Compartmental Ligands. Part 2.[1] Mononuclear Transition-metal Complexes of Acyclic Schiff Bases derived from 1,3,5-Triketones

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A series of acyclic Schiff bases (1) derived from 1,3,5-triketones and α,ω-alkanediamines has been prepared, and their mononuclear complexes with Cu^{II}, Ni^{II}, UO_2, and VO are described. Phenyl-substituted alicyclic bases are prepared by the reaction of 1-*p*-X-phenylhexane-1,3,5-trione (X = H, Br, Me, or OMe) (2 mol) and ethane-1,2-diamine (en) (1 mol) in ethanol; the condensation of 7,7-dimethyloctane-2,4,6-trione with en similarly yields 2,2,7,12,17,17-hexamethyl-8,11-diazaoctadeca-6,12-diene-3,5,14,16-tetraone (1l). 6,11-Dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone, (1a), is prepared by acid hydrolysis of the macrocyclic Schiff base 5,9,14,18-tetramethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (2a). Treatment of the alicyclic bases with metal acetates gives the corresponding mononuclear complexes. The ligands (1) are potentially tetra-anionic and have two available dissimilar compartments for complex formation, one comprising N_2O_2 and the other O_2O_2 donor sites. The co-ordination selectivity of (1) is established as a necessary prerequisite for the formation of pure heterobinuclear chelates of these ligands. The reaction of $Cu[O_2CMe]_2$ with (1a) gives three products: the two N_2O_2 and O_2O_2 positional isomers, (5a) and (6a)$\cdot H_2O$, and a homobinuclear complex. The mononuclear complexes of Ni, UO_2, and VO show N_2O_2, O_2O_2, and O_2O_2 site occupancy respectively. The preference of Ni for the N_2O_2 site is reinforced in its reaction with the phenyl-substituted bases, but here Cu shows a preference for O_2O_2 as do VO and UO_2. The site selectivity of Ni is further exemplified in the reaction of (5a; M = Cu) with $Ni[O_2CMe]_2$ in which the Ni replaces the Cu in the ligand. The complexes have been characterised by chemical analysis and spectral measurements, and the potential role of magnetic studies in establishing the site occupancy has been investigated.

THE syntheses and properties of macrocyclic Schiff-base ligands derived from symmetrical 1,3,5-triketones and α,ω-alkanediamines were reported in Part 1.[1] The preparation of mononuclear transition-metal complexes was also presented. It is possible to envisage the preparation of acyclic Schiff bases (1) from similar reactants. This class of ligands presents the exciting prospect of the co-ordination of two different metal atoms in the adjacent dissimilar compartments A and B, so enabling the investigation of modifications in spectral, magnetic, and chemical properties brought about by this juxtaposition. To a first approximation the ligand may be regarded as a fusion of a 1,3-diketone (B) and its Schiff base (A), and so the properties of a metal present in either compartment would be expected to parallel those of the metal in the

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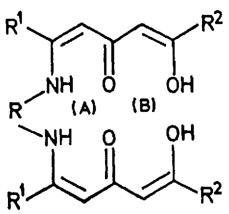
[1] D. E. Fenton and S. E. Gayda, preceding paper.

parent mononuclear complex. That is, $[M(N_2O_2)]$ would behave in a manner similar to [M(Schiff base)] and $[M(O_2O_2)]$ would resemble $[M(diketonate)_2]$. The vast literature available on the properties of 1,3-diketones [2] and their Schiff-base derivatives [3] would then allow one to study the mononuclear complexes of the acyclic systems in a straightforward way.

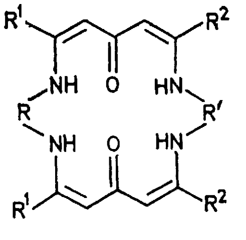


	R	R^1	R^2
(1a)	$[CH_2]_2$	Me	Me
(1b)	CH(Me)CH_2	Me	Me
(1c)	$[CH_2]_3$	Me	Me
(1g)	$[CH_2]_2$	Pr^n	Pr^n
(1l)	$[CH_2]_2$	Me	Bu^t
(1m)	$[CH_2]_2$	Me	Ph
(1n)	$[CH_2]_2$	Me	C_6H_4OMe-*p*
(1o)	$[CH_2]_2$	Me	C_6H_4Me-*p*
(1p)	$[CH_2]_2$	Me	C_6H_4Br-*p*

In this paper we report the synthesis of alicyclic Schiff-base ligands derived from 1,3,5-triketones and experiments to establish their co-ordination selectivity towards transition-metal ions. The isolation of pure, mononuclear, positional isomers of such complexes is regarded as a necessary prerequisite for the unambiguous formation of pure heterobinuclear metal complexes. Preliminary communication of this work has been made.[4,5]

RESULTS AND DISCUSSION

Alicyclic Schiff Bases (1).—The condensation of symmetrical 1,3,5-triketones with α,ω-alkanediamines led only to the formation of macrocyclic Schiff bases.[1] However, when a $CHCl_3$ solution of the macrocycle 5,9,14,18-tetramethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (2a) was stirred with a dilute aqueous solution containing 2 equivalents of ethanoic acid, the acyclic Schiff base 6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraone (1a) was recovered from the chloroform layer. Hydrolysis of one of the diamine bridges has thus taken place under acid conditions. When excess of ethanoic acid was used both bridges were hydrolysed and heptane-2,4,6-trione (3a) was recovered. Reaction in the presence of sodium hydroxide did not lead to cleavage of the macrocycle. Compound (1a) is soluble in most common organic solvents, unlike its predecessor (2a).



	R	R'	$R^1 = R^2$
(2a)	$[CH_2]_2$	$[CH_2]_2$	Me

The unsymmetrical 1-phenylhexane-1,3,5-trione and ethane-1,2-diamine (en) react, in 2 : 1 ratio in ethanol, to give bright yellow crystals of the acyclic Schiff base 5,10-dimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1m).[6] Similarly reaction of the corresponding *p*-methoxy-, *p*-methyl-, and *p*-bromophenyl-triketones with en led to isolation of the acyclic Schiff bases (1n), (1o), and (1p). When 7,7-dimethyloctane-2,4,6-trione was condensed with en in ethanol, 2,2,7,12,17,17-hexamethyl-8,11-diazaoctadeca-6,12-diene-3,5,14,16-tetraone (1l) was isolated. In all the reactions with the unsymmetrical triketones, condensation with the amine group occurred only at the carbonyl group adjacent to the methyl group. A similar behaviour pattern is observed with 1,3-diketones and may arise from electronic, or steric, effects. 5,5-Dimethylhexane-2,4-dione and 1-phenylbutane-1,3-dione condense only at the keto-group adjacent to the methyl substituent,[7,8] and 2,2,6,6-tetramethylheptane-3,5-dione and 1,3-diphenylpropane-1,3-dione are not reported to condense with en. The introduction of substituents into the phenyl ring did not induce ring closure.

