Compartmental Ligands. Part I. Mononuclear Macrocyclic Schiff-base Transition-metal Complexes derived from 1,3,5-Triketones

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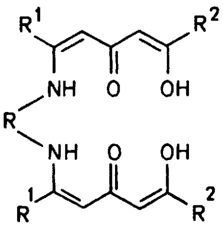
A series of macrocyclic Schiff bases derived from 1,3,5-triketones and α,ω-alkanediamines has been prepared and their mononuclear complexes with Cu^{II}, Ni^{II}, and Co^{II} are described. The symmetrical macrocycles are derived from the reaction of heptane-2,4,6-, nonane-3,5,7-, undecane-4,6,8-, or 2,8-dimethylnonane-3,5,7-trione (2 mol) with ethane-1,2-, propane-1,2-, propane-1,3-, or butane-1,4-diamine (2 mol), in ethanol, and are potentially tetra-anionic ligands. Treatment of the pre-formed macrocycle with metal acetate, or a template reaction involving the triketone, diamine, and metal salt, gives the corresponding mononuclear transition-metal derivative. The complexes are characterised by their i.r., diffuse-reflectance, and mass spectra and room-temperature magnetic moments. Positional isomers of the copper(II) complex of the macrocycle derived from heptane-2,4,6-trione (2 mol), ethane-1,2-diamine (1 mol), and propane-1,2-diamine (1 mol) are reported. Complexes of other unsymmetrical macrocyclic Schiff bases prepared by similar routes are described. The symmetrical macrocycle derived from heptane-2,4,6-trione and benzene-1,2-diamine is also reported.

LIGANDS capable of bringing two, or more, metal atoms into close proximity have been presented in the recent literature.[1,2] In general, the impetus for this work has come from a requirement to understand the magnetic interactions present in oligometallic clusters. Observations on the formation of bimetallic complexes derived from using transition-metal Schiff-base complexes as ligands for metal β-diketonates[3,4] led us to the realisation that fusion of a β-diketonate, with oxygen donor atoms, and a Schiff base, with oxygen and nitrogen donor atoms, could in principle provide a single ligand capable of complex formation with either two identical metal atoms (homobinuclear) or to two different metal atoms (heterobinuclear).

The general form of this class of ligand is depicted in (1). Clearly this provides a framework upon which a wide variety of modifications can be made in donor atoms, functional diamine, and substituent groups, to produce a versatile class of ligands whose predominant feature would be the availability of two adjacent, yet different, co-ordination compartments. The reaction of 1,3,5-triketones with α,ω-alkanediamines was therefore investigated and found to yield two classes of ligand, depending on the nature of the substituents present in the triketone. Alicyclic ligands of type (**1**) were obtained when R^1 = Me and R^2 = Bu^t or C_6H_4X-*p* (X = OMe, Me or Br), and macrocyclic ligands of type (2) were obtained when $R^1 = R^2$ = Me, Et, or Pr^n. A range of α,ω-alkanediamines was used. The ligands are potentially tetra-anionic and their selectivity towards various metals has been investigated. Preliminary communication of this work has been made.[5-7] This paper will



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

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[1] M. D. Glick and R. L. Lintvedt, *Progr. Inorg. Chem.*, 1976, **21**, 233.

[2] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391.

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

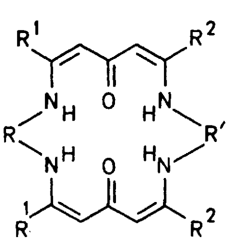
[4] D. E. Fenton and S. E. Gayda, unpublished work.

[5] D. E. Fenton and S. E. Gayda, *J.C.S. Chem. Comm.*, 1974, 960.

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

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

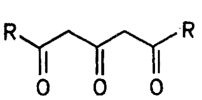
be concerned with the macrocyclic ligands (2) and the mononuclear transition-metal complexes derived from them.



	R	R′	R¹=R²
(2a)	$[CH_2]_2$	$[CH_2]_2$	Me
cis-(2b)	$CH(Me)CH_2$	$CH(Me)CH_2$	Me
trans-(2b)	$CH(Me)CH_2$	$CH_2CH(Me)$	Me
(2c)	$[CH_2]_3$	$[CH_2]_3$	Me
(2d)	$[CH_2]_4$	$[CH_2]_4$	Me
(2e)	$[CH_2]_2$	$[CH_2]_2$	Et
cis-(2f)	$CH(Me)CH_2$	$CH(Me)CH_2$	Et
trans-(2f)	$CH(Me)CH_2$	$CH_2CH(Me)$	Et
(2g)	$[CH_2]_2$	$[CH_2]_2$	Pr^n
(2h)	$[CH_2]_2$	$CH(Me)CH_2$	Me

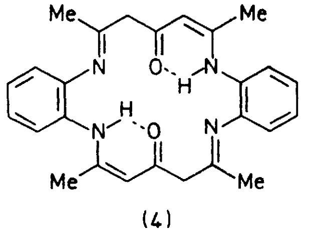
RESULTS AND DISCUSSION

Macrocyclic Schiff Bases.—The symmetrical 1,3,5-triketones (3; R = Me, Et, Pr^n, or Pr^i) were prepared by literature methods [8-10] as precursors for the synthesis



