g; $M^1 = M^2 =$ Cu)		1 580	1 506	
(8l; $M^1 = M^2 =$ Cu)		1 567	1 498	
(*b*) Phenyl-substituted acyclic Schiff bases				
(9m; $M^1 =$ Ni, $M^2 =$ Cu)	1 589	1 571	1 502	
(9m; $M^1 =$ Ni, $M^2 =$ VO)	1 620	1 580	1 510	981 V=O
(9m; $M^1 =$ Ni, $M^2 =$ Zn)·H_2O	1 589	1 570	1 500	3 440 H_2O
(9m; $M^1 =$ Ni, $M^2 = UO_2$)·EtOH	1 600	1 524	1 510	3 420 O–H 904 O=U=O (ν_3)
(8m; $M^1 = M^2 =$ Cu)	1 582	1 578	1 500	
(8r; $M^1 = M^2 =$ Cu)·C_6H_6	1 610	1 583	1 530	
(8n; $M^1 = M^2 =$ Cu)	1 600	1 581	1 510	
(8t; $M^1 = M^2 =$ Cu)·H_2O	1 601	1 580	1 520	3 420 H_2O
(8o; $M^1 = M^2 =$ Cu)	1 580	1 562	1 510	
(8u; $M^1 = M^2 =$ Cu)	1 615	1 579	1 511	
(8p; $M^1 = M^2 =$ Cu)	1 620	1 575	1 518	

The diffuse-reflectance spectra of the binuclear dicopper(II) complexes (Table 2) gave bands in the 615—700 nm region and compare favourably with bands observed in the spectra of other binuclear Schiff-base copper(II) complexes.[9] The heterobinuclear complexes (9; $M^1 =$ Cu) have a band, or a shoulder, in the 600—635 nm region, while the dinickel(II) and heterobinuclear complexes (9; $M^1 =$ Ni) exhibit bands in the 555—680 nm region. Definite identification of the stereochemistry about the metal atoms in the heterobinuclear complexes has not been made from these spectra.

Mass spectra were used in the characterisation of the complexes in order to show that pure heterobinuclear complexes were formed without the presence of homobinuclear species. All the complexes, with the exception of the species containing UO_2, gave mass spectra in which intense parent-ion peaks were obtained. None of the spectra of the heterobinuclear complexes contained peaks due to the presence of homobinuclear species. This is taken as an indication of their purity. The spectra are very simple in the high-mass region and show P^+ and P^{2+} as the most intense peaks. With the exception of (9a) ($M^1 =$ Cu, $M^2 =$ Zn; $M^1 =$ Ni, $M^2 =$ Cu), all the complexes showed peaks resulting from the loss of one or two mass units. These peaks are presumed to arise from loss of hydrogen atoms from the ethylenediamine bridge. This would give a product in which the conjugated π system extends throughout the ligand system. It is interesting to comment at this stage that the single-crystal *X*-ray structure of (6a; M = UO_2)·MeOH indicates the presence of two species. One is the

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[7] K. Nakamoto, Y. Morimato, and A. E. Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 4553.

[8] L. Cattalini, U. Croatto, S. Degetto, and E. Tondello, *Inorg. Chim. Acta Rev.*, 1971, **5**, 19.

[9] H. Okawa and S. Kida, *Bull. Chem. Soc. Japan*, 1972, **45**, 1759.

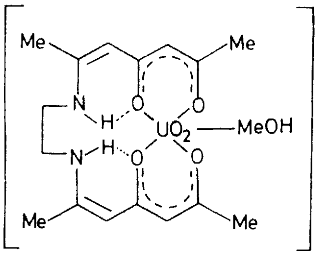
complex suggested by the formula unit (I), whilst the second form (II) shows the presence of an olefinic bridge, and not an aliphatic chain, between the nitrogen atoms.[10]

TABLE 2

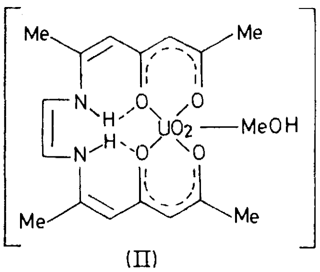
Major diffuse-reflectance bands (nm) for homo- and hetero-binuclear complexes of acyclic Schiff bases (s = strong, m = medium, w = weak, sh = shoulder, br = broad)