TABLE 1

Infrared bands (cm^{-1}) for acyclic Schiff bases (KBr disc; br = broad, s = strong, m = medium, w = weak, sh = shoulder)

(1a)	3 385w, 3 140m,br, 3 075w, 2 998w, 2 975w, 2 955w, 2 930w, 1 700s, 1 600s,br, 1 470s, 1 510s, 1 456m, 1 437m, 1 372s, 1 352s, 1 308s, 1 280s, 1 237s, 1 220s, 1 190m, 1 144m, 1 111m, 1 079s, 1 018m, 994m, 932m, 868s, 836m, 750s, 738m, 648w
(1m)	3 430w,br, 3 200w,br, 1 600s, 1 587s, 1 568s, 1 547s, 1 518s, 1 490m, 1 448s, 1 401m, 1 325m, 1 280s, 1 220m, 1 170s, 1 093s, 1 077m, 1 070m, 972s, 822s, 780s, 759m, 718m, 691s, 665m, 636m
(1n)	3 420w,br, 1 580s, 1 568s, 1 560 (sh), 1 542s, 1 519s, 1 455m,br, 1 440m, 1 428m, 1 328m, 1 281s, 1 256s, 1 208m, 1 178s, 1 112m, 1 021m, 973m, 840m, 818s, 700m, 650m
(1o)	3 400w, br, 1 580s, br, 1 545s, br, 1 508m, 1 456m, 1 420m, 1 390m, 1 370m, 1 325m, 1 280s, 1 206m, 1 187m, 1 170s, 1 112m, 1 088s, 1 070m, 1 018m, 972s, 840m, 809s, 700m, 656m
(1p)	3 420w,br, 1 582s,br, 1 545s,br, 1 432m, 1 425s,br, 1 322m, 1 270s, 1 205m, 1 181m, 1 170m, 1 104m, 1 088m, 1 069m, 1 009s, 972s, 840m, 812s, 749m, 708m, 651m
(1l)	3 410w,br, 3 200w,br, 2 960m, 1 625 (sh), 1 580s,br, 1 545s, 1 519s, 1 477m, 1 455m, 1 432s, 1 408m, 1 375m, 1 360m, 1 324s, 1 280s, 1 210s, 1 179s, 1 127m, 1 092s, 1 030w, 975s, 942m, 901m, 850m, 818s, 758w, 733m, 720m

The i.r. spectra of the acyclic bases (1) (Table 1) showed

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

[3] R. H. Holm, G. W. Everett, jun., and H. Chakavorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

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

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

[6] R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Zuszay, *Inorg. Chem.*, 1976, **15**, 1633.

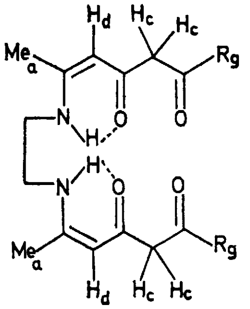
[7] L. F. Lindoy and W. E. Moody, *J. Amer. Chem. Soc.*, 1975, **97**, 2275.

[8] P. J. McCarthy, R. J. Horey, K. Ueno, and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.

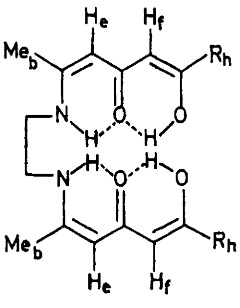
broad bands in the 3 000—3 400 cm^{-1} region, attributed to O–H $\cdots$ O and N–H $\cdots$ O stretches. Compound (1a) showed a strong free-carbonyl band at 1 700 cm^{-1} indicating that the Schiff base exists mainly as its keto-tautomer in the solid state, but none of the aromatic substituted Schiff bases had bands in this region indicating the predominance of their enol tautomers in the solid state. Compound (1l) also gave no absorption at *ca.* 1 700 cm^{-1}.

The mass spectra of all the compounds (1) showed peaks of low relative abundance corresponding to the parent molecular ions, and gave fragmentation patterns consistent with loss of one of the triketone moieties followed by amine-bridge loss. Compound (1l) alone showed loss of one substituent group, and (1m) gave a peak consistent with loss of two phenyl groups.

The ^{1}H n.m.r. spectrum of compound (1a) in CDCl$_3$ showed that two tautomers were present. When the spectrum was recorded immediately after dissolution, the keto-tautomer (I; R = Me) was present in almost 100% abundance with only a trace amount of the enol tautomer (II; R = Me). However, when a second spectrum was run after the solution had been allowed to stand for 2—3 weeks, the concentration of the enol tautomer increased to 30.3%. Assignments to the resonances observed are given in Table 2, with references to the structures shown. Compound (1l) also showed the presence of two isomers (R = Bu^t), this time in approximately equal amounts. Compound (1m) gave a ^{1}H n.m.r. spectrum in CDCl$_3$ consistent with the presence of an additional tautomer (III; R = Ph). The solution contained 22.1% of the diketo-tautomer (I), 43.6% of the monoenol tautomer (III), and 34.3% of the dienol tautomer (II). Compounds (1n)—(1p) were insufficiently soluble for spectra to be obtained.

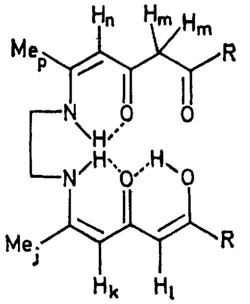


(I)



(II)

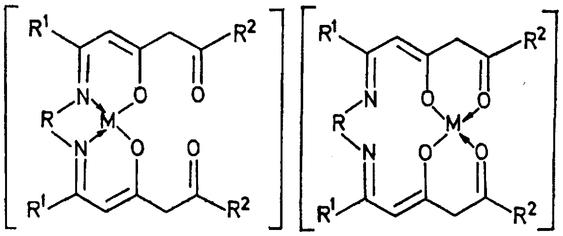
Mononuclear Metal Complexes.—It is established that certain metal ions have a specific preference for binding to particular donor atoms under competitive conditions. Therefore it is conceivable that in the acyclic ligands (1) the possibility of positional isomerism, in which a particular metal may be co-ordinated in either of the available compartments, will occur. Metal ions may co-ordinate to either the N$_2$O$_2$ or O$_2$O$_2$ compartments in these potentially tetra-anionic ligands. The complex formed may then be compared with chelates of well characterised 1,3-diketonates and their Schiff-base derivatives in order to establish the co-ordination present.



