Metal-ion Template Effects in the Synthesis of Polydentate Schiff-base Ligands. Part 1. Complexes of a Potentially Octadentate ' N_6O_2 ' Ligand and the Crystal and Molecular Structure of a Ten-co-ordinate Barium(II) Complex

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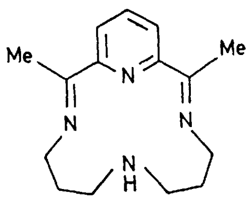
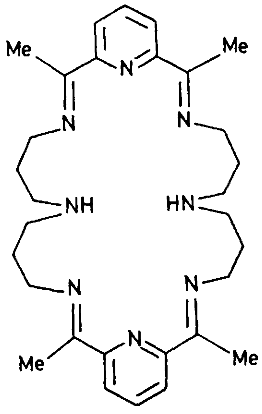
The Sr^{2+} and Ba^{2+} ions are effective templates for the Schiff-base condensation of 2 mol of 2,6-diacetylpyridine with 1 mol of 3,6-diazaoctane-1,8-diamine to give the complexes $[ML(ClO_4)_2]$ where M = Sr or Ba and L is an open-chain potentially octadentate ' N_6O_2 ' ligand. No macrocyclic products were obtained, and attempts to effect ring closure in the diketone L by reaction of $[BaL(ClO_4)_2]$ with a range of primary diamines of varying chain length were unsuccessful. Crystals of $[BaL(ClO_4)_2]$ are orthorhombic with a = 17.651(9), b = 13.870(7), c = 12.710(11) Å, Z = 4, and space group *Pnaa*. 1 468 Reflections above background have been measured by diffractometer, of which 1 062 were used in refinement to R 0.068. The Ba^{2+} ion is ten-co-ordinate being bonded to all eight donor atoms of L and to two ClO_4^- ions. Ba–N and Ba–O bond lengths are in the range 2.81(2)—2.92(2) Å. The conformation of the ligand is such that the two planar keto-pyridyl-imine segments are inclined at 80.2° to each other forming a cleft in which the two ketonic carbon atoms are separated by 5.21 Å. It is suggested that the failure of L to ring-close may be due to a steric barrier to the entry of the difunctional nucleophile into the cleft. Metal-exchange reactions carried out on solutions of $[BaL(ClO_4)_2]$ afforded the complexes $[ML][ClO_4]_2$ (M = Mn^{II}, Fe^{II}, Co^{II}, or Ni^{II}) and the binuclear complex $[Cu_2L(OH)(OH_2)][ClO_4]_3$. Physical data show the iron(II), cobalt(II), and nickel(II) complexes to have distorted octahedral structures in which the unco-ordinated acetyl groups are twisted out of the plane of the pyridine rings. The iron(II) complex is low spin (S = 0) while the cobalt(II) complex exists in a thermally controlled (S = 2) $\rightleftharpoons$ (S = 4) spin equilibrium in the temperature range 90—350 K. In the manganese(II) complex the carbonyl groups of L are co-ordinated and the metal ion appears to be eight-co-ordinate. An intramolecular hydroxo-bridge is suggested for the binuclear copper(II) complex which shows weak antiferromagnetic exchange.

THE effectiveness of metal ions as templates for the cyclic Schiff-base condensation of 2,6-diacetylpyridine with primary diamines leading to complexes of quadri-, quinque-, and sexi-dentate macrocyclic ligands has been amply demonstrated.[1] Of particular interest, recently, has been the observation that certain metal ions promote the synthesis in good yield of ' double ' rings *via* the condensation of two molecules of diketone with two molecules of primary diamine. Thus, while 2,6-diacetylpyridine reacts with 3,3′-diaminodipropylamine in the presence of salts of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} to give complexes of the 14-membered quadridentate macrocycle (1) in a ' 1 + 1 ' condensation, a ' 2 + 2 ' condensation leading to a binuclear complex of the 28-membered octadentate macrocycle (2) occurs when the template ion is Ag^I.[2]

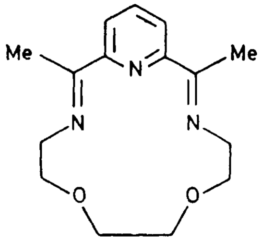


(1)



(2)

Again, it has been shown[3] that reaction of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of salts of Mg^{II}, Mn^{II}, Fe^{III}, Fe^{II}, and Co^{II} gives pentagonal-bipyramidal complexes of the 15-membered quinquedentate macrocycle (3), whereas when Pb^{II} or Ag^I are the templates the ' double ' 30-membered macrocycle (4) is formed in high yield.[4] Since the size of the template metal ion, in relation to the dimensions of the macrocycle cavity, is clearly one important factor in determining the preferred course of the template con-



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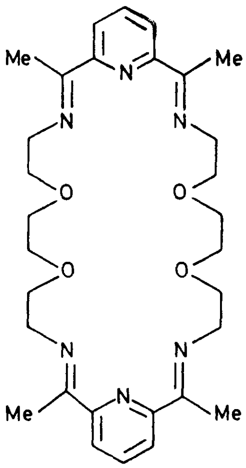
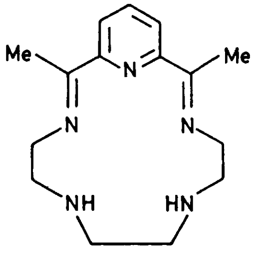


(4)

densation we have investigated the use of the large ions Sr^{II} and Ba^{II} in the reaction of 2,6-diacetylpyridine with 3,6-diazaoctane-1,8-diamine as possible templates for a '2 + 2' condensation. Earlier work[5] has shown that Mg^{II} and several of the (relatively small) first-row transition-metal ions, but not Ca^{II}, are effective templates for the synthesis of the '1 + 1' condensate (5).