	R
(3a)	Me
(3b)	Et
(3c)	Pr^n
(3d)	Pr^i

of the Schiff bases. Condensation of (3a) with the α,ω-alkanediamines, ethane-1,2-diamine (en), propane-1,2-diamine (pn), propane-1,3-diamine (pd), or butane-1,4-diamine (bd), in equimolar ratios in hot 95% ethanolic solution gave pale yellow crystalline solids. These compounds were found to be the macrocyclic Schiff bases (2a),[11] an equimolar mixture of *cis*- and *trans*-(2b), (2c), and (2d), respectively. The isomeric mixture was not separated and it was found that reactions in stoicheiometric amounts designed to yield acyclic species of type (1) led only to the formation of macrocycles. When (3b) was treated with en or pn in a similar manner, yellow crystals of the corresponding macrocyclic Schiff bases (2e) or an isomeric mixture of *cis*- and *trans*-(2f) were obtained. The macrocyclic Schiff base (2g) was prepared by a similar reaction using (3c) and en. The addition of en to the triketone (3d) did not afford an isolable product. Condensation of (3a) with benzene-1,2-diamine gave two products, the macrocyclic Schiff base (4) which was recovered as a red microcrystalline solid and 4-acetonyl-2-methyl-1*H*-1,5-benzodiazepine obtained as white needles.



(4)

Recrystallisation of the above compounds from ethanolic solution yielded the anhydrous Schiff bases with the exceptions of (2c)·$0.5H_2O$ and (4)·$0.5H_2O$. The diazepine contained one molecule of ethanol of solvation. The macrocycles were characterised on the basis of their i.r. and ^1H n.m.r. spectra, chemical analyses, and mass spectra.

The i.r. spectra of the macrocyclic Schiff bases (Table 1) recorded as KBr discs did not exhibit free carbonyl-stretching frequencies in the 1 700 cm^{-1} region as would be expected for the acyclic species. Sharp bands ascribable to N–H stretches were not observed, but broad weak absorptions attributable to hydrogen-bonded N–H · · · O were seen in the 3 000—3 500 cm^{-1} region. The mass spectra of the macrocycles all showed a strong peak corresponding to the mass of the parent molecular ion (P^+), except for (4) which gave a parent peak of relatively low abundance at *m*/*e* 425, corresponding to $[P - 3H]^+$. The macrocycles generally fragmented by loss of the bridging amine group, and by loss of the triketone moiety.

TABLE 1

Infrared bands (cm^{-1}) for macrocyclic Schiff bases (KBr disc)

(2a)	3 300br, 1 620 (sh), 1 580s, 1 510m, 1 420m, 1 320s, 1 265m, 1 238s, 1 169s, 1 094m, 897m, 717m
(2b)	3 300br, 1 590s, 1 534s, 1 512s, 1 475s, 1 435s, 1 370m, 1 355m, 1 320s, 1 244s, 1 123s, 1 038m, 795m, 721m
(2c)·$0.5H_2O$	3 450br, 1 632m, 1 570s, 1 482m, 1 462s, 1 300 (sh), 1 280s, 1 178s, 1 138s, 1 041m, 860m, 794s
(2d)	3 300br, 2 900m, 2 820m, 1 620 (sh), 1 560s, 1 520 (sh), 1 468m, 1 435m, 1 300s, 1 265s, 1 240s, 1 162s, 1 092s, 800s, 723m
(2e)	3 300br, 2 962m, 1 624s, 1 572s, 1 540m, 1 513s, 1 485m, 1 419m, 1 377m, 1 359m, 1 325s, 1 241s, 1 170m, 1 099s, 1 080m, 1 059m, 800s, 718s
(2f)	3 300br, 2 950m, 1 589s, 1 324m, 1 240m, 1 129m, 1 062m, 1 040m, 809m, 728s
(2g)	3 050br, 2 955m, 2 922m, 2 862m, 1 615 (sh), 1 580s, 1478m, 1 360m, 1 345m, 1 327s, 1 240s, 1 204m, 1 193m, 1 166m, 1 101s, 1 056m, 800s, 720s
(4)·$0.5H_2O$	3 400br, 1 658s, 1 627s, 1 579s, 1 479s, 1 402s, 1 360s, 1 326s, 1 195s, 1 180m, 981m, 960m, 918m, 802m, 741s
Diazepine·EtOH [a]	3 300s, 3 160s, 1 640s, 1 545s, 1 496s, 1 312s, 1 274m, 1 251s, 1 198s, 1 148m, 1 040m, 1 026m, 945m, 881s, 860s, 759s, 717m
(2h) [b]	3 300br, 1 590br, 1 560s, 1 510m, 1 310s, 1 240s, 1 200m, 1 163s, 1 095s, 1 040m, 798s, 723s

br = Broad, s = strong, m = medium, and sh = shoulder.

[a] Diazepine = 4-acetonyl-2-methyl-1*H*-1,5-benzodiazepine.

[b] Run as Nujol mull.

The ^1H n.m.r. spectra of the macrocycles in $CDCl_3$ solution (Table 2) were consistent with the formulated

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[8] J. R. Bethell and P. Maitland, *J. Chem. Soc.*, 1962, 3751.

[9] P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.*, 1969, **34**, 4049.

[10] S. S. Deshapande, *J. Indian Chem. Soc.*, 1932, **9**, 303.