Complex	
(8a; M^1 = M^2 = Cu)	667m, 448s
(8a; M^1 = M^2 = Cu)·py	735 (sh), 637m, 413 (sh), 356s,br
(8a; M^1 = M^2 = Cu)·4Me-py	746 (sh), 621m, 420s, 351s,br
(9a; M^1 = Cu, M^2 = VO)·H_2O	621m, 440s
(9a; M^1 = Cu, M^2 = Zn)	602m, 368s,br
(9a; M^1 = Cu, M^2 = UO_2)·EtOH	633 (sh), 505 (sh), 395s,br
(8a; M^1 = M^2 = Ni)·H_2O	935 (sh), 581m, 448 (sh), 406s, 370s
(8a; M^1 = M^2 = Ni)·2py	1 075w, 595m, 415s,br
(9a; M^1 = Ni, M^2 = Cu)	658m, 459 (sh), 437s
(9a; M^1 = Ni, M^2 = Cu)·py	794 (sh), 667 (sh), 556 (sh), 413s,br
(9a; M^1 = Ni, M^2 = VO)·H_2O	589m, 449s,br, 405s,br
(9a; M^1 = Ni, M^2 = Zn)·EtOH	571m, 532m, 435s,br, 397s
(9a; M^1 = Ni, M^2 = UO_2)·EtOH	599 (sh), 400s,br
(8b; M^1 = M^2 = Cu)	645m, 417 (sh), 341s,br
(8c; M^1 = M^2 = Cu)	667m,422 (sh), 394 (sh), 355s
(8g; M^1 = M^2 = Cu)	637m, 394s,br, 347s
(8l; M^1 = M^2 = Cu)	676m, 435 (sh), 386s
(9m; M^1 = Ni, M^2 = Cu)	676 (sh), 521 (sh), 495s
(9m; M^1 = Ni, M^2 = VO)	588 (sh), 472s, 433s,br
(9m; M^1 = Ni, M^2 = Zn)·H_2O	575 (sh), 474 (sh), 412s, br
(9m; M^1 = Ni, M^2 = UO_2)·EtOH	595 (sh), 420s,br
(8m; M^1 = M^2 = Cu)	632m, 480s,br, 383s,br
(8o; M^1 = M^2 = Cu)	637m, 472s, 400s,br
(8u; M^1 = M^2 = Cu)	671m, 438 (sh), 386s
(8n; M^1 = M^2 = Cu)	658m, 476s, br
(8t; M^1 = M^2 = Cu)	699m, 483s, br
(8p; M^1 = M^2 = Cu)·H_2O	662m, 459 (sh), 389s
(8r; M^1 = M^2 = Cu)·C_6H_6	615m, 424s

Only complexes (8g), (8n), and (8p) (M^1 = M^2 = Cu) showed peaks corresponding to the loss of one copper atom from the parent ion. The doubly charged parent-ion peaks probably arise from the presence of two metal ions per molecule. Such peaks are not observed in the mass spectra of the mononuclear species [1] and this reinforces the probability that the metal ions may stabilise the dipositive charge.



(I)



(II)

The room-temperature magnetic moments (Table 3) of the binuclear complexes can be used to help assign the compartmental occupancy of the ligand. Square-planar Ni^{II} is diamagnetic, and if in the absence of site exchange it retains its N_2O_2 occupancy then any paramagnetism must arise from O_2O_2 occupancy. On this assumption the observed moments for NiVO, NiCu, NiNi, and NiZn are those for isolated d^1, d^9, octahedral d^8, and d^{10} ions respectively. The complexes (8a)·2L [M^1 = M^2 = Ni, L = H_2O or pyridine (py)] therefore represent a class in which two similar metals having different spin states are held in juxtaposition by a single ligand. The high- and low-spin metal atoms are bridged by carbonyl functions (M^1 = Ni, M^2 = Ni·2H_2O). The observed moment of the binuclear nickel species also illustrates the achievement of co-ordinative saturation by the nickel atoms in the O_2O_2 compartment. The metal atoms in juxtaposition also have different co-ordination numbers and geometries. In (9a; M^1 = Ni, M^2 = Zn)·EtOH and in the NiUO_2 complexes an anomalous residual paramagnetism is observed; this suggests the possibility of some site exchange, leading to paramagnetic contamination, not evidenced by mass spectra, or a deviation from planarity.