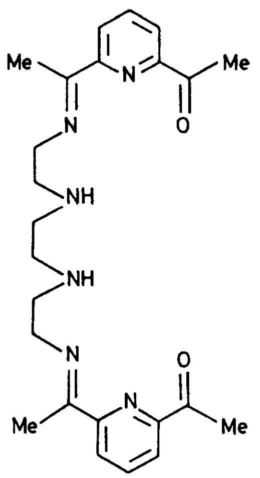
(5)

RESULTS AND DISCUSSION

Reaction of 2,6-diacetylpyridine with 3,6-diazaoctane-1,8-diamine in 1 : 1 mol ratio in the presence of an equimolar amount of $Sr[ClO_4]_2\cdot6H_2O$ or $Ba[ClO_4]_2$ in methanol for 30—60 min at ambient temperature yields colourless crystals (*ca.* 60% yield) of composition $[ML(ClO_4)_2]$, where M = Sr or Ba and L is the non-macrocyclic product [structure (6)] of a Schiff-base condensation of two molecules of diketone with one molecule of primary diamine (see Table 1) as discussed below. No macrocyclic products, either of a '1 + 1' or a '2 + 2' condensation, were isolated. Nor did longer reaction times, or the use of higher reaction temperatures, lead to macrocyclic products; instead, the yields of the complexes of L were diminished at the expense of an amorphous yellow material of low solubility and indefinite composition which gave broad, poorly resolved i.r. spectra suggestive of a polymeric constitution. Yields of $[ML(ClO_4)_2]$ were not appreciably increased by the use of a 2 : 1 ratio of diketone : amine in the synthesis. Reactions conducted in the absence of metal salt yielded only oils or gums.

Infrared spectra of the complexes $[ML(ClO_4)_2]$ (M = Sr or Ba) are virtually identical. Both exhibit a strong band at 1 690 and another at 1 640 cm^{-1} attributable to $\nu(C=O)$ and $\nu(C=N)$ respectively (Table 2). These bands together with the set of four pyridine-ring vibrations occurring between 1 400 and 1 600 cm^{-1} show that a Schiff-base condensation has occurred to yield a product having terminal acetylpyridyl groups. In agreement, only a single sharp N–H stretch at 3 290 cm^{-1}, assigned to the secondary amino-groups, was observed. The occurrence of $\nu(C=O)$ at 1 690 cm^{-1} in the complexes as compared to 1 703 cm^{-1} in uncomplexed diacetylpyridine is evidence, subsequently confirmed, that the carbonyl groups are co-ordinated to the metal. Both the asymmetric stretching (ν_3) and bending (ν_4) vibrations of ClO_4^- are split indicating that the anions are also co-ordinated. Mull i.r. spectra confirmed the absence of water or solvent molecules in the complexes. Electrical-conductance values for acetonitrile solutions are in the range characteristic of 2 : 1 electrolytes indicating that anion dissociation occurs in solution (Table 1).

These observations are fully consistent with the formulation of the ligand (L) as structure (6). Since L contains two residual carbonyl functions it seemed that it might be possible to effect ring closure by reaction of the complex with one equivalent of a suitable primary diamine. The co-ordination of the carbonyl groups indicated by i.r. spectra should encourage nucleophilic attack at the carbonyl carbon atoms. Accordingly, the barium(II) complex was treated in turn with a variety of primary diamines initially under the mild reaction conditions of ambient temperature and also at reflux tem-



(6) = L

TABLE 1

Analytical, magnetic, and electrical-conductance data for the complexes

	Analysis (%)								
	Found			Calculated				Λ[b]/S cm² mol⁻¹	
Complex	C	H	N	C	H	N	μeff.[a]/B.M.	Water	MeCN
$[BaL(ClO_4)_2]$	36.7	4.4	10.9	37.3	4.2	10.9		*c*	316
$[SrL(ClO_4)_2]$	38.1	4.5	11.4	39.8	4.5	11.6		*c*	334
$[MnL][ClO_4]_2$	41.5	4.7	12.3	41.8	4.7	12.2	5.85	340	302
$[FeL][ClO_4]_2$	41.8	4.5	12.0	41.7	4.7	12.2	0.95	328	281
$[CoL][ClO_4]_2$	41.4	4.6	12.1	41.5	4.6	12.1	3.59 [d]	348	334
$[NiL][ClO_4]_2$	41.4	4.7	12.0	41.5	4.6	12.1	3.27	325	305
$[Cu_2L(OH)(OH_2)][ClO_4]_3$	32.1	3.8	9.3	32.1	3.9	9.4	1.89 [d]	428 [e]	402 [e]

[a] At 293 K, corrected for diamagnetism of ligands. [b] For 10^{-3} mol dm^{-3} solutions at 25 °C. [c] Insoluble. [d] See also Figure 4. [e] Calculated for the binuclear complex.