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

structures (2). The amine bridging-group methylene protons appeared as multiplets and in (2a) irradiation at the NH resonance reduced the CH_2 multiplet to a single peak. The NH resonance appeared as a broad signal in the 10—11 p.p.m. region and is assigned to the four hydrogen-bonded NH protons. The methine protons (CH) were observed as singlets in the 4.6—4.8 p.p.m. region and there was no evidence to suggest that a second tautomer having CH_2 groups in the triketone spine was present. The delocalised tautomer (I) is therefore proposed for the aliphatic bridged species. The spectra of (2b) and (2f) showed broadening or multiplicity of resonances due to the presence of *cis* and *trans* isomers. The spectra are further complicated due to the presence of chiral centres in the amine bridges. No attempts were made to separate the isomers. The ^1H spectrum of (4) gave resonances corresponding to four CH_2 and two CH protons, and a broad signal due to only two N–H · · · O protons. Two methyl resonances were observed, and the structure is that in which there are two NH and two imine groups present; the nature of the isomer has not been proven.

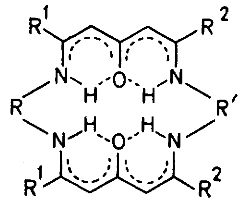

(I)

TABLE 2

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

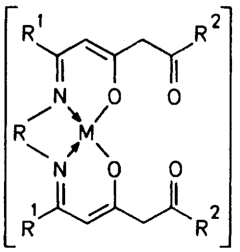
Base	δ/p.p.m. CH_3	CH	N–H · · · O	Terminal CH_2 and/or CH of bridge	Others
(2a)	1.84 (s)	4.73 (s)	10.80 (br)	3.30 [a]	
(2b)	1.87 (s)	4.62 (s) 4.64 (s)	10.0—11.1 [a]	3.25 [a] 3.64 (br)	1.24 (db) Bridge CH_3
(2c)	1.87 (s)	4.65 (s)	10.09 (br)	3.31 [a]	3.11 [a] Central CH_2 of bridge
(2d)	1.85 (s)	4.65 (s)	10.45 (br)	3.22 [a]	1.68 [a] Central CH_2 of bridge
(2e)	1.09 (t)	4.78 (s)	10.42 (br)	3.30 [a]	2.16 (q) CH_2 of Et group
(2f)	1.0—1.5 [b]	4.72 (s) 4.78 (s)	10.6—11.1 [a]	3.29 [a] 3.75 [a]	1.0—1.5 [c] Bridge CH_3 2.14 [d], 2.11 [d] } CH_2 of Et group
(2g)	0.96 (t)	4.76 (s)	10.10 (br)	3.31 [a]	1.52 [e], 2.0—2.2 [a] } CH_2 of Pr^n group
(4)	2.08 (s) 2.27 (s)	5.08 (s)	10.40 (br)		7.0—7.4 [a] Aromatic protons 2.88 (s) CH_2 (triketone)

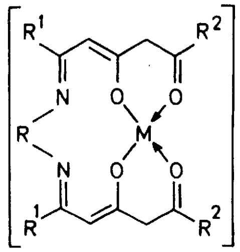
s = Singlet, db = doublet, t = triplet, q = quartet, and br = broad.

[a] Complex multiplet. [b] Two overlapping triplets. [c] Two doublets. [d] Two overlapping quartets. [e] Sextet.

The asymmetric macrocyclic Schiff base (2h) was prepared by condensation of the acyclic Schiff base (1a; $R^1 = R^2 = Me$, $R = [CH_2]_2$)[7] with pn. The macrocycle formed gave P^+ at *m/e* 346 in the mass spectrum and no indication of a carbonyl frequency in the i.r. An interesting feature of the mass spectrum was the presence of peaks attributable to (2a) and (2b). A physical mixture of (2a) and (2b) showed only peaks corresponding to those macrocycles, and so it is postulated that, in the ring-closure reaction, diamine exchange occurs to produce all three products. Diamine exchange has been observed in attempts to remove macrocyclic Schiff-base ligands such as 6,7,15,16-tetrahydrodibenzo-[*e,m*][1,4,8,11]dioxadiazacyclotetradecine from its nickel(II) complex by addition of pd.[12] Attempts to effect ring closure of (1a) with pd led only to amorphous oligomeric material being formed.

Mononuclear Metal Complexes.—The reaction of the macrocyclic ligands with Cu^{II} and Ni^{II} was investigated. It had previously been reported that the reaction of copper(II) acetate with (2a) yields the acyclic species (5a; M = Cu),[11] and that similarly uranyl nitrate and (2a), in the presence of Li[OH], yield (6a; M = UO_2)· MeOH.[13] These reactions were attributed to hydrolysis of the macrocycle facilitated by the presence of a metal atom which could enhance the electropositive nature of the azomethine carbon atom thus rendering it more susceptible to nucleophilic attack.[13]





	R	$R^1 = R^2$
(5a)	$[CH_2]_2$	Me
(5b)	CH(Me)CH_2	Me

	R	$R^1 = R^2$
(6a)	$[CH_2]_2$	Me

When $Cu[O_2CMe]_2 \cdot H_2O$, dissolved in 95% EtOH, was mixed with hot $CHCl_3$ solutions of the macrocyclic

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[12] L. G. Armstrong and L. F. Lindoy, *Inorg. Chem.*, 1975, **14**, 1322.

[13] P. A. Vigato, M. Vidali, U. Casellato, R. Graziani, and F. Benetollo, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 595.

