Metal-ion-controlled Transamination in the Synthesis of Macrocyclic Schiff-base Ligands. Part 2.[1] Stepwise Synthesis, Ring Expansion/Contraction, and the Crystal and Molecular Structure of a Ten-co-ordinate Barium(II) Complex

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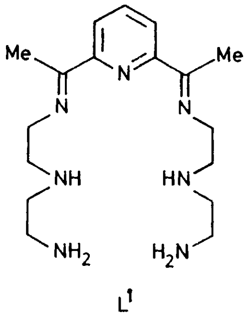
Reaction of 2,6-diacetylpyridine with diethylenetriamine in the presence of salts of the alkaline-earth metal ions Mg^{2+}—Ba^{2+} in methanol at room temperature yields complexes of the open-chain Schiff-base ligand L^1 derived from the condensation of one molecule of 2,6-diacetylpyridine with two molecules of diethylenetriamine. The use of higher reaction temperatures affords complexes (Mg^{II} excepted) of a macrocyclic ligand L^2 derived from the [2 + 2] condensation of two molecules of diketone with two molecules of diprimary amine, provided the amine is not present in excess. The intermediacy of the L^1 complexes in the L^2 macrocycle formation is demonstrated by their subsequent ring-closure reactions both in the presence and absence of added diketone. A transamination mechanism is suggested for the ring closures in the absence of diketone. Crystals of $[BaL^2(ClO_4)_2]$ are monoclinic with a = 19.427(12), b = 9.320(8), c = 9.768(11) Å, β = 116.1(1)°, Z = 2, and space group $P2_1/a$. 4 420 Reflections above background have been measured by diffractometer of which 2 312 were used in refinement to R 0.075. The macrocycle L^2 contains an 18-membered inner large ring and not the expected 24-membered ring L^3. The smaller (di-imine) ring may be considered as being derived from the larger (tetraimine) ring by nucleophilic addition of the two secondary amine groups across adjacent azomethine bonds with accompanying expulsion of two imidazolidine rings from the inner large ring. The Ba^{2+} ion is ten-co-ordinate being bonded to six nitrogens of the inner large ring in approximately planar array [Ba–N 2.841(7)—2.891(8) Å] and to four oxygen atoms of two perchlorate groups [Ba–O 2.923(10), 3.060(11) Å]. The single co-ordinated alkaline-earth metal ion in the L^2 complexes may be replaced by two copper(II) or two silver(I) ions with accompanying expansion of the macrocycle to the 24-membered (tetraimine) form L^3. The reversibility of the $L^2 \rightleftharpoons L^3$ ring expansion/contraction has been established.

IN the preceding paper [1] we reported on the chemistry of some Schiff-base condensation reactions between 2,6-diacetylpyridine (or related dicarbonyl) and 3,6-dioxaoctane-1,8-diamine in the presence of Ba^{2+} ion. By appropriate control of reaction conditions it was found that barium(II) complexes of the open-chain Schiff base derived from the condensation of one molecule of dicarbonyl with two molecules of diprimary amine could be isolated in good yield. That these non-macrocyclic complexes are possible intermediates in the formation of the 30-membered [2 + 2] macrocycles (comprising two dicarbonyl and two diamine moieties) was indicated by their subsequent ring-closure reaction with added dialdehyde or diketone. It was further shown in one case that ring closure could be effected in the absence of dicarbonyl and a mechanism consisting of a sequence of nucleophilic additions (followed by deamination) of NH_2 groups at co-ordinated C=N centres was proposed. The results demonstrated the facility and reversibility of amine exchange (transamination) and its importance in the metal-ion template synthesis of macrocyclic Schiff-base ligands. In this paper the study is extended to some alkaline-earth metal-ion-controlled reactions between 2,6-diacetylpyridine and diethylenetriamine. We will show that analogous open-chain complexes may be isolated for this system also and that these undergo self-condensation reactions to form complexes of a new macrocyclic ligand. The results include the crystal and molecular structure of a barium(II) complex of the macrocycle and its reversible ring expansion to give dicopper(II) and disilver(I) complexes.