TABLE 2

Infrared (cm^{-1}) and electronic spectral data for the complexes

Complex	ν(N–H)	ν(C=O)	ν(C=N)	ClO_4^-	Electronic spectra (10^3 cm^{-1}) [a,b] H$_2$O	MeCN
$[BaL(ClO_4)_2]$	3 285	1 691	1 640	1 105, 1 070 (sh),[c] 624, 610 [d]		
$[SrL(ClO_4)_2]$	3 283	1 691	1 648	1 110, 1 070,[c] 622, 610 [d]		
$[MnL][ClO_4]_2$	3 308	1 680	1 642	1 095,[c] 624, 614 (sh) [d]		
$[FeL][ClO_4]_2$	3 260	1 717		1 095,[c] 621 [d]	25.2 (3 600), 19.8 (4 100), 16.4 (10 100)	25.1 (3 700), 19.8 (4 200), 16.4 (10 400)
$[CoL][ClO_4]_2$	3 304	1 714	1 656	1 095,[c] 625 [d]	28.9 (1 900), *ca.* 21.7 (sh), *ca.* 18.5 (sh)	*ca.* 22.0 (sh), *ca.* 18.5 (sh)
$[NiL][ClO_4]_2$	3 300	1 718	1 660	1 095,[c] 626 [d]	*ca.* 19.0 (sh), 12.2 (35)	*ca.* 19.0 (sh), 12.1 (42)
$[Cu_2L(OH)(OH_2)][ClO_4]_3$	3 240	1 718, 1 680	1 656	1 090,[c] 626 [d]	16.2 (210)	16.0 (215)

[a] Values of ε/dm^3 mol^{-1} cm^{-1} are given in parentheses. [b] Spectra of the solid complexes are very similar to those of the solutions. [c] ν_3 Vibration. [d] ν_4 Vibration.

perature in methanol solution. The diamines included hydrazine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, *o*-phenylenediamine, and 3,6-diaza-octane-1,8-diamine itself. In every case these reactions failed to effect ring closure. The products isolated were usually amorphous solids, sometimes dark coloured gums or tars. Infrared spectra indicated that reaction of the carbonyl groups had occurred as judged by the intensity decrease or complete disappearance of the 1 690 cm^{-1} band. However, the spectra also showed broad absorption at *ca.* 3 400 cm^{-1} (in addition to the secondary N–H stretch at *ca.* 3 300 cm^{-1}) which we assign to residual unreacted primary amine functions. It thus seemed that the two carbonyl groups are not mutually well disposed for intramolecular linkage, at least with the diamines employed. In order to obtain further information on the structure of the complexes and, hopefully, to gain some insight into the reasons for the failure of the ring-closure reactions, a single-crystal *X*-ray structure determination of the barium(II) complex was undertaken.

Crystal Data.—$C_{24}H_{32}BaCl_2N_6O_{10}$, $M = 772.8$, Orthorhombic, $a = 17.651(9)$, $b = 13.870(7)$, $c = 12.710(11)$ Å, $U = 3\,111.6$ Å^3, $D_m = 1.60(2)$, $Z = 4$, $D_c = 1.61$ g cm^{-3}, μ(Mo-K_α) = 15.5 cm^{-1}, $\lambda = 0.710\,7$ Å, $F(000) = 1\,512$. Space group *Pnaa* (no. 56) from systematic absences $hk0$, $h = 2n + 1$, $h0l$, $h = 2n + 1$, $0kl$, $k + l = 2n + 1$.

A crystal with dimensions 0.33 × 0.5 × 1.0 mm was mounted with the (100) planes perpendicular to the instrument axis of a General Electric XRD5 apparatus which was equipped with manual goniostat, scintillation counter, and pulse-height discriminator. The stationary-crystal-stationary-counter method was used with a counting time of 10 s. Several standard reflections monitored during the course of the experiment showed no significant changes with intensity. 1 468 Reflections were measured with $2\theta < 40°$; 1 062 with $I > \sigma(I)$ were used in the subsequent refinement. An absorption correction was applied but no extinction correction.

Structure Determination.—The position of the barium atom was located from the Patterson map in special position (c) on a two-fold axis. Remaining atoms were located from a Fourier map. The Ba, Cl, and (perchlorate) O atoms were refined anisotropically and the C, N, and (ligand) O atoms refined isotropically. Hydrogen atoms were included in the structure-factor calculation in trigonal or tetrahedral positions but their parameters were not refined. The final R after full-matrix least-squares refinement was 0.068. A weighting scheme was chosen so that $w\Delta^2$ was constant over ranges of F_o and $(\sin\theta)/\lambda$. It was $w^{\frac{1}{2}} = 1$ for $F_o < 50$ and $50/F_o$ for $F_o > 50$. In the final cycle of refinement all shifts were less than 0.05σ and none of the unobserved reflections showed any serious discrepancy. The final difference Fourier showed no significant peaks. Final atomic co-ordinates are given in Table 3, bond lengths