TABLE 3

Room-temperature magnetic moments for homo- and hetero-binuclear complexes

Complex	T/K	$\mu_{\text{eff.}}$/B.M.
(9m; M^1 = Ni, M^2 = Cu)	297	1.83
(9m; M^1 = Ni, M^2 = Zn)·H_2O	295	0
(9m; M^1 = Ni, M^2 = UO_2)·EtOH	295	0.78
(9m; M^1 = Ni, M^2 = VO)	295	1.70
(8m; M^1 = M^2 = Cu)	293	0.37 *
(8a; M^1 = M^2 = Cu)	293	0.62 *
(8a; M^1 = M^2 = Cu)·py	296	0.54 *
(8a; M^1 = M^2 = Cu)·4Me-py	295	0.57 *
(9a; M^1 = Cu, M^2 = VO)·H_2O	296	0.88 *
(9a; M^1 = Cu, M^2 = UO_2)·EtOH	295	1.68
(8a; M^1 = M^2 = Ni)·2H_2O	295	3.05
(8a; M^1 = M^2 = Ni)·2py	297	3.16
(9a; M^1 = Ni, M^2 = Cu)	295	1.86
(9a; M^1 = Ni, M^2 = Cu)·py	295	2.00
(9a; M^1 = Ni, M^2 = VO)·H_2O	296	1.75
(9a; M^1 = Ni, M^2 = Zn)·EtOH	295	0.50
(9a; M^1 = Ni, M^2 = UO_2)·EtOH	295	0.69
(8l; M^1 = M^2 = Cu)	300	0.39 *

* Per metal ion

The heterobinuclear complexes derived from (5; M = Cu) are believed to follow the same pattern of incorporation as a consequence of the established co-ordination selectivities. As Cu^{II} has one unpaired electron it is not possible to make unambiguous assignment on the grounds of magnetism alone. Complex (9a; M^1 = Cu, M^2 = UO_2)·EtOH gave a moment of 1.68 B.M.,* slightly lower than the accepted range for d^9 Cu^{II}, and (9a; M^1 = Cu, M^2 = VO)·H_2O gave a moment of 0.88 B.M. per metal atom suggesting that a fairly strong antiferromagnetic interaction occurs between the copper(II) and oxovanadium(IV) ions. The results of magnetic measurements on binuclear oxovanadium(IV) complexes of a number of tridentate Schiff bases have been interpreted in terms of antiferromagnetic coupling *via* a direct metal–metal interaction between unpaired spins in the $3d_{xy}$ orbitals of the vanadium atoms.[11]

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* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

[10] R. Graziani, M. Vidali, U. Casellato, and P. A. Vigato, *Acta Cryst.*, 1976, **B32**, 1681.

[11] A. P. Ginsberg, H. J. Williams, and E. Koubek, *Inorg. Chem.*, 1966, **5**, 1656.

The homobinuclear complexes of Cu^{II} display reduced magnetic moments arising from antiferromagnetic behaviour, as is observed for copper(II) triketonates.[12] The ligands are presumed to be planar because of the extensive π systems, and the copper atoms have square-planar (N_2O_2) or square-based-pyramidal geometry [as in the adducted Cu atom co-ordinated in the O_2O_2 site of the complexes (8a)·L ($M^1 = M^2 =$ Cu; L = py or 4Me-py)]. In either geometry the $3d$ orbital of highest energy of the copper(II) ion is the $3d_{x^2-y^2}$ orbital [13] and this contains the unpaired electron. It will thus be the overlap of this orbital with the $2p_x$ orbitals on the bridging oxygen atoms of the ligand which will be involved in the superexchange mechanisms governing the magnetic properties. The room-temperature magnetic moments of the homobinuclear complexes are in accord with those observed for many binuclear copper(II) complexes in which antiferromagnetic behaviour predominates.[9,14,15]

Whilst no single technique establishes unambiguously the compartmental occupancy in these complexes, the use of several physical methods allows some assignment to be made. Single-crystal X-ray structural studies could act as the final arbiter for the solid state, unless the adjacent metals atoms have similar atomic numbers. During the latter stages of this work the structures of [9m; $M^1 =$ Ni, $M^2 =$ Zn(py)],[16] (9m; $M^1 =$ Ni, $M^2 =$ VO),[16] and [8m; $M^1 = M^2 =$ Ni(py)]·py [17] have been reported and confirm the preference of Ni for the N_2O_2 compartment.