(III)

Similar magnetic, spectral, and chemical properties would be expected for similar co-ordination environments.

When a chloroform solution of compound (2a) is stirred with an aqueous solution of a stoicheiometric amount of Cu[O$_2$CMe]$_2$ the CHCl$_3$ layer becomes purple. The mononuclear acyclic Schiff-base copper(II) complex (5a; M = Cu) is isolated as purple crystals from the CHCl$_3$ layer.[9] It has been proposed that the presence of the metal causes hydrolysis of the macrocycle by enhancing the electropositive nature of the azomethine carbon, rendering it prone to nucleophilic attack.[10] The preformed complex (7a; M = Cu) also undergoes hydrolytic cleavage on shaking in chloroform–water, and from the aqueous layer it is possible to recover small quantities of bis(heptane-2,4,6-trionato)dicopper(II), the product of complete hydrolysis of the macrocyclic complex. It is not certain that this is the definite mode of reaction, however, as acid-catalysed hydrolytic cleavage of (2a)



	R	R^1	R^2	
(5a)	[CH$_2$]$_2$	Me	Me	(6a)
(5b)	CH(Me)CH$_2$	Me	Me	
(5g)	[CH$_2$]$_2$	Pr^n	Pr^n	
(5l)	[CH$_2$]$_2$	Me	Bu^t	
(5m)	[CH$_2$]$_2$	Me	Ph	(6m)
	[CH$_2$]$_2$	Me	C$_6$H$_4$OMe-*p*	(6n)
	[CH$_2$]$_2$	Me	C$_6$H$_4$Me-*p*	(6o)
	[CH$_2$]$_2$	Me	C$_6$H$_4$Br-*p*	(6p)
	CH(Me)CH$_2$	Me	Ph	(6q)
	[CH$_2$]$_3$	Me	Ph	(6r)
	CH(Me)CH$_2$	Me	C$_6$H$_4$Br-*p*	(6s)

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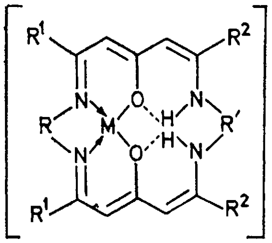
[9] T. Yano, T. Ushijima, M. Sasaki, H. Kobayashi, and K. Ueno, *Bull. Chem. Soc. Japan*, 1972, **45**, 2452.

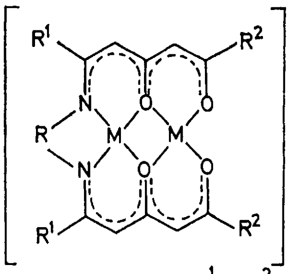
[10] M. Vidali, U. Casellato, P. A. Vigato, and R. Graziani, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1455.

yields (1a), and the acid used is ethanoic acid which would be released during reaction of Cu[O_2CMe]$_2$ with (2a) to yield (7a; M = Cu). It is possible that the metal *facilitates* cleavage, but when the same reaction conditions are used for nickel(ii) acetate and (2a) only the macrocyclic species (7a; M = Ni) is recovered. A similar proposition has been forwarded for the formation of (6a; M = UO_2)·MeOH from (2a), [UO_2][NO_3]$_2$·6H_2O, and Li[OH] in MeOH, (7a; M = UO_2) being proposed as an intermediate prior to hydrolysis.[10]



	R	R′	$R^1 = R^2$
(7a)	$[CH_2]_2$	$[CH_2]_2$	Me
(7g)	$[CH_2]_2$	$[CH_2]_2$	Pr^n

The purple complexes (5b) and (5g) (M = Cu) are isolated by the above method for (5a) from the macrocyclic ligands (2b) and (2g) respectively.[1] An analogous reaction with Cu[O_2CMe]$_2$ and (2c), however, leads [1] only to the isolation of the homobinuclear complex (8c; M = Cu). Complex (5l; M = Cu) was prepared by the reaction of equimolar amounts of Cu[O_2CMe]$_2$ and (1l) in 95% ethanol.



	R	R^1	R^2
(8a)	$[CH_2]_2$	Me	Me
(8c)	$[CH_2]_3$	Me	Me

Reaction of the free Schiff base (1a) with a stoicheiometric amount of Cu[O_2CMe]$_2$ in 95% ethanol led first to the precipitation of the green homobinuclear complex (8a; M = Cu). Removal of this complex resulted in the precipitation of a second, deep green, complex (6a; M = Cu)·H_2O. When this complex was removed from the mixture a purple solution remained from which (5a; M = Cu) was isolated. Thus in a single reaction the binuclear complex and two mononuclear positional isomers are formed with respective yields of 50, 25, and 25% based on copper. The reaction of (1a) and Ni[O_2CMe]$_2$·4H_2O under similar conditions to the above led only to the formation of (5a; M = Ni). In contrast, the reactions of dioxouranium(vi) acetate or oxovanadium(iv) acetate with (1a) in hot EtOH–$CHCl_3$ or MeOH–$CHCl_3$ yielded (6a; M = UO_2)·MeOH and (6a; M = VO) respectively. The dioxouranium(vi) complex was also prepared using a template procedure from [UO_2][O_2CMe]$_2$, en, and (3a) in hot MeOH.

Mononuclear transition-metal complexes of Schiff bases derived from unsymmetrical phenyl-substituted triketones are readily prepared by reaction of the ligand with the metal acetate dissolved in suitable solvent systems. The reaction of a hot acetone solution of (1m) with hot aqueous Ni[O_2CMe]$_2$ or [VO][O_2CMe]$_2$, in 1 : 1 ratio, gave the complexes (5m; M = Ni) and (6m; M = VO)·Me_2CO respectively; reaction of (1m) dissolved in hot $CHCl_3$ with hot ethanolic solutions of Cu[O_2CMe]$_2$ or [UO_2][O_2CMe]$_2$ in 1 : 1 ratios gave (6m; M = Cu)·H_2O and (6m; M = UO_2)·EtOH respectively. Similar reactions were used to prepare (6n)·$CHCl_3$, (6o), and (6p)·2H_2O (M = Cu). The *para* substituents did not appear to influence co-ordination selectivity.

The complexes were characterised by elemental analysis, and i.r., electronic, and mass spectra. Those with the metal in the N_2O_2 compartment are soluble in most common organic solvents, whilst those with the metal in the O_2O_2 compartment are less soluble in the common solvents and more soluble in co-ordinating solvents.