TABLE 3

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ba	6 056(1)	2 500(0)	2 500(0)
O(1)	5 049(12)	1 303(15)	3 608(16)
C(1)	4 591(18)	743(22)	3 179(24)
C(2)	4 470(17)	753(21)	2 047(22)
N(3)	4 941(12)	1 293(15)	1 501(16)
C(4)	4 820(15)	1 355(19)	451(19)
C(5)	5 414(16)	1 891(20)	− 148(21)
N(6)	6 032(13)	2 064(15)	287(16)
C(7)	6 670(15)	2 555(19)	− 244(24)
C(8)	7 420(16)	2 307(23)	266(23)
N(9)	7 471(12)	2 686(16)	1 330(16)
C(10)	8 099(16)	2 309(22)	1 951(20)
C(11)	4 152(18)	20(26)	3 886(20)
C(12)	3 869(16)	236(21)	1 608(22)
C(13)	3 757(17)	337(23)	503(25)
C(14)	4 231(16)	893(21)	− 59(25)
C(15)	5 206(21)	2 230(27)	−1 250(29)
Cl(1)	6 708(5)	− 308(6)	2 845(6)
O(10)	6 006(11)	− 756(17)	2 880(19)
O(11)	6 625(16)	563(18)	2 276(24)
O(12)	6 970(17)	− 112(29)	3 837(21)
O(13)	7 273(14)	− 834(20)	2 319(33)

TABLE 4

Molecular dimensions: distances (Å) and angles (°) *

Ba–O(1)	2.81(2)	O(1)–Ba–N(3)	56.3(6)
Ba–N(3)	2.88(2)	O(1)–Ba–N(6)	110.9(6)
Ba–N(6)	2.87(2)	O(1)–Ba–N(9)	148.1(6)
Ba–N(9)	2.92(2)	O(1)–Ba–O(11)	73.7(7)
Ba–O(11)	2.88(2)	O(1)–Ba–O(1$^{\rm I}$)	101.5(6)
N(6)–Ba–N(9)	62.6(6)	O(1)–Ba–N(3$^{\rm I}$)	71.9(6)
N(6)–Ba–O(11)	73.3(7)	O(1)–Ba–N(6$^{\rm I}$)	68.0(6)
N(6)–Ba–N(6$^{\rm I}$)	178.3(6)	O(1)–Ba–N(9$^{\rm I}$)	103.5(6)
N(6)–Ba–N(9$^{\rm I}$)	119.5(6)	O(1)–Ba–O(11$^{\rm I}$)	136.2(7)
N(6)–Ba–O(11$^{\rm I}$)	107.3(7)	N(3)–Ba–N(6)	55.7(6)
N(9)–Ba–O(11)	74.6(7)	N(3)–Ba–N(9)	114.3(6)
N(9)–Ba–N(9$^{\rm I}$)	62.3(6)	N(3)–Ba–O(11)	69.7(7)
N(9)–Ba–O(11$^{\rm I}$)	70.7(7)	N(3)–Ba–N(3$^{\rm I}$)	93.7(6)
O(11)–Ba–O(11$^{\rm I}$)	139.2(7)	N(3)–Ba–N(6$^{\rm I}$)	122.9(6)
Cl(1)–O(10)	1.39(2)	N(3)–Ba–N(9$^{\rm I}$)	139.3(6)
Cl(1)–O(11)	1.42(3)	N(3)–Ba–O(11$^{\rm I}$)	145.5(7)
Cl(1)–O(12)	1.37(3)		
Cl(1)–O(13)	1.40(3)	O(10)–Cl(1)–O(11)	108(2)
		O(10)–Cl(1)–O(12)	111(2)
		O(10)–Cl(1)–O(13)	115(2)
		O(11)–Cl(1)–O(12)	110(2)
		O(11)–Cl(1)–O(13)	106(2)
Ba–O(11)–Cl(1)	141(2)	O(12)–Cl(1)–O(13)	108(2)

* Remaining dimensions are given in SUP 22711. Superscript I refers to the equivalent position: $x, \frac{1}{2} - y, \frac{1}{2} - z$.

and angles in Table 4. Thermal parameters and structure factors are contained in Supplementary Publication No. SUP 22711 (9 pp.).* Calculations were done at the University of London Computer Centre using SHELX 76 (ref. 6). Scattering factors and dispersion corrections were taken from ref. 7.

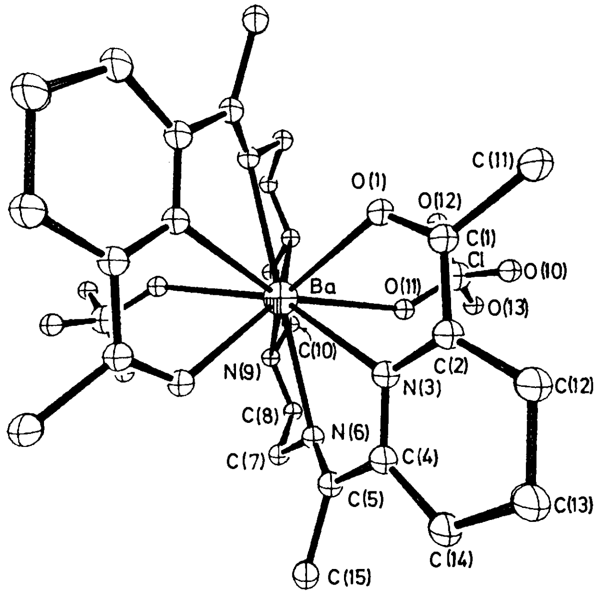


FIGURE 1 The structure of the complex $[BaL(ClO_4)_2]$ together with the atom-numbering scheme