Chemical evidence for the preference of Ni for N_2O_2 was seen in the reaction of Ni[O_2CMe]$_2$ with (5a; M = Cu) in which (5a; M = Ni) was isolated, facile metal exchange having occurred.[1] Insoluble (8a; $M^1 = M^2 =$ Cu) is also recovered from this reaction. In the reaction of (5a; M = Cu) with Zn[O_2CMe]$_2$ the first product observed is (9a; $M^1 =$ Cu, $M^2 =$ Zn) followed by a high-yield precipitation of (8a; $M^1 = M^2 =$ Cu). A possible path for this reaction involves initial co-ordination of the second metal atom to the vacant O_2O_2 compartment of the mononuclear complex. (This may not be necessary for nickel as direct replacement of Cu by Ni could occur.) In the CuNi intermediate, ready replacement of the copper occurs, the nickel jumping into the N_2O_2 site as expected according to the site selectivity. For the CuZn species this process is less ready as evidenced by the isolation of (9a; $M^1 =$ Cu, $M^2 =$ Zn). As the inner copper is replaced it becomes available for co-ordination by unchanged (5a; M = Cu) to yield (8a; $M^1 = M^2 =$ Cu). No evidence has been found for the presence of (9a; $M^1 =$ Cu, $M^2 =$ Ni), nor for the mononuclear zinc complex, as a consequence of these reactions. Zinc appears to prefer O_2O_2 as is seen in the formation of NiZn complexes and in reactions of (5a; M = Ni) with copper, or zinc, acetate no metal exchange is observed. A strong preference of Ni for N_2O_2 is thus indicated, and it could be that the relatively stronger affinity of Zn for O_2O_2 gives stability to the CuZn complex. Attempts to synthesise mononuclear zinc complexes were not successful, and so it is likely that this is why no mononuclear zinc complex is observed in the above. Both nickel and zinc appear to act as antagonists for copper in the N_2O_2 site of acyclic Schiff-base complexes.

Complex (9a; $M^1 =$ Cu, $M^2 =$ Ni)·$2H_2O$ has been reported,[18] but it was prepared by routes involving the formation of (5a; M = Cu)·Ni[ClO_4]$_2$ and its subsequent reaction with Li[OH]. Under our conditions we have only observed a metal-exchange reaction.

EXPERIMENTAL

Details of physical measurements were given in Part 1; [19] preparative details for the macrocyclic and acyclic Schiff bases and their mononuclear transition-metal complexes have also been reported.[1]

Syntheses of Homo- and Hetero-binuclear Complexes of Acyclic Schiff Bases.—[6,11-*Dimethyl*-7,10-*diazahexadeca*-5,11-*diene*-2,4,13,15-*tetraonato*(4−)-$N^7N^{10}O^4O^{13}$; $O^2O^4O^{13}O^{15}$]*dicopper*(II) (8a). Complex (5a; M = Cu) (1.0 g) was dissolved in hot 95% ethanol and an ethanolic solution of Cu[O_2CMe]$_2$·H_2O (0.54 g) was added. The reaction mixture immediately became deep green and a silky green precipitate was deposited. After the solution had been allowed to cool the product was collected by filtration and dried over silica gel *in vacuo*, yield 90% (Found: C, 44.3; H, 4.8; N, 6.2. $C_{16}H_{20}Cu_2N_2O_4$ requires C, 44.5; H, 4.6; N, 6.4%), P^+ at m/e 430 (2 × ^{63}Cu).

[6,11-*Dimethyl*-7,10-*diazahexadeca*-5,11-*diene*-2,4,13,15-*tetraonato*(4−)-$N^7N^{10}O^4O^{13}$; $O^2O^4O^{13}O^{15}$]*copper*(II)*oxovanadium*(II) *hydrate* (9a)·H_2O. Complex (5a; M = Cu) (1.0 g) dissolved in hot 95% ethanol was added to a stirred suspension of [VO][O_2CMe]$_2$ (0.5 g) in hot 95% ethanol (100 cm^3). The resulting mixture was stirred and heated under reflux for 2 h. The deep green solution was filtered whilst hot to remove any unchanged [VO][O_2CMe]$_2$. On cooling, a deep green microcrystalline solid was deposited which was collected by filtration and recrystallised from dichloromethane. The product was dried over silica gel *in vacuo*, yield 50% (Found: C, 42.8; H, 4.7; N, 6.1. $C_{16}H_{20}CuN_2O_5V$·H_2O requires C, 42.4; H, 4.9; N, 6.2%), P^+ at m/e 434 (^{63}Cu, ^{51}V).