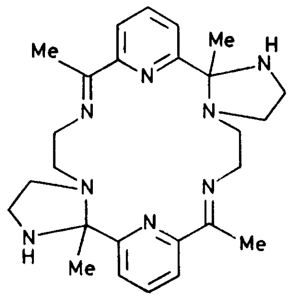
RESULTS AND DISCUSSION

Reaction of 2,6-diacetylpyridine with diethylenetriamine (dien) in the presence of a salt (perchlorate or nitrate) of Ba^{II}, Sr^{II}, Ca^{II}, or Mg^{II} in 1 : 1 : 1 molar proportions in MeOH at room temperature yielded the crystalline complexes $[ML^1]X_2 \cdot xH_2O$ ($X = ClO_4^-$ or NO_3^-, x = 0 or 1) where L^1 is the Schiff base derived from the condensation of one molecule of diacetylpyridine with two molecules of diethylenetriamine. Yields were in the range 30—40%. The same products were obtained using different ratios of diketone to amine although substantially increased yields were obtained by the use of an excess of amine.



L^1

When the reactions employing a 1 : 1 : 1 molar ratio of reactants were carried out in refluxing MeOH for 1—4 h different products were obtained where the template ion was Ba^{2+}, Sr^{2+}, or Ca^{2+}, but not for Mg^{2+}. It is shown later that the products of the ' high-temperature ' reaction are complexes of the macrocyclic ligand L^2. The formation of these complexes is suppressed in the presence of an excess of amine, even when the higher reaction temperature is employed. Evidence will be given later that the complexes of the open-chain ligand L^1 are intermediates in the formation of the macrocyclic complexes containing L^2. First we consider the L^1 series of complexes.



L^2

Complexes of the Open-chain Ligand L^1.—The nature of the ligand L^1 in the complexes was deduced by means of chemical analysis, i.r., and ^1H n.m.r. spectra (Table 1) and by the ring-closure reactions. The complexes have low to moderate solubility in methanol and generally a lower solubility in other solvents such as ethanol or acetonitrile. They are fairly stable in the solid state but show some discolouration on storage, especially in light. As judged by chemical analysis and mull i.r. spectra, all appear to be monohydrates except $[SrL^1][ClO_4]_2$ which is anhydrous. All exhibited two or three fairly strong bands between 3 250 and 3 400 cm^{-1} attributable to the ν(N–H) vibrations of primary and secondary amine groups, a moderately strong band at *ca.* 1 645 cm^{-1} characteristic of the co-ordinated C=N group, and a weak to moderate intensity absorption at *ca.* 1 600 cm^{-1} which we assign to the NH_2 bending mode, as well as various bands characteristic of the pyridine ring. The ν_3 and ν_4 vibrations of the ClO_4^- group occurring at *ca.* 1 090 and 620 cm^{-1} respectively, and of the nitrate group at 1 380 and 820 cm^{-1}, are unsplit suggesting that they are not co-ordinated to the metal. All the complexes exhibited 2 : 1 electrolyte behaviour in acetonitrile.