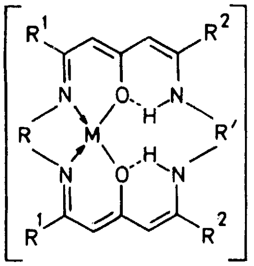
Schiff bases (2a), (2b), and (2e)—(2g) in equimolar ratios brown microcrystalline precipitates were obtained. The complexes so formed are the mononuclear (7a), (7b), and (7e)—(7g) (M = Cu). The reaction of Ni[$O_2CMe]_2\cdot 4H_2O$ with the macrocyclic Schiff bases under the same conditions yielded brown microcrystalline precipitates of the analogous mononuclear nickel species. Complex (7a; M = Co) may be prepared by treating Co[$O_2CMe]_2\cdot 4H_2O$, in 95% EtOH, with a hot $CHCl_3$ solution of (2a) under an atmosphere of dry dinitrogen. The complex forms as a red microcrystalline precipitate. The reaction of Co[$O_2CMe]_2\cdot 4H_2O$ with the remaining Schiff bases under the same reaction conditions led to inconsistent results. The reaction of twice as much metal(II) acetate with the Schiff bases under the same experimental conditions yielded only the mononuclear complexes. The macrocycles (2c), (2d), and (4) failed to form metal(II) complexes by reaction under the above conditions.

TABLE 3

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

Complex	I.r.				Diffuse reflectance
	ν(N–H)	$\nu(\mathrm{C\overset{\cdots}{-}O})$	$\nu(\mathrm{C\overset{\cdots}{-}O})$ + $\nu(\mathrm{C\overset{\cdots}{-}C})$	$\nu(\mathrm{C\overset{\cdots}{-}N})$	
(7a; M = Cu)	3 160	1 630	1 590	1 508	623m, 446 (sh), 427s, 378s
(7a; M = Ni)	3 200	1 640	1 590	1 510	584m, 450s, 417s,br, 382s,br
(7a; M = Co)	3 200	1 635	1 590	1 512	543 (sh), 477s,br, 446s,br
(7b; M = Cu)	3 160	1 630	1 590	1 510	615m, 498 (sh), 423s,br
(7b; M = Ni)	3 200	1 630	1 592	1 510	537m, 426s, 374s,br, 347s
(7e; M = Cu)	3 160	1 630	1 590	1 510	624m, 452s, 430s
(7e; M = Ni)	3 200	1 640	1 597	1 512	584m, 468s, 452s, 414s, 398 (sh), 344s
(7f; M = Cu)	3 150	1 629	1 590	1 505	619m, 493 (sh), 447s, 424 (sh), 365 (sh)
(7f; M = Ni)	3 200	1 630	1 592	1 510	568m, 460 (sh), 442s, 408 (sh), 382 (sh), 350s
(7g; M = Cu)	3 150	1 628	1 589	1 509	617s, 524 (sh), 465 (sh), 427s, 373 (sh)
(7g; M = Ni)	3 200	1 638	1 595	1 510	578s, 472s, 442s, 408s, 395 (sh), 344s
(7h; M = Cu)	3 160	1 635	1 592	1 500	591 (sh), 534s,br, 372 (sh)
(7h; M = Ni)	3 200	1 640	1 598	1 515	578s, 552 (sh), 481s, 450 (sh), 412br
(7j; M = Cu)	3 170	1 640	1 597	1 510	621s, 502s,br, 424 (sh), 373m
(7i; M = Cu)	3 250	1 622		1 510	633 (sh), 543 (sh), 520s,br, 454s,br, 420s, 370br
(7i; M = Ni)	3 270	1 625		1 510	585m, 463s, 435s, 405s, 342s
(7k; M = Cu)	3 250	1 620		1 500	621 (sh), m, 549s,br, 481s,br, 413s, 369s,br

br = Broad, s = strong, m = medium, w = weak, and sh = shoulder.



	R	R′	$R^1=R^2$
(7a)	$[CH_2]_2$	$[CH_2]_2$	Me
cis-(7b)	CH(Me)CH_2	CH(Me)CH_2	Me
trans-(7b)	CH(Me)CH_2	CH_2CH(Me)	Me
(7e)	$[CH_2]_2$	$[CH_2]_2$	Et
cis-(7f)	CH(Me)CH_2	CH(Me)CH_2	Et
trans-(7f)	CH(Me)CH_2	CH_2CH(Me)	Et
(7g)	$[CH_2]_2$	$[CH_2]_2$	Pr^n
(7h)	$[CH_2]_2$	CH_2CH(Me)	Me
(7i)	$[CH_2]_2$	$[CH_2]_3$	Me
(7j)	CH(Me)CH_2	$[CH_2]_2$	Me
(7k)	CH(Me)CH_2	$[CH_2]_3$	Me

Metal complexes of unsymmetrical Schiff bases were prepared by utilisation of the ring closure of their acyclic precursors. Thus (5a; M = Cu or Ni) [7] reacted with alkanediamines in hot ethanol to give symmetrical or unsymmetrical macrocyclic products. Reaction with en yielded (7a; M = Cu or Ni), and reaction with pn or pd yielded (7h) or (7i) (M = Cu or Ni). Ring-closure reactions also take place between (5b; M = Cu) and alkanediamines to give (7b), (7j), and (7k) (M = Cu). The complexes (7h) were also prepared by the reaction of (2h) with either M[$O_2CMe]_2$ (M = Cu or Ni). All the complexes gave a weak i.r. absorption in the 3 150—3 300 cm^{-1} region, assigned to a hydrogen-bonded NH stretch (Table 3). Strong or medium bands in the 1 500—1 700 cm^{-1} region are characteristic of $\nu(\mathrm{C\overset{\cdots}{-}O})$, $\nu(\mathrm{C\overset{\cdots}{-}C})$, and $\nu(\mathrm{C\overset{\cdots}{-}N})$; no bands occur in the range 1 700—1 800 cm^{-1} confirming the absence of unco-ordinated carbonyls due to hydrolysis. The complexes (7h) and (7j), derived from ring closure of (5a) and (5b) (M = Cu) respectively, give different i.r. spectra. This indicates that positional isomerisation is present; the Cu^{II} can exist in either of the two different N_2O_2 donor compartments offered by the unsymmetrical macrocycle.