(9a; $M^1 =$ Cu, $M^2 =$ Zn). Complex (5a; M = Cu) (1.0 g) dissolved in hot 95% ethanol was added to a hot ethanolic solution of Zn[O_2CMe]$_2$·$2H_2O$ (0.59 g). The mixture was warmed on a steam-bath and a green solid was precipitated which was collected by filtration whilst the solution was still hot. The filtrate then precipitated (8a; $M^1 = M^2 =$ Cu) immediately. When the first precipitate of (9; $M^1 =$ Cu, $M^2 =$ Zn) was not removed from the reaction mixture while it was still hot, (8a; $M^1 = M^2 =$ Cu) was also precipitated on cooling to give a mixture of the two complexes. Yield of (9a; $M^1 =$ Cu, $M^2 =$ Zn) 10% (Found: C, 43.5; H, 5.3; N,

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6.7. $C_{16}H_{20}CuN_2O_4Zn$ requires C, 44.3; H, 4.6; N, 6.4%), P^+ at *m/e* 431 (^{63}Cu, ^{64}Zn).

(9a; M^1 = Cu, M^2 = UO_2)·EtOH. Complex (5a; M = Cu) (*1.0* g) dissolved in hot 95% ethanol was added to a hot ethanolic solution of $[UO_2][O_2CMe]_2 \cdot 2H_2O$ (1.15 g). The reaction mixture was warmed on a steam-bath for *ca.* 5 min and the resulting brown solution was allowed to cool. The brown microcrystalline precipitate was collected by filtration and dried over silica gel *in vacuo*, yield 90% (Found: C, 31.3; H, 3.9; N, 4.3. $C_{16}H_{20}CuN_2O_6U \cdot EtOH$ requires C, 31.6; H, 3.8; N, 4.1%).

(9a; M^1 = Ni, M^2 = VO)·H_2O. Complex (5a; M = Ni) (1.0 g) dissolved in hot 95% ethanol was added to a stirred suspension of $[VO][O_2CMe]_2$ (0.51 g) in hot 95% ethanol. The resulting mixture was stirred at the reflux temperature for 2 h. The hot solution was filtered to remove any unchanged $[VO][O_2CMe]_2$ and allowed to cool. The green microcrystalline precipitate was collected by filtration and dried over silica gel *in vacuo*, yield 50% (Found: C, 42.8; H, 4.7; N, 6.9. $C_{16}H_{20}N_2NiO_5V \cdot H_2O$ requires C, 42.8; H, 4.9; N, 6.2%), P^+ at *m/e* 429 (^{58}Ni, ^{51}V).