The i.r. spectra of the complexes (Table 3) fall into two categories: those that have strong bands in the 1 700 cm^{-1} region arising from unco-ordinated carbonyl groups, and those in which these bands are absent but which show hydrogen bonded N–H stretches at *ca.* 3 200 cm^{-1}. The former group have the metal co-ordinated in the N_2O_2 compartment of the ligand. Complexes (5a; M = Cu or Ni) show two strong bands in the 1 700 cm^{-1} region suggesting two different orientations of the unco-ordinated carbonyl groups in the solid state. The spectra of these complexes in $CDCl_3$ solution show only one carbonyl stretch. The i.r. spectrum of (5m; M = Ni) shows a strong band at 1 675 cm^{-1}. The second category of complexes have the metal atom co-ordinated in the O_2O_2 compartment and show bands assigned to the N–H stretch, but no free-carbonyl band. There are bands present in the 1 500—1 600 cm^{-1} region assigned to ν(C $\overset{...}{-}$ O) and ν(C $\overset{...}{-}$ C).

Mass spectra were used to show that the mononuclear complexes were pure, and that no binuclear species were present. The spectra showed strong peaks corresponding to the mass of the parent molecular ions, P^+, but did not give peaks corresponding to the double charged molecular ion.

The diffuse reflectance spectra of the copper complexes (5) (Table 3) exhibited a band in the vicinity of 550 nm. The visible spectra of $CHCl_3$ solutions of these complexes also showed a band in this region. This compares directly with a value of 545 nm for [Cu(acen)] [acen = *NN′*-ethylenebis(acetylacetoneiminate)] [11] which has a square-planar copper atom co-ordinated in an N_2O_2

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[11] S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, 1961, **35**, 105.

donor site. Complex (6a; M = Cu)·H_2O has two bands at 558 and 671 nm compared with 550 and 650 nm for [Cu(acac)$_2$] (acac = pentane-2,4-dionate).[11] Complex (5a; M = Ni) has a band at 555 nm which may be compared with 565 nm for [Ni(acen)].[12] The complex [Ni(acac)$_2$]·$2H_2O$ has two bands at 650 and 645 nm,[13] and the nickel achieves six-co-ordination through addition of two water molecules. Similar behaviour patterns were observed for the diffuse reflectance spectra of complexes of (1m).

TABLE 2

Hydrogen-1 n.m.r. spectra of acyclic Schiff bases in $CDCl_3$

	δ [a]/p.p.m.				
	CH_3	CH	N–H · · · O	CH_2 of bridge	Others
(1a)	1.87 (s, h) 1.92 (s, g) 2.20 (s, a and b)	4.64 (s, f) 4.98 (s, d) 5.04 (s, e)	10.93 (br)	3.56 [b]	3.34s (c) CH_2 (triketone) 10.16 (br) O–H · · · O
(1m)	1.81 (s, b) 1.89 (s, j) 1.94 (s, p) 2.02 (s, a)	4.83 (s, k) 4.89 (s, d) 5.04 (s, e) 5.11 (s, n) 5.77 (s, f) 5.79 (s, l)	10.92 (br)	3.34—3.55 [b]	3.91 (s, m), 3.93 (s, c) } CH_2 (triketone) 10.36 (br) O–H · · · O 7.36—8.09 [b] Aromatic
(1l)	1.92 (s, b) 1.94 (s, a)	4.72 (s, f) 5.00 (s, d) 5.12 (s, e)	10.89 (br)	3.42 [b]	3.46 (c) CH_2 (triketone) 10.17 (br) O–H · · · O 1.13 (s, h), 1.15 (s, g) } Me of Bu^t

[a] Assignments to protons are given in parentheses after the multiplicity; the letters refer to the protons in structures (I)—(III). [b] Complex multiplet. s = Singlet, br = broad.

TABLE 3

Major i.r. bands (cm^{-1}, KBr disc) and diffuse-reflectance bands (nm) for mononuclear complexes of acyclic Schiff bases

	I.r.					
Complex	ν(N–H)	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{O})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{O})$ + $\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{C})$	$\nu(\mathrm{C} \overset{\cdots}{-} \mathrm{N})$	Other bands	Diffuse reflectance
(5a; M = Cu)			1 591	1 518	1 721, 1 705 } C=O unco-ordinated	549m, 379 (sh), 345s
(6a; M = Cu)·H_2O	3 170	1 618	1 600	1 525	3 440 H_2O	671w, 558w, 481 (sh), 394 (sh), 360s
(5a; M = Ni)			1 588	1 510	1 720, 1 695 } C=O unco-ordinated	555m, 420 (sh), 385s
(6a; M = VO)	3 220	1 618	1 592	1 534	984 V=O	685w, 581w, 481 (sh), 402 (sh), 369s
(6a; M = UO_2)·MeOH	3 160	1 630	1 610	1 532	3 420 O–H 908 O=U=O (ν_3)	413s, br
(5b; M = Cu) *			1 590	1 500	1 700 C=O unco-ordinated	
(5g; M = Cu)			1 590	1 505	1 710 C=O unco-ordinated	545m, 370s, br
(5l; M = Cu)			1 588	1 502	1 700 C=O unco-ordinated	543m, 385s
(5m; M = Ni)			1 600	1 510	1 675 C=O unco-ordinated	555 (sh), 474s, 435s, 373s
(6m; M = Cu)·H_2O	3 140	1 641	1 598, 1 544	1 527	3 400 H_2O	574 (sh), 450s
(6m; M = VO)·Me_2CO	3 055	1 627	1 600, 1 588	1 527	981 V=O 1 702 unco-ordinated Me_2CO	694 (sh), 641m, 450 (sh), 412s 413s, br
(6m; M = UO_2)·EtOH	3 260	1 620	1 608, 1 583	1 535	892 O=U=O (ν_3)	686m, 431 (sh), 402s, 373 (sh)
(6q; M = Cu)	3 040	1 583	1 570, 1 540	1 520		598m, 445s, 406 (sh)
(6r; M = Cu)	3 040	1 610	1 573	1 535		
(6n; M = Cu)·$CHCl_3$	3 140	1 640	1 600	1 521	1 223, 758, 665 $CHCl_3$	602m, 446s
(6o; M = Cu)	3 020	1 630	1 608, 1 582	1 521		633w, 495 (sh), 417s, br
(6p; M = Cu)·$2H_2O$	3 160	1 628	1 600, 1 580	1 511	3 300 H_2O	633m, 469s
(6s; M = Cu)	3 060	1 610	1 599, 1 581	1 510		630m, 503s, 467s

* Nujol mull on NaCl plates.

s = Strong, m = medium, w = weak, sh = shoulder, and br = broad.