The diffuse-reflectance spectra of the copper(II) complexes gave a medium or strong band in the 491—633 nm region (Table 3), with the exception of (7h), (7i), and (7k) which gave only shoulders. These bands lie within the range for square-planar (N_2O_2) copper(II) co-ordination.[14] The spectra of the nickel(II) complexes gave strong or medium bands in the 537—585 nm region indicating square-planar co-ordination for Ni^{II}.[14] Complex (7a; M = Co) gave a band at 543 nm which does not correspond well with that for [Co(acen)] [acen = *NN*′-ethylenebis(acetylacetoneiminate)], at 454 nm, which has a square-planar Co^{II} co-ordinated in an N_2O_2 donor site,[15] verified by an *X*-ray crystal-structure determination.[16] This suggests that the cobalt(II) ion may not necessarily be square planar in (7a).

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

[15] G. Costa, G. Mestroni, G. Tauzher, and L. Stefani, *J. Organometallic Chem.*, 1966, **6**, 181.

[16] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 386.

The mass spectra of the complexes gave intense peaks corresponding to the mass of the parent molecular ions P^+. Only the complexes (7a; M = Cu) and (7h; M = Cu or Ni) gave peaks consistent with loss of the metal atoms, with peaks of relatively low abundance corresponding to the ligand monocations. None of the complexes gave peaks at higher mass indicative of the formation of bimetallic species. Peaks were observed in the spectra of the unsymmetrical Schiff-base complexes corresponding to the presence of symmetric species, *e.g.* (7h; M = Ni) showed also (7a) and (7b). It is probable that these are the products of amine-exchange processes during the syntheses of the complexes. A similar behaviour pattern was observed for the free ligands.

The room-temperature magnetic moments (Table 4) for the copper(II) complexes were consistent with the presence of one unpaired electron. The nickel(II) complexes, however, were not rigorously diamagnetic as would be expected in square-planar nickel(II) complexes and suggest a deviation from planarity or a residual temperature-independent paramagnetism (t.i.p.). The complex (7a; M = Co) gave an anomalous moment of 3.20 B.M.,* further indicating that the metal may not be in a square-planar environment.

TABLE 4

Room-temperature magnetic moments for mononuclear macrocyclic Schiff-base complexes

Complex	T/K	$\mu_{eff.}$/B.M.
(7a; M = Cu)	296	1.70
(7a; M = Ni)	295	0.72
(7a; M = Co)	295	3.20
(7b; M = Cu)	293	2.05
(7b; M = Ni)	297	0.78
(7e; M = Cu)	291	1.74
(7e; M = Ni)	297	0.68
(7h; M = Cu)	297	1.76
(7h; M = Ni)	295	0.38
(7j; M = Cu)	293	1.76
(7i; M = Cu)	296	1.80
(7i; M = Ni)	295	0.21
(7k; M = Cu)	295	1.70

Whilst the physical measurements for the copper(II) and nickel(II) complexes support the proposed structures as having square-planar (or slightly distorted square-planar) geometry about the metal in the N_2O_2 site, a different structure appears likely for the cobalt complex. The magnetic susceptibility of (7a; M = Co), χ_g, is 10.64×10^{-6} c.g.s. units at 295 K, which would give a magnetic moment of 2.26 B.M. per cobalt ion in a dimeric structure. This value lies in the region for low-spin Co^{II}, and the moment found for optically inactive [Co(salen)][salen = *NN'*-ethylenebis(salicylideneiminate)] is 2.5 B.M.[17] The structure of this complex is dimeric, each cobalt being made five-co-ordinate by sharing an oxygen atom from a salen ligand.[18,19] The possibility of an equilibrium between high- and low-spin forms of (7a; M = Co) is also present.[17]

The formation of the unsymmetrical bridged macrocyclic complexes (7h) and (7j) (M = Cu) shows that positional isomerism may exist in these complexes. Mass-spectroscopic evidence, however, indicates an inability for the macrocyclic Schiff bases to form even trace amounts of homobinuclear metal complexes under the reaction conditions cited in this work. This does not preclude the possibility that under different reaction conditions such homo-, or hetero-, binuclear complexes could be prepared.

EXPERIMENTAL

Infrared spectra were recorded, as KBr discs, in the 250—4 000 cm^{-1} region using a Perkin-Elmer 457 grating instrument, ^{1}H n.m.r. spectra at 100 MHz using a Varian HA100, or a JEOL JNM-PS-100 Fourier-transform spectrometer, and electronic spectra as powder diffuse-reflectance spectra using a Cary 14 spectrometer. Magnetic moments were measured by the Gouy method at room temperature; Pascal's constants were used for diamagnetic correction and tris(ethane-1,2-diamine)nickel(II) thiosulphate was used as a calibrant. Microanalyses were by Miss M. A. McKinnon of these laboratories.