Discussion of the Structure.—The $[BaL(ClO_4)_2]$ molecule has crystallographically imposed C_2 symmetry. The structure is illustrated, together with the numbering scheme, in Figure 1. The barium atom is ten-co-ordinate, being bonded to all eight donor atoms of the ligand (six nitrogen and two oxygen atoms) and to one oxygen atom from each of the two perchlorate ions. The Ba–O and Ba–N bond lengths are similar, falling in the range 2.81(2)—2.92(2) Å. This is the normal range for Ba–O distances;[8] the perchlorate-oxygen atoms appear to be just as strongly bound as the ligand-oxygen atoms. Less information is available on Ba–N bond distances but, once again, the values found for the present complex are close to those reported for other systems, for example, ref. 9 where several structures listed therein have Ba–N bond lengths in the range 2.86—3.18 Å.

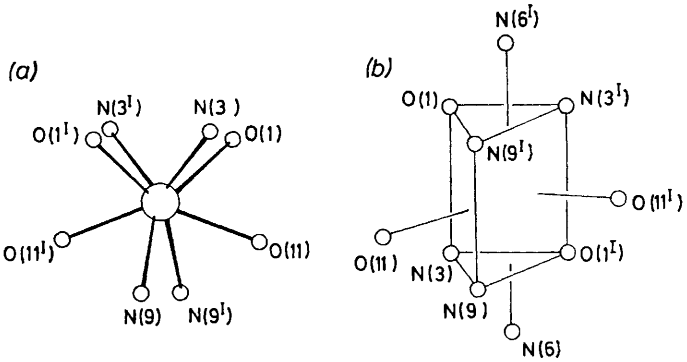


FIGURE 2 View of the co-ordination sphere in $[BaL(ClO_4)_2]$: (*a*) down the N(6) · · · N(6$^{\rm I}$) vector (these two atoms omitted for clarity); (*b*) as a C_{2v} polyhedron (2 : 2 : 2 : 4) based on a bicapped-trigonal prism with the triangular faces capped

The geometry of the co-ordination sphere does not conform to any of the usual ten-co-ordinate polyhedra (the bicapped-square antiprism or the 4,6-expanded dodecahedron) despite the ten equivalent bond lengths. Constraints within the polydentate ligand may dominate the choice of geometry. Moreover, the metal–donor atom bond lengths are comparatively long and therefore repulsions between atoms in the co-ordination sphere are relatively small. There is just one angle subtended at the metal close to 180° [N(6)–Ba–N(6$^{\rm I}$) at 178.3°] but a projection down the N(6) · · · N(6$^{\rm I}$) vector shows that the structure is no closer to a bicapped-square antiprism than it is to a bicapped cube [Figure 2(*a*)]. However, Figure 2(*a*) does show that the geometry can be described in terms of a C_2 polyhedron (2 : 2 : 2 : 4 down the C_2 axis) [see Figure 2(*b*)]. This geometry, analysed previously for a [Pb(macrocycle)(NCS)] complex,[10,†] is derived from the eight-co-ordinate bicapped-trigonal prism by capping the two triangular faces of the prism [Figure 2(*b*)]. The root-mean-square deviation from the C_{2v} geometry is 0.092 Å.

Least-squares planes in Table 5 show no unexpected features except that N(6) and C(7) are pulled rather a long way out of the pyridine-ring plane. There are no significantly short intermolecular distances.

It remains to consider whether the apparent failure of the co-ordinated ligand to undergo ring-closure reactions with primary diamines can be related to the geometry of the complex. The structural analysis shows that the two planar keto-pyridyl-imine segments of the ligand are inclined at 80.2° with respect to each other [angle of

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† Structure analysed by M. G. B. Drew (*Co-ordination Chem. Rev.*, 1977, **24**, 179).

TABLE 5

Distances of atoms from least-square planes

Plane 1: C(2) 0.01, N(3) 0.00, C(4) −0.01, C(12) −0.01, C(13) 0.00, C(14) 0.01, Ba* 0.34, C(1)* 0.09, O(1)* 0.31, C(11)* −0.10, C(5)* −0.16, C(15)* 0.21, N(6)* −0.54, C(7)* −0.77
Plane 2: Ba, N(6), N(9) 0.00, C(7)* 0.54, C(8)* −0.21
Plane 3: Ba, N(9), N(9^{I}), C(10)* 0.38, C(10^{I})* −0.38

Atoms marked with an asterisk are not included in the calculation of the plane.

intersection between plane 1 (Table 3) and the symmetry related plane] and giving a separation between the two carbonyl-carbon atoms C(1) and C(1^{I}) of 5.21 Å. Three possible modes of attack of a difunctional nucleophile may be envisaged. (In the arguments which follow it is assumed that the ligand conformation in solution is similar to that in the solid.) The mechanism most likely to lead to an intramolecular bridge between C(1) and C(1^{I}) is a concerted attack from inside the cleft formed by the acetylpyridyl groups. However, as shown by molecular models and by Figure 3 there is obvious steric hindrance to the simultaneous entry of two amino-groups. Alternatively, a concerted attack at C(1) and C(1^{I}) from outside the cleft, or one in which one NH_2 group approaches from inside the cleft [say, from the lower face of segment (1)] and the other NH_2 approaches from outside [*i.e.* from the upper surface of segment (1^{I})] is possible. However, this would require a highly improbable serpentine conformation on the part of the (long-chain) primary diamine. Thirdly, a step-wise process in which one amino-group reacts and the resulting complex rearranges so that the second amino-group can readily approach the second carbonyl function is possible, but, again, unlikely.