The remaining binuclear complexes of (1a) were prepared by the following general method. Complex (5a; M = Ni) (0.003 mol) dissolved in hot 95% ethanol was added to a hot ethanolic solution of the metal acetate (0.003 mol). The reaction mixture was warmed on a steam-bath for 5 min and then allowed to cool. The microcrystalline precipitate was collected by filtration and dried over silica gel *in vacuo*, yields averaged 80%. Complex (5a; M = Ni) and $Ni[O_2CMe]_2 \cdot 4H_2O$ yielded a green precipitate of (8a; M^1 = M^2 = Ni)·2H_2O (Found: C, 42.1; H, 5.3; N, 5.9. $C_{16}H_{20}N_2Ni_2O_4 \cdot 2H_2O$ requires C, 41.9; H, 5.2; N, 6.1%), P^+ at *m/e* 420 (2 × ^{58}Ni). Recrystallisation from hot pyridine afforded a deep green microcrystalline solid found to be (8a; M^1 = M^2 = Ni)·2py (Found: C, 53.8; H, 5.2; N, 9.8. $C_{26}H_{30}N_4Ni_2O_4$ requires C, 53.8; H, 5.2; N, 9.6%). Complex (5a; M = Ni) and $Cu[O_2CMe]_2 \cdot H_2O$ yielded deep green microcrystals of (9a; M^1 = Ni, M^2 = Cu) (Found: C, 45.5; H, 5.3; N, 6.3. $C_{16}H_{20}CuN_2NiO_4$ requires C, 45.0; H, 4.7; N, 6.5%), P^+ at *m/e* 425 (^{63}Cu, ^{58}Ni). Recrystallisation from hot pyridine yielded (9a; M^1 = Ni, M^2 = Cu)·py as a deep green microcrystalline solid (Found: C, 49.6; H, 5.1; N, 8.5. $C_{21}H_{25}CuN_3NiO_4$ requires C, 49.8; H, 4.9; N, 8.3). Complex (5a; M = Ni) and $Zn[O_2CMe]_2 \cdot 2H_2O$ yielded (9a; M^1 = Ni, M^2 = Zn)·EtOH as a brown precipitate (Found: C, 45.2; H, 5.9; N, 5.6. $C_{16}H_{20}N_2NiO_4Zn \cdot EtOH$ requires C, 45.5; H, 5.5; N, 5.9%), P^+ at *m/e* 426 (^{58}Ni, ^{64}Zn). Complex (5a; M = Ni) and $[UO_2][O_2CMe]_2 \cdot H_2O$ yielded (9a; M^1 = Ni, M^2 = UO_2)·EtOH as a brown microcrystalline solid (Found: C, 30.8; H, 4.0; N, 3.9. $C_{16}H_{20}N_2NiO_6U \cdot EtOH$ requires C, 30.6; H, 3.6; N, 4.2%).

[6,12-*Dimethyl*-7,11-*diazaheptadeca*-5,12-*diene*-2,4,14,16-*tetraonato*(4−)-$N^7N^{11}O^4O^{14}$; $O^2O^4O^{14}O^{16}$]*dicopper*(II) (8c). Copper(II) acetate monohydrate (0.56 g) was dissolved in water (100 cm^3) and added to a chloroform solution of (1c) (1.0 g in 100 cm^3). The two phases were intimately mixed by stirring at room temperature for 1 h. The mixture was poured into a separating funnel, the lower green chloroform layer was collected, and the solvent was removed by evaporation under reduced pressure. The green oil obtained was redissolved in a small volume of fresh chloroform and eluted with chloroform down a column containing neutral Brock activated alumina (25 g). A green fraction was collected and removal of the solvent by evaporation under reduced pressure yielded a green solid, which was dried over silica gel *in vacuo*, yield 25% (Found: C, 45.4; H, 5.3; N, 5.9. $C_{17}H_{22}Cu_2N_2O_4$ requires C, 45.8; H, 4.9; N, 6.2%), P^+ at *m/e* 444 (2 × ^{63}Cu).

[2,2,7,12,17,17-*Hexamethyl*-8,11-*diazaoctadeca*-6,12-*diene*-3,5,14,16-*tetraonato*(4−)-$N^8N^{11}O^5O^{14}$; $O^3O^5O^{14}O^{16}$]*dicopper*(II) (8l). Compound (1l) (1.0 g) dissolved in hot 95% ethanol (50 cm^3) was added to a hot ethanolic solution of $Cu[O_2CMe]_2 \cdot H_2O$ (1.2 g in 50 cm^3). A green filamentous solid was precipitated immediately and the reaction mixture was allowed to cool. The product was collected by filtration and recrystallised from a small volume of hot chloroform. It was then re-collected and dried over silica gel *in vacuo*, yield 80% (Found: C, 49.7; H, 6.2; N, 4.9. $C_{22}H_{32}Cu_2N_2O_4$ requires C, 51.2; H, 6.2; N, 5.4%), P^+ at *m/e* 514 (2 × ^{63}Cu).

The remaining two binuclear copper(II) complexes of this type were prepared by the following method. The mononuclear copper(II) complex (0.001 mol) dissolved in hot 95% ethanol was added to a hot ethanolic solution of $Cu[O_2CMe]_2 \cdot H_2O$ (0.001 mol). A green solid was immediately precipitated and was collected by filtration after the reaction mixture had been allowed to cool. It was dried over silica gel *in vacuo*, yields averaged 80%. Complex (5b; M = Cu) yielded [6,8,11-trimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(4−)-$N^7N^{10}O^4O^{13}$; $O^2O^4O^{13}O^{15}$]dicopper(II) (8b) (Found: C, 45.8; H, 5.1; N, 5.8. $C_{17}H_{22}Cu_2N_2O_4$ requires C, 45.8; H, 4.9; N, 6.2%), P^+ at *m/e* 444 (2 × ^{63}Cu) and (5 g; M = Cu) yielded [8,13-di-n-propyl-9,12-diazaeicosa-7,13-diene-4,6,15,17-tetraonato(4−)-$N^9N^{12}O^6O^{15}$;$O^4O^6O^{15}O^{17}$]dicopper(II) (8g) (Found: C, 53.2; H, 6.9; N, 5.4. $C_{24}H_{36}Cu_2N_2O_4$ requires C, 53.0; H, 6.6; N, 5.1%), P^+ at *m/e* 542 (2 × ^{63}Cu).