Heptane-2,4,6-trione, nonane-3,5,7-trione, undecane-4,6,-8-trione, and 2,8-dimethylnonane-3,5,7-trione were synthesised according to reported methods.[8-10]

Syntheses of Macrocyclic Schiff Bases.—6,10,17,21-*Tetramethyl*-5,9,16,20-*tetrahydrodibenzo*[b,k][1,4,10,13]*tetra-azacyclo-octadecine*-8,19-*dione* (4).—Freshly recrystallised benzene-1,2-diamine (1.0 g) was dissolved in hot 95% ethanol and added to a warm solution of heptane-2,4,6-trione (3a) (1.3 g) also dissolved in 95% ethanol. A brown solution was immediately formed which darkened further on heating on a steam-bath with stirring. After 0.5 h the solution was removed from the steam-bath and set aside to cool. When cooled to room temperature, water (*ca.* 300 cm^3) was added and a cloudy solution was formed which became clear again on standing at room temperature. This solution was slowly concentrated on a steam-bath to a volume of *ca.* 160 cm^3 when the solution became cloudy and was then allowed to cool to room temperature. After leaving the solution in a refrigerator for 2 d, an orange-brown solid was precipitated on allowing the solution to warm to room temperature. On allowing the solution to stand, more colourless needles also crystallised. Separation of the orange solid and colourless needles was effected by heating the mixture until the needles dissolved leaving the orange-red solid which was collected by filtration. The colourless needles were recrystallised from the filtrate on allowing to stand. The orange-red solid was found to be (4) (Found: C, 71.5; H, 6.5; N, 13.1. $C_{26}H_{28}N_4O_2\cdot 0.5H_2O$ requires C, 71.4; H, 6.4; N, 12.8%), P^+ in mass spectrum at *m/e* 428. The colourless needles, after recrystallising from ethanol, were found to be 4-acetonyl-2-methyl-1*H*-1,5-benzodiazepine (Found: C, 69.4; H, 7.1; N, 11.3. $C_{13}H_{14}N_2O\cdot C_2H_5OH$ requires C, 69.2; H, 7.7; N, 10.7%), P^+ at *m/e* 214.

2,5,9,14,18-*Pentamethyl*-1,4,10,13-*tetra-azacyclo-octadeca*-5,8,14,17-*tetraene*-7,16-*dione* (2h). An ethanolic solution of (1a)[7] 6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,-15-tetraone (2.0 g) was heated and to it was added propane-1,2-diamine (pn) (0.48 g) in ethanol. The reaction mixture

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[17] L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 1972, **11**, 457.

[18] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671.

[19] R. De Iasi, S. L. Holt, and B. Post, *Inorg. Chem.*, 1970, **10**, 1498.

was heated for 15 min. The resulting yellow precipitate was filtered off after cooling to give (2h) (Found: C, 65.7; H, 8.8; N, 16.8. $C_{19}H_{30}N_4O_2$ requires C, 65.8; H, 8.7; N, 16.1%), P^+ at *m/e* 346.

The experimental procedure used for the remaining macrocyclic Schiff bases was as follows. The triketone (0.01 mol) dissolved in hot 95% ethanol (30 cm^3) was mixed with an alkanediamine (0.01 mol) also dissolved in 95% ethanol (5 cm^3). The mixture was heated on a steam-bath for 5 min whereupon either pale yellow crystals were precipitated while the solution was still hot or crystallisation occurred on cooling. The Schiff bases obtained were collected by filtration and dried over silica gel *in vacuo*.

Condensation of (3a) with ethane-1,2-diamine yielded 5,9,14,18-tetramethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (2a) (Found: C, 64.7; H, 8.3; N, 16.8. $C_{18}H_{28}N_4O_2$ requires C, 65.0; H, 8.4; N, 16.8%), P^+ at *m/e* 332. Reaction of (3a) with pn yielded an equimolar mixture of the two isomers 2,5,9,11,14,18-hexamethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (*trans*-2b) and 2,5,9,12,14,18-hexamethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (*cis*-2b) (Found: C, 66.9; H, 9.0; N, 15.5. $C_{20}H_{32}N_4O_2$ requires C, 66.6; H, 8.9; N, 15.5%), P^+ at *m/e* 360. Compound (3a) and propane-1,3-diamine (pd) yielded 6,10,16,20-tetramethyl-1,5,11,15-tetra-azacycloeicosa-6,9,16,19-tetraene-8,18-dione (2c) (Found: C, 64.9; H, 9.0; N, 14.9. $C_{20}H_{32}N_4O_2 \cdot 0.5H_2O$ requires C, 65.1; H, 8.8; N, 15.1%), P^+ at *m/e* 360. Compound (3a) and butane-1,4-diamine (bd) yielded 7,11,18,22-tetramethyl-1,6,12,17-tetra-azacyclodocosa-7,10,18,21-tetraene-9,20-dione (2d) (Found: C, 68.2; H, 9.4; N, 14.9. $C_{22}H_{36}N_4O_2$ requires C, 68.0; H, 9.3; N, 14.4), P^+ at *m/e* 388.

Nonane-3,5,7-trione (3b) and en gave 5,9,14,18-tetraethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (2e) (Found: C, 68.0; H, 9.4; N, 14.3. $C_{22}H_{36}N_4O_2$ requires C, 68.0; H, 9.3), P^+ at *m/e* 388. Compound (3b) and pn gave an equimolar mixture of the two isomers 5,9,14,18-tetraethyl-2,11-dimethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (*trans*-2f) and 5,9,14,18-tetraethyl-2,12-dimethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (*cis*-2f) (Found: C, 70.0; H, 9.4; N, 13.7. $C_{24}H_{40}N_4O_2$ requires C, 69.2; H, 9.6; N, 13.4%), P^+ at *m/e* 416.