Magnetic-moment measurements were carried out for the mononuclear complexes (Table 4). The copper(II) and oxovanadium(IV) complexes gave moments consistent with the presence of one unpaired electron per molecule. Complex (5a; M = Ni) consistently gave a high moment of 1.20 B.M.,* whereas it was expected that this complex would be diamagnetic. The diffuse-reflectance spectrum suggests a square-planar geometry and it is possible

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

[12] S. Yamada, E. Ohno, Y. Kuge, A. Takeuchi, S. Yamanouchi, and K. Iwasaki, *Co-ordination Chem. Rev.*, 1968, **3**, 247.

[13] G. Maki, *J. Chem. Phys.*, 1958, **29**, 162.

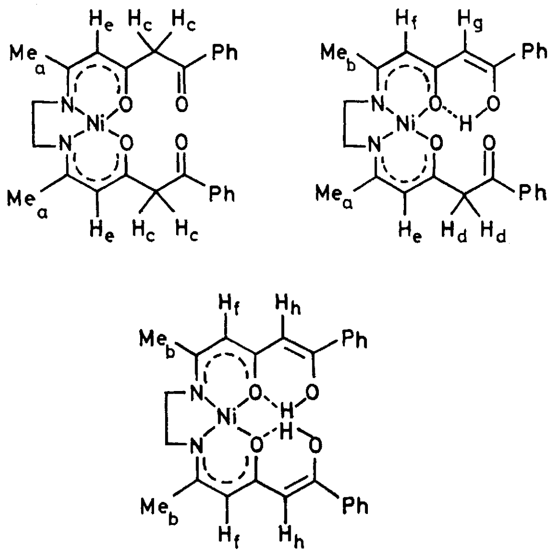
that the magnetism arises from a distortion from this geometry. However, close inspection of the mass spectrum shows the presence of a trace quantity of the dinickel complex, (8a; M = Ni), which would be expected to contain the second nickel in the O_2O_2 site. By analogy with [Ni(acac)$_2$] it is expected that this second nickel atom would be six-co-ordinate through co-ordination by solvent, or oligomerisation, and thus paramagnetic. The presence of the binuclear complex could then cause the high observed moment. The ^1H n.m.r. spectrum of (5a; M = Ni) gave broad resonances also indicating the presence of paramagnetism.

TABLE 4

Room-temperature magnetic moments for mononuclear complexes of acyclic Schiff bases

Complex	T/K	$\mu_{eff.}$/B.M.
(5a; M = Cu)	296	1.76
(6a; M = Cu)·H_2O	295	1.80
(5a; M = Ni)	294	1.20
(6a; M = VO)	295	1.73
(6a; M = UO_2)·MeOH	296	0.46
(5m; M = Ni)	295	0
(6m; M = Cu)·H_2O	297	1.70
(6m; M = VO)·Me_2CO	295	1.77
(6m; M = UO_2)·EtOH	296	0.65

Complex (5m; M = Ni) is rigorously diamagnetic and this is also shown by the ^1H n.m.r. in $CDCl_3$ solution. The spectrum suggests the presence of diketo-, monoenol, and dienol tautomers. The tautomers and the spectral assignment are shown in the Figure. The dioxouranium(VI) complexes also exhibit a small residual paramagnetism; these complexes also retain a molecule of solvation so that the uranium atom might achieve its preferred seven-co-ordination.



Hydrogen-1 n.m.r. data for (5m; M = Ni): 1.77 (a), 1.81 (b), 2.95 (c), 2.99 (d), 3.70 (CH_2, bridge), 4.83 (e), 4.91 (f), 5.01 (g), 5.43 (h), 7.20—8.20 (aromatic), and 10.61 p.p.m. (Ph–OH)

The single-crystal X-ray structures of (6a; M = UO_2)·MeOH,[14] prepared by the template method, (6m; M = VO),[15] and (6m; M = Cu) [6] have been independently determined during the course of this investigation. The structures confirm the use of the O_2O_2 compartment, and the achievement of seven-co-ordination by U^{VI}. The complexes of UO_2 and VO are monomers, whilst that of Cu is a dimer. The magnetic moment of the latter is 1.86 B.M. at 297 K and little, or no, magnetic exchange occurs.[6]

The co-ordination selectivity of the ligands (1a) and (1m) is demonstrated by the formation of the pure mononuclear chelates (5a) and (5m) (M = Ni), (6a) and (6m) (M = VO), and (6a) and (6m) (M = UO_2). The difference between the two ligands in their selective behaviour is evidenced in their reaction with copper where, for (1a), a mixture of the positional isomers (5a) and (6a) is recovered together with bis(heptane-2,4,6-trionato)dicopper(II), and where, for (1m), complex (6m) is formed.

It has been suggested [5,10] that the mode of incorporation may be viewed as a preference of the 'harder' species, UO_2 and VO, for the O_2O_2 compartment, and the 'softer' species, Ni and Cu, for the N_2O_2 compartment. Copper(II) does, however, give an ambiguous selectivity. There is an absence of detailed stability-constant data for related Schiff-base systems, and concerning $[UO_2]^{2+}$, $[VO]^{2+}$, and pentane-2,4-dione, but for this diketone the sequence Cu > Ni is well characterised.[16]

The preference of Ni for the N_2O_2 compartment in (1a) is well illustrated by the addition of Ni[O_2CMe]$_2$ to (5a; M = Cu) in hot EtOH. The nickel replaces the copper and so releases copper into the solution. This is readily incorporated into the outside compartment of (5a; M = Cu) to give (8a; M = Cu), which being insoluble in EtOH is precipitated. Interestingly, there is no evidence for the presence of either the mixed complex (8a; M = Ni, Cu) or (6a; M = Cu) in the work up, only (5a; M = Ni) being recovered from the solution.

The preparation of pure, mononuclear, positional isomers of the acyclic Schiff-base ligands has been achieved, and, as evidenced by the formation of (8a; M = Cu), these can act as precursors in the synthesis of binuclear species.

EXPERIMENTAL

Details concerning physical measurements have been given in Part 1,[1] as were the preparative details for the macrocyclic Schiff bases. 1-Phenylhexane-1,3,5-trione was prepared by the method of Miles *et al.*,[17,18] and the remaining substituted triketones by this method using the corresponding methyl ester in place of methyl benzoate.

Syntheses of Acyclic Schiff Bases.—6,11-*Dimethyl*-7,10-*diazahexadeca*-5,11-*diene*-2,4,13,15-*tetraone* (1a). The

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

[15] R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, and D. P. Gavel, *Inorg. Chem.*, 1976, **15**, 1646.

[16] G. Gutnikov and H. Freiser, *Analyt. Chem.*, 1968, **40**, 39.

[17] M. L. Miles, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 1007.