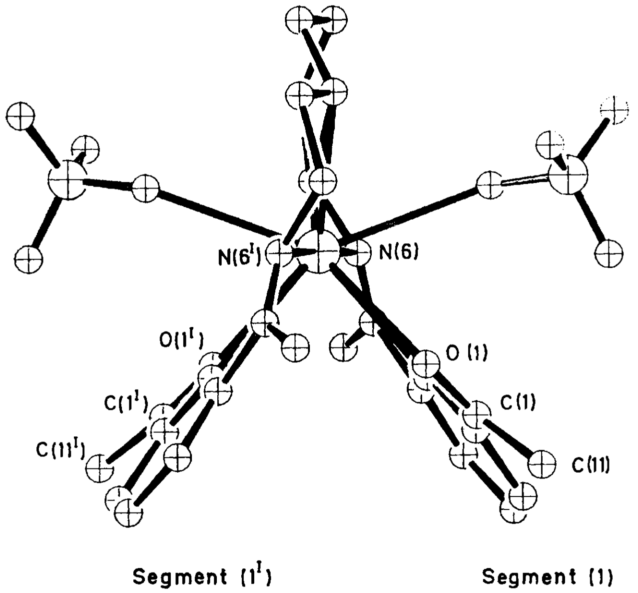
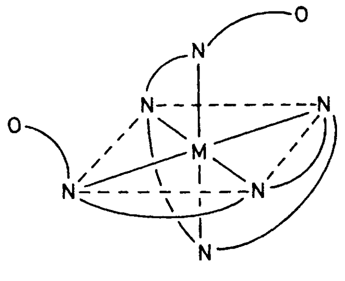


FIGURE 3 Projection of [$BaL(ClO_4)_2$] showing the cleft between the two planar keto-pyridyl-imine planes

Metal Exchange Reactions.—Attempts to recover the free ligand L from its barium(II) complex were unsuccessful. However, it was found that the Ba^{2+} and Sr^{2+} ions are readily replaced by other metal ions in solution by treatment with an excess of a salt of the metal ion to be introduced. In this way, mononuclear complexes of Mn^{II}, Fe^{II}, Co^{II}, and Ni^{II} of stoicheiometry $[ML][ClO_4]_2$ were prepared (Table 1). Reactions employing $Cu[ClO_4]_2{\cdot}6H_2O$ yielded a binuclear complex for which the best fit to the analytical data is $[Cu_2(OH)(OH_2)][ClO_4]_3$.

The i.r. spectra of the cobalt(II) and nickel(II) complexes are virtually identical and very similar to that of the iron(II) complex. The spectra do differ, however, in one significant respect, namely, the intensity of the ν(C=N) vibration at *ca.* 1 660 cm^{-1} (Table 2). In the nickel(II) complex the relative intensity of this mode is comparable to that in the spectra of the strontium(II) and barium(II) complexes, *i.e.* somewhat lower than that of the adjacent ν(C=O) band. In the cobalt(II) complex the relative intensity of ν(C=N) is significantly reduced while in the spectrum of the iron(II) complex it has virtually disappeared. We attribute these variations in intensity not to alterations in the nature of the ligand but to differences in the spin state of the metal ion to which it is co-ordinated (see below). In the spectra of all three complexes the ν(C=O) vibration occurs at a higher frequency (1 715 cm^{-1}) than in the barium(II) and strontium(II) complexes, higher even than in unco-ordinated diacetylpyridine (1 703 cm^{-1}). This is seen as an indication not only that the carbonyl groups are unco-ordinated but also that the acetyl groups are twisted out of the plane of the pyridine rings resulting in some loss of conjugation. On the assumption of an octahedral co-ordination mode in which only the six nitrogen donors of the ligand are bonded to the metal ion, molecular models clearly show that such twisting out-of-plane of the acetyl groups is necessary to relieve steric crowding between the carbonyl oxygens and the co-ordinated imino-groups. The molecular models further suggest that the ligand conformation illustrated in structure (7), in which the pyridine nitrogens occupy *cis* positions on the octahedron, and with the acetyl groups directed away from each other, is the only one possible.



(7)

Thus, once again, the two keto-groups are unfavourably disposed for intramolecular condensation with a primary diamine, and could not be spanned by a molecule of shorter chain length than $NH_2{-}(CH_2)_4{-}NH_2$.

In the i.r. spectrum of the manganese(II) complex ν(C=O) occurs at 1 680 cm^{-1} and it is concluded that like the alkaline-earth complexes the carbonyl groups are co-ordinated in this case also. The occurrence of the ν_3 and ν_4 modes of the ClO_4^- ion as unsplit bands (Table 2) in the spectra of the iron(II), cobalt(II), and nickel(II) complexes is consistent with their formulation as salts of the octahedrally co-ordinated cations $[ML]^{2+}$. In the spectrum of the manganese(II) complex slight splitting of the ν_4 mode of ClO_4^- was observed but not for the ν_3 mode. It is therefore probable that the anions are unco-ordinated in this case also.