TABLE 1

	Analysis (%) [a]			I.r. absorption bands (cm^{-1})			Λ [b]
Complex	C	H	N	ν(NH)	ν(C=N)	ClO_4^-	S cm^2 mol^{-1}
$[BaL^1][ClO_4]_2\cdot H_2O$	29.9 (29.9)	4.9 (4.8)	14.4 (14.3)	3 375, 3 315	1 640	1 100, 628	253
$[BaL^1]Br_2\cdot H_2O$	31.1 (31.5)	4.9 (4.9)	15.1 (15.1)	3 300, 3 240, 3 208	1 624		[c]
$[SrL^1][ClO_4]_2$	32.6 (32.9)	4.9 (5.0)	15.4 (15.8)	3 378, 3 298	1 643	1 090, 628	270
$[CaL^1][ClO_4]_2\cdot H_2O$	33.9 (34.6)	5.4 (5.6)	16.6 (16.6)	3 370, 3 335, 3 308	1 645	1 096, 622	300
$[CaL^1][NO_3]_2\cdot H_2O$	39.0 (39.6)	6.4 (6.5)	24.5 (24.5)	3 340, 2 385	1 642	1 380, 820 [d]	[c]
$[MgL^1][ClO_4]_2\cdot H_2O$	36.2 (35.5)	5.7 (5.8)	17.0 (17.1)	3 350, 3 300	1 652	1 100, 628	268
$[BaL^2(ClO_4)_2]$	38.7 (39.2)	4.4 (4.5)	13.8 (14.0)	3 270	1 640	1 125, 1 050, 632, 625, 620	321
$[BaL^2Br_2]\cdot 2\ H_2O$	40.1 (39.5)	4.9 (5.1)	14.1 (14.2)	3 286	1 634		[c]
$[SrL^2(ClO_4)_2]$	41.8 (41.8)	4.9 (4.9)	14.8 (15.0)	3 300	1 638	1 125, 1 050, 630, 625	337
$[SrL^2(NO_3)_2]\cdot 2\ H_2O$	44.2 (44.1)	5.5 (5.7)	19.8 (19.8)	3 334	1 635	1 388, 1 337, 830 [d]	[c]
$[CaL^2(NO_3)_2]\cdot 2\ H_2O$	47.4 (47.3)	5.9 (6.1)	21.3 (21.2)	3 285	1 642	1 385, 1 315, 815 [d]	[c]
$[CaL^2(NO_3)_2]\cdot MeCN$	51.1 (50.3)	6.1 (5.9)	22.7 (23.0)	3 302, 3 290	1 638	1 390, 1 320 [d] 818	[c]
$[Ag_2L^3][ClO_4]_2$	35.6 (35.7)	4.1 (4.1)	12.7 (12.8)	3 270	1 651, 1 612	1 085, 622	291
$Cu_2L^3(ClO_4)_4$	31.5 (31.7)	3.6 (3.7)	11.4 (11.4)	3 230	1 652, 1 620	1 095, 632, 623	468
$Cu_2L^3(NO_3)_4\cdot 3\ H_2O$	35.2 (35.2)	4.7 (4.5)	18.6 (18.9)	3 200	1 654, 1 620	1 385, 1 332, 825 [d]	
$[Cu(dap)(dien)][ClO_4]_2$	29.4 (29.6)	4.2 (4.2)	10.6 (10.6)	3 340, 3 285, 3 255	1 702 [e]	1 090 (br), 622	

[a] Calculated values are given in parentheses. [b] For 10^{-3} mol dm^{-3} solutions in MeCN. [c] Poorly soluble. [d] Nitrate absorptions. [e] ν(C=O).

A few of the complexes were sufficiently soluble in CD_3OD or CD_3CN for ^1H n.m.r. spectra to be measured. Spectra of $[CaL^1][ClO_4]_2\cdot H_2O$, $[CaL^1][NO_3]_2\cdot H_2O$, and $[MgL^1][ClO_4]_2\cdot H_2O$ were initially virtually identical although in the case of $[CaL^1][NO_3]_2\cdot H_2O$, time-dependent changes were observed. These changes could be identified with formation of the macrocyclic complex $[CaL^2(NO_3)_2]$. The initial spectrum of this complex in CD_3OD consisted of five resonances with relative intensities 3 : 4 : 4 : 8 : 6 at 8.19 (m), 3.76 (t), 2.98 (t), 2.76 (s), and 2.51 (s) p.p.m. downfield from $SiMe_4$. These are assigned to the pyridine protons, the CH_2 groups adjacent to the C=N bonds, the neighbouring CH_2 groups, the CH_2 groups linking the NH and NH_2 functions, and the methyl groups respectively. In addition, a strong singlet which altered in position (4.5—5.5 p.p.m.) and intensity on addition of D_2O is assigned to rapidly exchanging NH, NH_2, and H_2O protons.

Ring-closure Reactions.—When the complexes of L^1, the magnesium(II) complex excepted, were treated with one equivalent of 2,6-diacetylpyridine (MeOH or MeCN, 1 h at 65 °C or *ca.* 15 h at 20 °C) the corresponding complexes of the macrocyclic ligand were obtained in 40—70% yield. These are the same complexes as obtained in the initial ' high-temperature ' template reactions starting from equimolar amounts of diketone and amine.

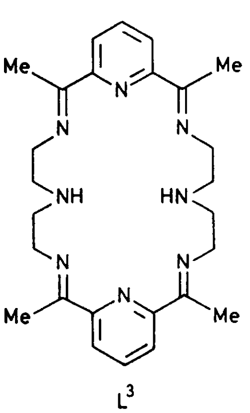
More interesting is the observation that the same set of complexes may be obtained, in the *absence* of diketone, merely by heating the L^1 complexes in methanol for *ca.* 1 h (or standing at ambient temperature for 12—24 h). As before, ring closure was not observed in the case of the magnesium(II) complex. Overall yields of product calculated on equation (1) ranged from 50 to 70%.

$$2[ML^1]X_2 \longrightarrow [ML^2X_2] + M^{2+} + 2X^- + 2\text{dien} \quad (1)$$

The possibility that the ring closure in the absence of added diketone might have resulted from a partial hydrolysis of the L^1 complexes followed by a different recombination of hydrolysis products to give the macrocyclic complexes was ruled out by repeating the preparations in dried solvent in the presence of 2,2-dimethoxypropane without loss in yield.