Undecane-4,6,8-trione and en yielded 5,9,14,18-tetra-n-propyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dione (2g) (Found: C, 69.4; H, 9.6; N, 13.1. $C_{26}H_{44}N_4O_2$ requires C, 70.8; H, 9.1; N, 12.7%), P^+ at *m/e* 444. Yields averaged 80%.

Syntheses of Symmetrical Mononuclear Macrocyclic Schiff-base Complexes.—(*a*) *Copper*(II) *complexes*. The complexes were prepared by the following general method. The macrocyclic Schiff base (0.01 mol) dissolved in the minimum volume of hot chloroform was added to a solution of copper(II) acetate monohydrate (0.01 mol) dissolved in the minimum volume of hot 95% ethanol. The resulting solution immediately became deep green and after warming on a steam-bath a fine shiny brown microcrystalline solid was precipitated. The more highly substituted Schiff-base complexes generally required more heating before precipitation occurred. The mixture was allowed to cool and the product was collected by filtration. The complex was purified by suspending in hot benzene and filtering which was carried out three times. The pure complex was dried over silica gel *in vacuo*.

Compound (2a) yielded [5,9,14,18-tetramethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato-(2−)-$N^1N^4O^7O^{16}$]copper(II) (7a; M = Cu) (Found: C, 54.6; H, 6.7; N, 14.3. $C_{18}H_{26}CuN_4O_2$ requires C, 54.8; H, 6.6; N, 14.2%), P^+ at *m/e* 393 (^{63}Cu). Alternatively, (7a; M = Cu) could be prepared by condensing an equimolar ratio of [6,11-dimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(2−)-$N^7N^{10}O^4O^{13}$]copper(II) (5a) and en in hot 95% ethanolic solution.

The equimolar isomeric mixture of *trans*- and *cis*-(2b) yielded an isomeric mixture of [2,5,9,11,14,18-hexamethyl-1,4,10-13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato(2−)-$N^1N^4N^7O^{16}$]copper(II) *trans*-(7b; M = Cu) and [2,5,9,12,14,18-hexamethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato(2−)-$N^1N^4O^7O^{16}$]-copper(II) *cis*-(7b; M = Cu) (Found: C, 56.6; H, 7.3; N, 13.1. $C_{20}H_{30}CuN_4O_2$ requires C, 57.1; H, 7.1; N, 13.2%), P^+ at *m/e* 421 (^{63}Cu). Complex (7b; M = Cu) could also be prepared by reaction of an equimolar ratio of [6,8,11-trimethyl-7,10-diazahexadeca-5,11-diene-2,4,13,15-tetraonato(2−)-$N^7N^{10}O^4O^{13}$]copper(II) (5b) and pn in hot 95% ethanolic solution.

Compound (2e) yielded [5,9,14,18-tetraethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato-(2−)-$N^1N^4O^7O^{16}$]copper(II) (7e; M = Cu) (Found: C, 58.9; H, 7.6; N, 12.7. $C_{22}H_{34}CuN_4O_2$ requires C, 58.7; H, 7.6; N, 12.4%), P^+ at *m/e* 449 (^{63}Cu).

The equimolar isomeric mixture of *trans*- and *cis*-(2f) yielded an isomeric mixture of [5,9,14,18-tetraethyl-2,11-dimethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato(2−)-$N^1N^4O^7O^{16}$]copper(II) *trans*-(7f; M = Cu) and [5,9,14,18-tetraethyl-2,12-dimethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato-(2−)-$N^1N^4O^7O^{16}$]copper(II) *cis*-(7f; M = Cu) (Found: C, 60.6; H, 8.2; N, 11.6. $C_{24}H_{38}CuN_4O_2$ requires C, 60.2; H, 8.0; N, 11.7%), P^+ at *m/e* 477 (^{63}Cu).

Compound (2g) yielded [5,9,14,18-tetra-n-propyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato-(2−)-$N^1N^4O^7O^{16}$]copper(II) (7g; M = Cu) (Found: C, 61.1; H, 8.2; N, 10.8. $C_{26}H_{42}CuN_4O_2$ requires C, 61.6; H, 8.3; N, 11.0%), P^+ at *m/e* 505 (^{63}Cu).

Yields averaged 60%.

(*b*) *Nickel*(II) *complexes*.—The procedure used for the copper(II) complexes was followed. The complexes were recovered as brown shiny microcrystalline solids.