Strong support for a six-co-ordinate, approximately octahedral, structure for the iron(II), cobalt(II), and nickel(II) complexes is provided by the magnetic properties and the electronic spectra (see Tables 1 and 2). The iron(II) complex is low-spin. The magnetic moment of 0.95 B.M.* at 293 K, while slightly greater than expected on the basis of temperature-independent paramagnetism, clearly defines the complex as having a spin-singlet ground state.[11] This result is fully consistent with expectation for an octahedral ' N_6 ' donor set comprising two α-di-imine groups, and inconsistent with most other co-ordination geometries that might be envisaged. The isomer shifts, relative to natural iron, of 0.25 and 0.33 mm, at 293 and 77 K respectively, are typical of $^1A_{1g}$ ground states.[12] The quadrupole splittings (1.04 and 1.00 mm s^{-1} at 293 and 77 K respectively) are large for low-spin iron(II) complexes and presumably reflect some splitting of the t_{2g} orbital set as a result of sterically induced distortion from O_h symmetry. The apparent inactivity of the ν(C=N) mode in the i.r. spectrum now finds a natural explanation in terms of chelate-ring electron delocalisation arising from $t_{2g} \rightarrow p_\pi^*$ back co-ordination. This causes an alteration in the position and intensity, or both, of the characteristic frequencies of constituent groups and is an often noted feature of low-spin iron(II) and cobalt(III) complexes of α-di-imine and related ligands.[13]

The proposed $d_\pi \rightarrow p_\pi^*$ back bonding is confirmed by the intense visible absorption spectrum consisting of a band at 16 400 cm^{-1} (ε_M = 10 100 dm^3 mol^{-1} cm^{-1}) and another at 19 800 cm^{-1} (ε_M = 4 200 dm^3 mol^{-1} cm^{-1}) which we attribute to a charge transfer from the (split) t_{2g} level to the antibonding p_π^* orbitals of the ligand. A third broad band at *ca.* 25 000 cm^{-1} may be a transition of the co-ordinated ligand (Table 2).

The complex $[CoL][ClO_4]_2$ exhibits a temperature-dependent moment (Table 1 and Figure 4) ranging from 3.83 B.M. at 333 K to 2.21 B.M. at 93 K. Figure 4 shows that the magnetic moment appears to approach a lower limit of *ca.* 2.0 B.M. as the temperature is decreased. This behaviour strongly indicates the occurrence of a thermally controlled $(S = 2) \rightleftharpoons (S = 4)$ spin transition. Spin cross-over in six-co-ordinate cobalt(II) complexes of α-di-imine and related ligands is a fairly commonly observed phenomenon [14] and its observation here is further evidence for a distorted octahedral structure in $[CoL][ClO_4]_2$. Electronic spectra (solid and solution) consist of three overlapping bands between 18 000 and 30 000 cm^{-1} and are probably due to transitions of the co-ordinated ligand (at 28 900 cm^{-1}) along with *d–d* bands derived from transitions from the $^2E_{2g}$ ground state of the low-spin form; *d–d* bands due to the high-spin form were not detected, presumably because of their lower intrinsic intensities.

The complex $[NiL][ClO_4]_2$ has a magnetic moment of 3.27 B.M. (at 293 K) consistent with a six-co-ordinate configuration.[11] The expected $^3A_{2g} \rightarrow {}^3T_{2g}$ transition occurs as a weak nearly symmetrical band at 12 100 cm^{-1} (ε_M = 35 dm^3 mol^{-1} cm^{-1}). The $^3A_{2g} \rightarrow {}^3T_{1g}$ transition is seen as a shoulder at *ca.* 19 000 cm^{-1} on the side of the much more intense co-ordinated ligand absorption; the $^3A_{2g} \rightarrow T_{1g}(P)$ transition is completely obscured. The observed *Dq* of 1 210 cm^{-1} in this complex is typical for octahedral nickel(II) complexes of unsaturated nitrogen ligands.

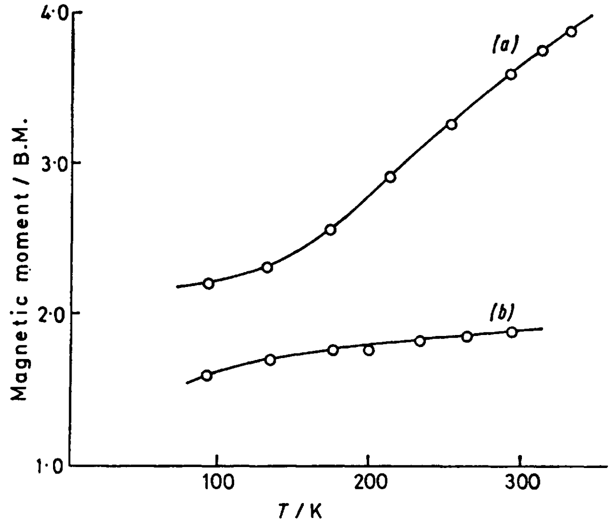


FIGURE 4 The magnetic moments as a function of temperature of (*a*) $[CoL][ClO_4]_2$ and (*b*) $[Cu_2L(OH)(OH_2)][ClO_4]_3$

The magnetic moment of $[MnL][ClO_4]_2$ is 5.85 B.M. at 293 K as expected for an orbitally degenerate $^6A_{2g}$ ground-state complex for which no orbital contribution to the magnetic moment is expected.[11] As pointed out above, the i.r. evidence indicates that the carbonyl groups are co-ordinated and that the perchlorate ions are probably not. On the reasonable assumption that all six nitrogen donors are also co-ordinated the manganese(II) ion is concluded to be eight-co-ordinate in this complex.