To account for the ring closure in the absence of added diacetylpyridine the transamination mechanism described in the preceding paper [1] is proposed. This consists of the intermolecular nucleophilic addition of an unco-ordinated NH_2 group of one $[ML^1]^{2+}$ ion across the co-ordinated C=N group of a second $[ML^1]^{2+}$ ion followed by elimination of a molecule of dien. A second nucleophilic addition, intramolecular this time, and deamination, leads to the formation of the macrocycle (see Scheme 3 of preceding paper).

The nature of the ligand L^2 in the complexes was deduced from analytical, i.r., and ^1H n.m.r. data and, in particular, by an *X*-ray analysis of one member of the series. The i.r. spectra are similar to those of the complexes of L^1 but differ in the following important respects. Only a single sharp band at *ca.* 3 330 cm^{-1} occurs in the NH stretching region and the weak to moderate intensity band present at *ca.* 1 600 cm^{-1} in the spectra of the complexes of L^1 was absent in the spectra of the L^2 series of complexes. These observations are taken as evidence for the absence of primary amine groups and the presence of secondary amine groups. A further point of difference is the occurrence of well defined splitting in the two absorptions characteristic of ClO_4^- and NO_3^- indicating co-ordination of these ions to the metal.



L^3

Neither chemical analysis nor i.r. spectra allow a distinction to be made between L^2 and the isomeric form L^3 which was the expected ring-closure product. The nature of the macrocycle was determined by a single-crystal *X*-ray analysis of the structure of $[BaL^2(ClO_4)_2]$ described in the Experimental section.

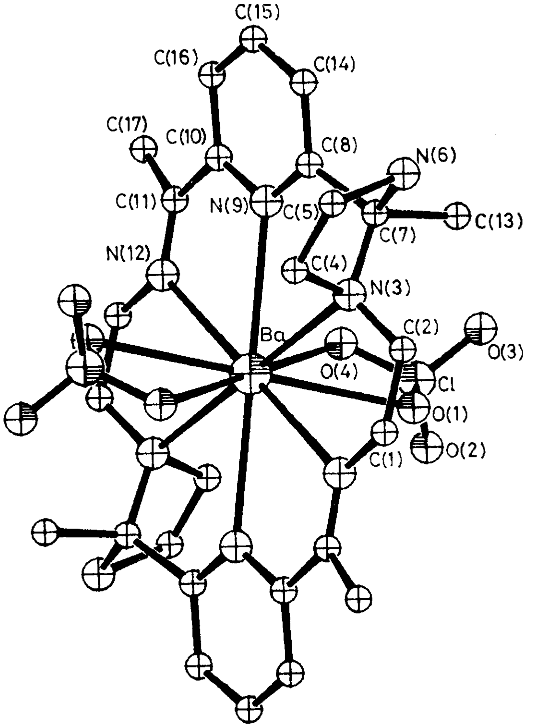


FIGURE 1 Structure of $[BaL^2(ClO_4)_2]$ together with atomic numbering scheme

Discussion of the Structure.—The structure of $[BaL^2(ClO_4)_2]$ is shown in Figure 1, together with the atomic numbering scheme. The barium atom is positioned on a centre of symmetry being bonded to six nitrogen atoms of the macrocycle L^2 and to four oxygen atoms of two perchlorate groups. The BaN_6 moiety is approximately planar (maximum deviation 0.06 Å, Table 2) and as the adjacent N–Ba–N angles are close to 60°, the macrocycle can be considered to form a hexagonal girdle around the metal ion.