[18] M. L. Miles, T. M. Harris, and C. R. Hauser, *Org. Synth.*, 1966, **46**, 57.

macrocyclic Schiff base (2a) (5g) was dissolved in chloroform (300 cm^3). Dilute aqueous acetic acid (1.8 cm^3, 17 mol dm^{-3} in 200 cm^3 of water) was added. The mixture was stirred so that the two phases were mixed intimately and stirring was continued for 1.5 h at room temperature. The mixture was then poured into a separating funnel (2 l) and the lower chloroform layer was collected. The chloroform was removed by evaporation under reduced pressure until a pale yellow oil remained. The oil was dissolved in 95% ethanol (20 cm^3) and any unchanged insoluble (2a) was removed by filtration. Cooling of the solution afforded fine pearly plates which were collected by filtration after crystallisation was complete. The crystals were dried over silica gel *in vacuo*, yield 20% (Found: C, 61.6; H, 7.9; N, 8.7. $C_{16}H_{24}N_2O_4$ requires C, 62.3; H, 7.8; N, 9.0%), P^+ at *m/e* 308.

The remaining acyclic Schiff bases were prepared by the following general method. The triketone (0.01 mol) was dissolved in hot 95% ethanol (50 cm^3) and ethane-1,2-diamine (en) (0.005 mol) dissolved in 95% ethanol (5 cm^3) was added. The resulting orange or brown solution was stirred and warmed on a steam-bath for 5 min whereupon the Schiff base either was precipitated or slowly crystallised on cooling. The product was collected by filtration, dried in air, and crystallised from the minimum volume of hot chloroform. The pure Schiff base was then collected by filtration and dried over silica gel *in vacuo*. Condensation of 1-phenylhexane-1,3,5-trione and en yielded 5,10-dimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1m) as small bright yellow crystals (Found: C, 72.0; H, 6.4; N, 6.4. $C_{26}H_{28}N_2O_4$ requires C, 72.1; H, 6.5; N, 6.4%), P^+ at *m/e* 432. H_2mba [H_2mba = 1-(*p*-methoxyphenyl)hexane-1,3,5-trione] and en yielded bright yellow crystals of 1,14-di(*p*-methoxyphenyl)-5,10-dimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1n) (Found: C, 68.0; H, 6.6; N, 5.9. $C_{28}H_{32}N_2O_6$ requires C, 68.2; H, 6.5; N, 5.7%), parent peak of very low relative intensity at m_4e 392 [P − 100]$^+$ (P^+ at *m/e* 492 was not present). H_2pmb [H_2pmb = 1-(*p*-tolyl)hexane-1,3,5-trione] and en yielded bright yellow crystals of 5,10-dimethyl-1,14-di(*p*-tolyl)-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1o) (Found: C, 73.2; H, 6.9; N, 6.0. $C_{28}H_{32}N_2O_4$ requires C, 73.2; H, 7.0; N, 6.0%), P^+ at *m/e* 460. H_2pba [H_2pba = 1-(*p*-bromophenyl)hexane-1,3,5-trione] and en yielded bright yellow crystals of 1,14-di(*p*-bromophenyl)-5,10-dimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraone (1p) (Found: C, 53.1; H, 4.7; Br, 29.8; N, 4.6%. $C_{26}H_{26}Br_2N_2O_4$ requires C, 52.9; H, 4.4; Br, 27.0; N, 4.7%), P^+ at *m/e* 592 (^{81}Br). H_2pva [H_2pva = 7,7-dimethyloctane-2,4,6-trione] and en yielded pale yellow pearly plates of 2,2,7,12,17,-17-hexamethyl-8,11-diazaoctadeca-6,12-diene-3,5,14,16-tetraone (1l) (Found: C, 67.9; H, 9.3; N, 7.1. $C_{22}H_{36}N_2O_4$ requires C, 67.3; H, 9.2; N, 7.1%), P^+ at *m/e* 392.

Syntheses of Mononuclear Transition-metal 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). Copper(II) acetate monohydrate (0.6 g) dissolved in water (50 cm^3) was added to a solution of (2a) (0.1 g) in chloroform (50 cm^3) and the two phases were intimately mixed by stirring. Stirring was continued for 1.5 h at room temperature during which the chloroform layer first became deep green and then purple. The mixture was poured into a separating funnel and the lower chloroform layer was collected and evaporated under reduced pressure to yield a purple solid. The solid was redissolved in a small volume of fresh chloroform and the resulting solution was eluted with chloroform down a column of neutral Brock activated alumina (50 g). A purple fraction was collected and removal of the solvent by evaporation under reduced pressure left a purple crystalline solid which was recrystallised from hexane–chloroform as a deep purple microcrystalline solid, yield 20% (Found: C, 51.8; H, 6.2; N, 7.5. $C_{16}H_{22}CuN_2O_4$ requires C, 52.0; H, 5.9; N, 7.3%), P^+ at *m/e* 369 (^{63}Cu). The aqueous layer was found to contain small quantities of bis(heptane-2,4,6-trionato)dicopper(II) and of (7a; M = Cu) by comparison with authentic samples.

[6,11-*Dimethyl*-7,10-*diazahexadeca*-5,11-*diene*-2,4,13,15-*tetraonato*(2−)-$O^2O^4O^{13}O^{15}$]*copper*(II) *hydrate*, (6a)·H_2O. Copper(II) acetate monohydrate (0.65 g) was dissolved in hot 95% ethanol and added to a hot ethanolic solution of (1a) (1.0 g). The solution immediately became deep green and (8a; M = Cu) [5] was precipitated (50% yield based on copper). The complex (8a) was removed by filtration whilst the solution was still hot and the deep green filtrate was allowed to cool. Deep green crystals of (6a; M = Cu)·H_2O (25% yield based on copper) were then collected by filtration and dried over silica gel *in vacuo*. The solvent was removed from the remaining purple filtrate leaving a purple oil which was dissolved in a small volume of chloroform and eluted with chloroform down a column containing neutral Brock activated alumina (25 g). A purple fraction was collected and removal of the solvent yielded (5a; M = Cu) as a purple microcrystalline solid (25% yield based on copper) (Found: C, 49.3; H, 5.8; N, 7.0. $C_{16}H_{22}CuN_2O_4$·H_2O requires C, 49.5; H, 6.2; N, 7.2%), P^+ at *m/e* 369 (^{63}Cu).