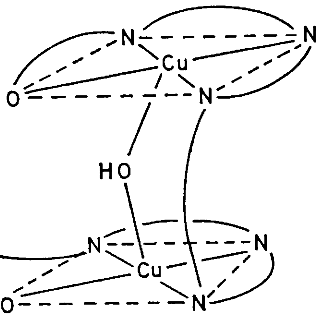
The copper(II) complex differs from all others prepared in containing two metal ions per ligand molecule. The analytical data (Table 1) indicate the stoicheiometry $[Cu_2L(OH)(OH_2)][ClO_4]_3$. The i.r. spectra (KBr and Nujol mull) show a strong OH absorption with a poorly resolved splitting ($\nu_{max.}$ 3 580 and 3 520 cm^{-1}) consistent with two inequivalent O–H stretching modes. The 1 600—1 750 cm^{-1} region is more complex than in the spectra of the mononuclear complexes (Table 2); a total

* Throughout this paper: 1 B.M. = 9.274 × 10^{-24} A m^2.

of five bands occur. The highest-energy band at 1 713 cm^{-1} can be assigned to unco-ordinated ν(C=O) and the bands at 1 652 and 1 600 cm^{-1} to, respectively, ν(C=N) and the highest-energy pyridine-ring vibration, as in the mononuclear complexes. The additional band at 1 678 cm^{-1} is in the region associated with co-ordinated ν(C=O), so for this complex the i.r. evidence points to one co-ordinated and one unco-ordinated acetyl group. The weak absorption at *ca.* 1 625 cm^{-1} is attributed to the bending mode of water. The ν_3 and ν_4 modes of the ClO_4^- ion are unsplit and therefore presumably unco-ordinated.

The magnetic moment at 293 K is 1.89 B.M. per copper(II) ion, but falls gradually with descending temperature to a value of 1.61 B.M. at 93 K (Figure 4) suggesting weak antiferromagnetic coupling between the two paramagnetic centres of the binuclear complex. We suggest therefore, that the copper(II) ions are intramolecularly linked *via* a single OH^- bridge as demonstrated recently[15] for a related (macrocyclic) binuclear copper(II) complex. Solid-state and solution (MeCN, H_2O) electronic spectra are virtually identical and the electrical conductances in the same solvents are in the range associated with 3 : 1 electrolyte behaviour (Table 1) suggesting that the intramolecular bridge is retained on dissolution. The visible electronic spectra (Table 2) consist of a broad band centred at *ca.* 16 200 cm^{-1}, which is at least consistent with a square-pyramidal based structure.

On the basis of the foregoing evidence and of molecular models a binuclear structure such as that illustrated in structure (8) is suggested, in which the ligand is folded so as to bring the two planar segments of the ligand into a roughly parallel relationship. Each copper(II) ion is assumed to have an approximately square-pyramidal geometry, the two metal ions being linked intramolecularly *via* the OH^- group in the axial positions.



(8)

The molecular models indicate that two arrangements of the kind shown in (8) differing in the mutual orientations of the two ' N_3O ' square planes with respect to each other are possible. In one of these (the one illustrated) the acetyl groups are disposed at the same side of the binuclear complex, whereas in the other they are disposed at opposite sides. For the former situation the formation of a closed macrocycle *via* reaction with a primary diamine would seem a possibility. However, attempts to do so using 1,2-diaminoethane and 1,3-diaminopropane were unsuccessful.

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine and 3,6-diazaoctane-1,8-diamine were used as supplied.

[BaL(ClO_4)$_2$] *and* [SrL(ClO_4)$_2$]. 2,6-Diacetylpyridine (0.01 mol), 3,6-diazaoctane-1,8-diamine (0.01 mol), and Sr[ClO_4]$_2$·6H_2O or Ba[ClO_4]$_2$ were stirred in methanol (500 cm^3) for 30—60 min at room temperature. The solution was concentrated to *ca.* 100 cm^3 on a rotary evaporator keeping the bath temperature below 50 °C. White crystals separated on standing in 60—65% yield based on diamine.

In experiments designed to effect ring closure, [BaL(ClO_4)$_2$] (0.01 mol) was treated in turn with various diamines (hydrazine, 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, *o*-phenylenediamine, and 3,6-diazaoctane-1,8-diamine) (0.01—0.02 mol) in methanol (500 cm^3) for varying periods (1—6 h) at temperatures ranging from ambient to reflux. Resulting reaction mixtures were concentrated by evaporation of solvent and the residues examined and recrystallized or extracted using methanol where possible.

The transition-metal complexes were obtained by treatment of [BaL(ClO_4)$_2$] (0.01 mol) in methanol (300 cm^3) with the appropriate hydrated metal perchlorate (0.01—0.02 mol). Mixing was carried out at room temperature and the reaction mixture kept at 30—40 °C for 1—2 h. This was then concentrated by rotary evaporation to *ca.* 100 cm^3. The products separated on standing in 40—60% yield.

Physical measurements were carried out as described in earlier papers.[1]

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