[5,10-*Dimethyl*-1,14-*diphenyl*-6,9-*diazatetradeca*-4,10-*diene*-1,3,12,14-*tetraonato*(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]*dicopper*(II) (8m). Compound (1m) (1.0 g) dissolved in hot chloroform (200 cm^3) was added to $Cu[O_2CMe]_2 \cdot H_2O$ (0.92 g) dissolved in 95% ethanol (200 cm^3) . A green-brown precipitate was immediately deposited and the mixture was allowed to cool. The product was collected by filtration and recrystallised from hot pyridine as fine green-brown needles, which were collected by filtration and dried over silica gel *in vacuo*, yield 70% (Found: C, 55.8; H, 4.6; N, 4.6. $C_{26}H_{24}Cu_2N_2O_4$ requires C, 56.1; H, 4.3; N, 5.0%), P^+ at *m/e* 556 (2 × ^{63}Cu).

[5,10-*Dimethyl*-1,14-*diphenyl*-6,9-*diazatetradeca*-4,10-*diene*-1,3,12,14-*tetraonato*(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]-*nickel*(II)*oxovanadium*(IV) (9m). Oxovanadium(IV) acetate (0.38 g) dissolved in hot water was added dropwise to (5m; M = Ni) (1.0 g) dissolved in hot acetone (150 cm^3). The resulting deep brown mixture was warmed on a steam-bath for 5 min and allowed to cool. The deep green precipitate was collected by filtration and dried over silica gel *in vacuo*, yield 60% (Found: C, 56.0; H, 4.9; N, 5.0. $C_{26}H_{24}N_2NiO_5V$ requires C, 56.3; H, 5.3; N, 5.3%), P^+ at *m/e* 553 (^{58}Ni, ^{51}V).

The remaining heterobinuclear complexes of (1m) were prepared by the following method. Complex (5m; M = Ni) (0.002 mol) dissolved in hot acetone (150 cm^3) was added to the metal acetate (0.002 mol) dissolved in 95% ethanol (150 cm^3). The resulting solution was warmed on a steam-bath for 5 min and allowed to cool. The precipitated solid was collected by filtration and dried over silica gel *in vacuo*, yields averaged 80%. Complex (1m; M = Ni) and $Cu[O_2CMe]_2 \cdot H_2O$ yielded (9m; M^1 = Ni, M^2 = Cu) as a brown solid (Found: C, 57.3; H, 4.7; N, 4.9. $C_{26}H_{24}CuN_2NiO_4$ requires C, 56.7; H, 4.3; N, 5.0%), P^+ at *m/e* 549 (^{63}Cu, ^{58}Ni); $Zn[O_2CMe]_2 \cdot 2H_2O$ yielded (9m; M^1 = Ni, M^2 =

Zn)·H_2O as a light brown solid (Found: C, 54.8; H, 5.7; N, 5.0. $C_{26}H_{24}N_2NiO_4Zn{\cdot}H_2O$ requires C, 54.7; H, 4.5; N, 4.9%), P^+ at *m/e* 550 (^{58}Ni, ^{64}Zn); and $[UO_2][O_2CMe]_2{\cdot}2H_2O$ yielded (9m; M^1 = Ni, M^2 = UO_2)·EtOH as a deep brown solid which was further washed by suspending in boiling 95% ethanol (Found: C, 42.2; H, 4.0; N, 3.4. $C_{26}H_{24}N_2NiO_6U{\cdot}EtOH$ requires C, 41.8; H, 3.7; N, 3.5%), P^+ at *m/e* 756 (^{58}Ni, ^{238}U).