Compound (2a) yielded (7a; M = Ni) (Found: C, 56.2; H, 6.7; N, 14.7. $C_{18}H_{26}N_4NiO_2$ requires C, 55.5; H, 6.7; N, 14.4%), P^+ at *m/e* 388 (^{58}Ni). This complex was also prepared by condensing an equimolar ratio of (5a; M = Ni) with en in hot 95% ethanolic solution. The equimolar isomeric mixture of *trans*- and *cis*-(2b) yielded an isomeric mixture of *trans*- and *cis*-(7b; M = Ni) (Found: C, 57.3; H, 7.2; N, 13.6. $C_{20}H_{30}N_4NiO_2$ requires C, 57.5; H, 7.2; N, 13.4%), P^+ at *m/e* 416 (^{58}Ni). Compound (2e) yielded (7e; M = Ni) (Found: C, 59.3; H, 7.7; N, 12.5. $C_{22}H_{34}N_4NiO_2$ requires C, 59.3; H, 7.7; N, 12.5%), P^+ at *m/e* 444 (^{58}Ni). The equimolar isomeric mixture of *trans*- and *cis*-(2f) yielded an isomeric mixture of *trans*- and *cis*-(7f; M = Ni) (Found: C, 60.6; H, 8.0; N, 12.0. $C_{24}H_{38}N_4NiO_2$ requires C, 60.9; H, 8.0; N, 11.8%), P^+ at *m/e* 472 (^{58}Ni). Compound (2g) yielded (7g; M = Ni) (Found: C, 62.5; H, 8.4; N, 11.9. $C_{26}H_{42}N_4NiO_2$ requires C, 62.2; H, 8.4; N, 11.1%), P^+ at *m/e* 500 (^{58}Ni).

Yields averaged 60%.

(*c*) [5,9,14,18-*Tetramethyl*-1,4,10,13-*tetra-azacyclo-octa-*

deca-5,8,14,17-*tetraene*-7,16-*dionato*(2−)-$N^1N^4O^7O^{16}$]*cobalt*(II) (7a; M = Co). Cobalt(II) acetate tetrahydrate (0.01 mol) dissolved in hot 95% ethanol was placed in a conical flask. The flask was flushed with a stream of dry nitrogen gas and (2a) (0.01 mol) dissolved in hot chloroform was added. The resulting orange-brown mixture was heated with stirring until the reflux temperature was reached, a dry nitrogen atmosphere being maintained at all times. After 5 min the deep red microcrystalline precipitate was collected by filtration whilst the solution was still hot, and dried over silica gel *in vacuo*, yield 70% (Found: C, 55.5; H, 6.8; N, 14.6. $C_{18}H_{26}CoN_4O_2$ requires C, 55.5; H, 6.7; N, 14.3%), P^+ at *m*/*e* 389 (^{59}Co).

Syntheses of Unsymmetrical Mononuclear Macrocyclic Schiff-base Complexes.—(*a*) *Copper*(II) *complexes.* The following general method was used. Complex (5a) or (5b) (M = Cu) was dissolved in a minimum volume of hot 95% ethanol and an equimolar amount of an alkanediamine dissolved in a small volume of 95% ethanol was added. The purple reaction mixture slowly became deep brown on heating on a steam-bath for *ca.* 10 min. The mixture was cooled and the shiny brown microcrystalline precipitate was collected by filtration and dried over silica gel *in vacuo*. Complex (5a) and pn yielded [5,9,11,14,18-pentamethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato(2−)-$N^1N^4O^7O^{16}$]copper(II) (7h; M = Cu) (Found: C, 55.6; H, 7.1; N, 13.8. $C_{19}H_{28}CuN_4O_2$ requires C, 55.9; H, 6.9; N, 13.7%), P^+ at *m*/*e* 407 (^{63}Cu). Complex (5a) and pd yielded [5,9,15,19-tetramethyl-1,4,10,14-tetra-azacyclononadeca-5,8,15,18-tetraene-7,17-dionato(2−)-$N^1N^4O^7O^{17}$]copper(II) (7i; M = Cu) (Found: C, 55.4; H, 7.2; N, 13.4. $C_{19}H_{28}CuN_4O_2$ requires C, 55.9; H, 6.9; N, 13.7%), P^+ at *m*/*e* 407 (^{63}Cu). Complex (5b) and en yielded [2,5,9,14,18-pentamethyl-1,4,10,13-tetra-azacyclo-octadeca-5,8,14,17-tetraene-7,16-dionato(2−)-$N^1N^4O^7O^{16}$]-copper(II) (7j; M = Cu) (Found: C, 56.3; H, 6.9; N, 13.9. $C_{19}H_{28}CuN_4O_2$ requires C, 55.9; H, 6.9; N, 13.7%), P^+ at *m*/*e* 407 (^{63}Cu). Complex (5b) and pd yielded [2,5,9,15,19-pentamethyl-1,4,10,14-tetra-azacyclononadeca-5,8,15,18-tetraene-7,17-dionato(2−)-$N^1N^4O^7O^{17}$]copper(II) (7k; M = Cu) (Found: C, 57.1; H, 7.2; N, 13.6. $C_{20}H_{30}CuN_4O_2$ requires C, 56.9; H, 7.1; N, 13.2%), P^+ at *m*/*e* 421 (^{63}Cu). Yields averaged 60%.

(*b*) *Nickel*(II) *complexes.* The method used for the copper (II) complexes was followed using (5a; M = Ni). The nickel complexes were recovered as shiny purple or green microcrystalline solids. Complex (5a; M = Ni) and pn yielded (7h; M = Ni) (Found: C, 56.1; H, 7.2; N, 14.1. $C_{19}H_{28}N_4NiO_2$ requires C, 56.6; H, 7.0; N, 13.9%), P^+ at *m*/*e* 402 (^{58}Ni). Complex (5a) and pd yielded (7i; M = Ni) (Found: C, 56.6; H, 6.9; N, 13.7. $C_{19}H_{28}N_4NiO_2$ requires C, 56.6; H, 7.0; N, 13.9%), P^+ at *m*/*e* 402 (^{58}Ni).

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