(6a; M = VO). Compound (1a) (2.0 g) dissolved in hot 95% ethanol–chloroform was added to a stirred suspension of oxovanadium(IV) acetate (1.2 g) in hot 95% ethanol. The reaction mixture was stirred and heated under reflux for 4 h. The deep green solution was filtered whilst hot to remove any unchanged [VO][O_2CMe]$_2$ and the filtrate was reduced to small volume (*ca.* 25 cm^3) on a steam-bath. After the solution had been allowed to cool, the deep green precipitate was collected by filtration and dried over silica gel *in vacuo*, yield 50% (Found: C, 51.4; H, 6.1; N, 7.6. $C_{16}H_{22}N_2O_5V$ requires C, 51.4; H, 5.8; N, 7.5%), P^+ at *m/e* 373 (^{51}V).

(6a; M = UO_2)·MeOH. Compound (3a) (3.0 g) dissolved in hot methanol and en (0.6 g), also dissolved in methanol, were simultaneously added to a hot methanolic solution of dioxouranium(VI) acetate dihydrate (4.48 g). The mixture was heated on a steam-bath for *ca.* 2 min when an orange solid was precipitated. The solution was allowed to cool and the product was collected by filtration and dried over silica gel *in vacuo*, yield 80%.

Alternatively, this complex was prepared by reaction of (1a) (1.0 g) and [UO_2][O_2CMe]$_2$·$2H_2O$ (1.38 g) in hot methanolic solution where the product was precipitated as an orange solid, yield 90% (Found: C, 33.7; H, 4.4; N, 4.5%. $C_{16}H_{22}N_2O_6U$·MeOH requires C, 33.5; H, 4.3; N, 4.6%).

(5a; M = Ni). Compound (1a) (1.0 g) dissolved in hot 95% ethanol was added to a hot ethanolic solution of nickel(II) acetate tetrahydrate (0.81 g). The resulting brown solution was warmed on a steam-bath for 5 min and allowed to cool. The brown solid was collected by filtration, recrystallised from 95% ethanol, and recollected. The brown shiny crystals were dried over silica gel *in vacuo*, yield 60% (Found: C, 52.1; H, 6.3; N, 8.0. $C_6H_{22}N_2NiO_4$ requires C, 52.6; H, 6.0; N, 7.6%), P^+ at *m/e* 364 (^{58}Ni).

The complex was also prepared from (5a; M = Cu) by the following method. Complex (5a; M = Cu) (1.0 g) dissolved in hot 95% ethanol was added to a hot ethanolic solution of Ni[O$_2$CMe]$_2$·4H$_2$O (0.81 g). The complex (8a; M = Cu) was precipitated immediately and was removed by filtration after the solution had been allowed to cool. The brown filtrate was evaporated under reduced pressure to remove the solvent, leaving a brown-green solid which was dissolved in a small volume of chloroform. The brown chloroform solution was eluted with chloroform down a column containing neutral Brock activated alumina (25 g) and a brown-red fraction was collected. Removal of the solvent left a brown solid, P^+ at *m/e* 364 (^{58}Ni) with a minor peak at *m/e* 369 corresponding to (5a; M = Cu).

[6,8,11-*Trimethyl*-7,10-*diazahexadeca*-5,11-*diene*-2,4,13,15-*tetraonato*(2−)-N^{7}N^{10}O^{4}O^{13}]*copper*(II) (5b). The method for the preparation of (5a; M = Cu) was followed using (2b)[1] (1.8 g) and Cu[O$_2$CMe]$_2$·H$_2$O (1.0 g). The product was obtained as a purple oil which could not be crystallised (Found: C, 55.6; H, 6.8; N, 7.8. C$_{17}$H$_{24}$CuN$_2$O$_4$ requires C, 53.1; H, 6.3; N, 7.3%), P^+ at *m/e* 383 (^{63}Cu).

[8,13-*Di-n-propyl*-9,12-*diazaeicosa*-7,13-*diene*-4,6,15,17-*tetraonato*(2−)-N^{9}N^{12}O^{6}O^{15}]*copper*(II) (5g). The method used for (5a; M = Cu) was followed using Cu[O$_2$CMe]$_2$·H$_2$O (0.27 g) and (2 g)[1] (0.6 g). The purple oil obtained was dissolved in a small volume of fresh chloroform and eluted with ethyl acetate down a column containing neutral Brock activated alumina (25 g). A brown fraction was collected and removal of the solvent by evaporation under reduced pressure left a brown oil. Addition of ethanol precipitated a brown microcrystalline solid which was removed by filtration and was found to be (7g; M = Cu). The solvent was removed from the filtrate by evaporation under reduced pressure to yield a purple-brown oil which recrystallised from a small volume of hot chloroform as a purple-brown solid (Found: C, 60.3; H, 7.7; N, 6.3. C$_{24}$H$_{38}$CuN$_2$O$_4$ requires C, 59.7; H, 7.9; N, 5.8%), P^+ at *m/e* 481 (^{63}Cu).

[2,2,7,12,17,17-*Hexamethyl*-8,11-*diazaoctadeca*-6,12-*diene*-3,5,14,16-*tetraonato*(2−)-N^{8}N^{11}O^{5}O^{14}]*copper*(II) (5l). Compound (1l) (1.0 g) dissolved in hot 95% ethanol (50 cm^3) was added to a hot ethanolic solution of Cu[O$_2$CMe]$_2$·H$_2$O (0.51 g in 50 cm^3) immediately forming a deep green solution. The mixture was warmed on a steam-bath for 2 h and the resulting deep purple solution was allowed to stand overnight at room temperature. The solvent was removed by evaporation under reduced pressure and the purple oil obtained was dissolved in a small volume of chloroform and eluted with chloroform down a column containing neutral Brock activated alumina (50 g). A purple fraction was collected and the solvent was removed by evaporation under reduced pressure. The resulting purple oil was recrystallised from a small volume of hot chloroform to yield fine purple-brown needles which were collected by filtration, washed with a small volume of light petroleum (b.p. 80—100 °C), and dried over silica gel *in vacuo*, yield 60% (Found: C, 57.9; H, 7.6; N, 5.9. C$_{22}$H$_{34}$CuN$_2$O$_4$ requires C, 58.1; H, 7.5; N, 6.1%), P^+ at *m/e* 453 (^{63}Cu).

[5,10-*Dimethyl*-1,14-*diphenyl*-6,9-*diazatetradeca*-4,10-*diene*-1,3,12,14-*tetraonato*(2−)-O^{1}O^{3}O^{12}O^{14}]*copper*(II) *hydrate* (6m)·H$_2$O. Compound (1m) (1.0 g) dissolved in hot chloroform (150 cm^3) was added to a solution of Cu[O$_2$CMe]$_2$·H$_2$O (0.46 g) in hot 95% ethanol (150 cm^3). Initially a green-brown solid appeared which dissolved on warming on a steam-bath. The reaction was warmed for 5 min and the deep green mixture was allowed to cool. The fine deep green crystals were collected by filtration and dried over silica gel *in vacuo*, yield 80% (Found: C, 61.2; H, 5.4; N, 5.6. C$_{26}$H$_{26}$CuN$_2$O$_4$·H$_2$O requires C, 60.9; H, 5.5; N, 5.4%), P^+ at *m/e* 493 (^{63}Cu).