Complexes of acyclic Schiff bases derived from substituted-phenyl 1,3,5-triketones and ethane-1,2-diamine (en) were prepared by the following procedure. The Schiff base (0.002 mol) dissolved in hot chloroform (100 cm^3) was added to $Cu[O_2CMe]_2{\cdot}H_2O$ (0.004 mol) dissolved in hot 95% ethanol (150 cm^3). A green or green-brown precipitate was immediately deposited. After the mixture had been allowed to cool, the precipitate was collected by filtration and dried over silica gel *in vacuo*, yields averaged 80%. Compound (1n) yielded [1,14-di(*p*-methoxyphenyl)-5,10-dimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]dicopper(II) (8n) (Found: C, 54.0; H, 5.0; N, 4.6. $C_{28}H_{28}Cu_2N_2O_6$ requires C, 54.6; H, 4.5; N, 4.5%), P^+ at *m/e* 614 (2 × ^{63}Cu); (1o) yielded [5,10-dimethyl-1,14-di(*p*-tolyl)-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato-(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]dicopper(II) (8o) (Found: C, 57.9; H, 5.1; N, 4.8. $C_{28}H_{28}Cu_2N_2O_4$ requires C, 57.6; H, 4.8; N, 4.8%), P^+ at *m/e* 582 (2 × ^{63}Cu); and (1p) yielded [1,14-di(*p*-bromophenyl)-5,10-dimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]dicopper(II) (8p) (Found: C, 42.3; H, 3.4; Br, 23.6; N, 3.6. $C_{26}H_{22}Br_2Cu_2N_4O_2{\cdot}H_2O$ requires C, 42.6; H, 3.3; Br, 21.8; N, 3.8%), P^+ at *m/e* 714 (2 × ^{63}Cu, 2 × ^{81}Br).

The remaining homobinuclear complexes of this type were prepared by the following method. The *triketone* (0.004 mol) dissolved in hot 95% ethanol and the alkanediamine (0.002 mol) also dissolved in 95% ethanol were mixed and heated on a steam-bath for 15 min. The yellow solution was then added to $Cu[O_2CMe]_2{\cdot}H_2O$ (0.004 mol) dissolved in hot 95% ethanol. The resulting deep green mixture precipitated a green solid on further heating for 5 min. The product was collected by filtration, after the solution had been allowed to cool, and was dried over silica gel *in vacuo*, yields averaged 70%. 1-Phenylhexane-1,3,5-trione and propane-1,3-diamine (pd) yielded [5,11-dimethyl-1,15-diphenyl-6,10-diazapentadeca-4,11-diene-1,3,13,15-tetraonato(4−)-$N^6N^{10}O^3O^{13}$; $O^1O^3O^{13}O^{15}$]dicopper(II) (8r) (Found: C, 59.8; H, 4.8; N, 3.7. $C_{27}H_{26}Cu_2N_2O_4$ requires C, 56.9; H, 4.6; N, 4.9%). Recrystallisation from benzene yielded (8r)·C_6H_6 (Found: C, 60.6; H, 5.4; N, 3.9. $C_{27}H_{26}Cu_2N_2O_4{\cdot}C_6H_6$ requires C, 61.1; H, 4.9; N, 4.3%), P^+ at *m/e* 568 (2 × ^{63}Cu). H_2mba and propane-1,2-diamine (pn) yielded [1,14-di(*p*-methoxyphenyl)-5,7,10-trimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(4−)-$N^6N^9O^3O^{12}$; $O^1O^3O^{12}O^{14}$]dicopper(II) (8t) (Found: C, 53.7; H, 5.0; N, 4.3. $C_{29}H_{30}Cu_2N_2O_6$ requires C, 53.7; H, 4.9; N, 4.3%), $[P - 2\ H]^+$ at *m/e* 828 (2 × ^{63}Cu). H_2pmb and pd yielded [5,11-dimethyl-1,15-di(*p*-tolyl)-6,10-diazapentadeca-4,11-diene-1,3,13,15-tetraonato(4−)-$N^6N^{10}O^3O^{13}$; $O^1O^3O^{13}O^{15}$]dicopper(II) (8u) (Found: C, 58.0; H, 5.3; N, 4.5. $C_{29}H_{30}Cu_2N_2O_4$ requires C, 58.2; H, 5.0; N, 4.6%), P^+ at *m/e* 596 (2 × ^{63}Cu).

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