[5,10-*Dimethyl*-1,14-*diphenyl*-6,9-*diazatetradeca*-4,10-*diene*-1,3,12,14-*tetraonato*(2−)-N^{6}N^{9}O^{3}O^{12}]*nickel*(II) (5m). Nickel (II) acetate tetrahydrate (0.58 g) dissolved in a small volume of hot water (20 cm^3) was added dropwise to a solution of (1m) (1.0 g) dissolved in hot acetone (200 cm^3). The resulting deep red-brown solution was boiled on a steam-bath for 5 min and set aside to cool for 2 h. The acetone was removed by evaporation under reduced pressure until brown crystals began to appear. These were redissolved in a minimum volume of hot acetone and on standing small red-brown needles were deposited which were collected by filtration and dried over silica gel *in vacuo*, yield 70% (Found: C, 64.0; H, 5.4; N, 5.6. C$_{26}$H$_{26}$N$_2$NiO$_4$ requires C, 63.8; H, 5.3; N, 5.7%), P^+ at *m/e* 488 (^{58}Ni).

(6m; M = VO)·Me$_2$CO. Oxovanadium(IV) acetate (0.43 g) dissolved in hot water (25 cm^3) was added dropwise to (1m) (1.0 g) dissolved in hot acetone (200 cm^3). The resulting green solution was boiled for 5 min and allowed to cool. The green crystals were collected by filtration, recrystallised from a small volume of hot dichloromethane, recollected, and dried over silica gel *in vacuo*, yield 70% (Found: C, 62.7; H, 5.8; N, 5.4. C$_{26}$H$_{26}$N$_2$O$_5$V·Me$_2$CO requires C, 62.7; H, 5.7; N, 5.0%), P^+ at *m/e* 497 (^{51}V).

(6m; M = UO$_2$)·EtOH. Compound (1m) (1.0 g) dissolved in hot chloroform (150 cm$_3$) was added to [UO$_2$]-[O$_2$CMe]$_2$·2H$_2$O (0.98 g) dissolved in hot 95% ethanol (150 cm^3). The deep brown solution was warmed on a steam-bath for 5 min and allowed to cool. The deep maroon precipitate was collected by filtration and washed by suspending in boiling 95% ethanol. The orange-red solid was collected by filtration and dried over silica gel *in vacuo*, yield 70% (Found: C, 44.8; H, 4.3; N, 3.6. C$_{26}$H$_{26}$N$_2$O$_6$U·EtOH requires C, 45.1; H, 4.0; N, 3.7%), P^+ at *m/e* 700 (^{238}U).

Complexes of acyclic Schiff bases derived from en and the *para*-substituted-phenyltriketones were prepared by the following general method. The Schiff base (0.002 mol) dissolved in hot chloroform (100 cm^3) was added to Cu[O$_2$CMe]$_2$·H$_2$O (0.002 mol) dissolved in hot 95% ethanol (100 cm^3). The resulting deep green solution was warmed for 5 min on a steam-bath and allowed to cool. The deep green microcrystalline 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(2−)-*O*^{1}*O*^{3}*O*^{12}*O*^{14}]copper(II)–chloroform(1/1) (6n)·CHCl$_3$ (Found: C, 51.7; H, 4.6; N, 4.1. C$_{28}$H$_{30}$CuN$_2$O$_6$·CHCl$_3$ requires C, 51.8; H, 4.9; N, 3.7%, P^+ at *m/e* 553 (^{63}Cu); (1o) yielded [5,10-dimethyl-1,14-di(*p*-tolyl)-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-*O*^{1}*O*^{3}*O*^{12}*O*^{14}]copper(II) (6o) (Found: C, 61.0; H, 5.8; N, 4.9. C$_{28}$H$_{30}$CuN$_2$O$_4$ requires C, 60.2; H, 5.7; N, 5.0%), P^+ at *me/* 521 (^{63}Cu); and (1p) yielded [1,14-di(*p*-bromophenyl)-5,10-dimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-*O*^{1}*O*^{3}*O*^{12}*O*^{14}]-copper(II) dihydrate (6p)·2H$_2$O (Found: C, 47.1; H, 3.8; Br, 23.9; N, 3.9. C$_{26}$H$_{24}$Br$_2$CuN$_2$O$_4$·2H$_2$O requires C, 47.2; H, 3.9; Br, 22.4; N, 3.9%), P^+ at *m/e* 653 (^{63}Cu, 2 × ^{81}Br).

The remaining mononuclear complexes were prepared by the following general template procedure. The triketone (0.004 mol) dissolved in hot 95% ethanol and the alkanediamine (0.002 mol) also dissolved in 95% ethanol were mixed and warmed on a steam-bath for 15 min. The resulting yellow solution was added to $Cu[O_2CMe]_2 \cdot H_2O$ (0.002 mol) dissolved in hot 95% ethanol. The deep green solution was heated on a steam-bath for 15 min and allowed to cool. The deep green microcrystalline solid was collected by filtration and dried over silica gel *in vacuo*, yields averaged 70%. 1-Phenylhexane-1,3,5-trione and pn yielded [5,7,10-trimethyl-1,14-diphenyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-$O^1O^3O^{12}O^{14}$]copper(II) (6q) (Found: C, 63.3; H, 6.0; N, 5.4. $C_{27}H_{28}CuN_2O_4$ requires C, 63.8; H, 5.5; N, 5.5%), P^+ at *m/e* 507 (^{63}Cu); the same 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(2−)-$O^1O^3O^{13}O^{15}$]copper(II) (6r) (Found: C, 63.5; H, 5.8; N, 5.3. $C_{27}H_{28}CuN_2O_4$ requires C, 63.8; H, 5.5; N, 5.5%), P^+ at *m/e* 507 (^{63}Cu). H_2pda and propane-1,2-diamine (pn) yielded [1,14-di(*p*-bromophenyl)-5,7,10-trimethyl-6,9-diazatetradeca-4,10-diene-1,3,12,14-tetraonato(2−)-$O^1O^3O^{12}O^{14}$]copper(II) (6s) (Found: C, 48.7; H, 4.5; Br, 23.7; N, 4.2. $C_{27}H_{26}Br_2CuN_2O_4$ requires C, 48.7; H, 3.9; Br, 24.0; N, 4.2%), P^+ at *m/e* 667 (^{63}Cu, 2 × ^{81}Br).

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