The Ba–N distances are 2.841(7), 2.887(8), and 2.891(8) Å. These values are similar to those found [2] for another ten-co-ordinate barium(II) complex of a related (non-macrocyclic) Schiff-base ligand. The two Ba–O distances are slightly different at 2.923(10), 3.060(11) Å. This is

TABLE 2

Least-squares planes. Distances of atoms from the planes are given in Å. Atoms not contributing to the plane are marked with an asterisk

Plane	
(1)	Ba 0.00, N(3) −0.06, N(9) 0.07, N(12) −0.07, N(3*) 0.06, N(6*) −0.07, N(12*) 0.07
(2)	N(3) −0.23, C(4) 0.12, C(5) 0.01, N(6) −0.16, C(7) 0.27
(3)	Ba, N(3), N(9), C(7) * 0.45, C(8) * −0.05
(4)	Ba, N(3), N(12*), C(1) * −0.07, C(2) * 0.39
(5)	C(8) 0.02, N(9) −0.01, C(10) −0.00, C(14) −0.02, C(15) 0.00, C(16) 0.01, Ba * 0.62
(6)	Ba, O(1), O(4), N(12) * 0.32, N(12*) * −0.32

Angle between planes (1) and (2), 70.4, between (1) and (5), 10.8°.

probably due to the non-equivalent positions of the two oxygen atoms with respect to the macrocycle. As can be seen from Figure 2, the perchlorate groups avoid both the five-membered imidazolidine rings and the methyl groups which protrude from the N_6 macrocycle plane. Thus, the perchlorate group is arranged such that the Cl, O(1), O(4) plane is almost parallel to the N(12)–Ba–N(12*) vector [deviation of N(12) from this plane, 0.32 Å]. The molecule thus does not have C_s symmetry, possible only if the four-membered BaO_2Cl chelate ring were aligned parallel or perpendicular to the N(9)–Ba–N(9*) vector.

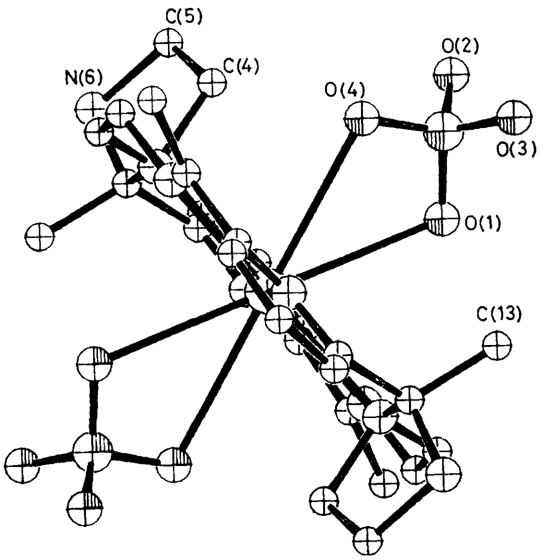


FIGURE 2 Structure of $[BaL^2(ClO_4)_2]$ viewed along the macrocycle plane showing the perchlorate ion co-ordination

The conformation of the macrocycle L^2 in this complex is relatively strain-free as is apparent from the following observations: (*i*) the saturated rings are puckered, (*ii*) the Ba–N bond lengths are equivalent and no longer than usual, and (*iii*) the near planarity of the BaN_6 atom set (Table 2). The displacement of 0.62 Å of the metal atom from the plane of the pyridine ring is a device whereby steric strain may be minimised without weakening the metal–ligand bonds, and is observed in a number of complexes containing this trimethine group.[3]

The geometry of the co-ordination polyhedron is unique belonging to none of the usual ten-co-ordinate geometries. Just as the ideal geometries in ten-co-ordination such as the bicapped dodecahedron and the bicapped square antiprism are related to eight-co-ordinate analogues,[4] so the geometry found in $[BaL^2(ClO_4)_2]$ (a 2 : 6 : 2 type) is related to the hexagonal bipyramid with each of the axial atoms replaced by a chelating perchlorate group.

There are no significant contacts less than the sum of van der Waals distances between atoms.

The most significant aspect of the structure of $[BaL^2(ClO_4)_2]$ is that the macrocycle has the structure L^2 (containing an 18-membered inner large ring) rather than the expected structure L^3 (containing a 24-membered inner large ring). The $[24] \longrightarrow [18]$ ring contraction (see later) can thus be seen as a consequence of the nucleophilic addition of the two secondary amine functions of L^3 across adjacent azomethine bonds. This causes the expulsion of two five-membered imidazolidine rings from the inner large ring and a reduction in the denticity of the macrocycle (towards a centrally complexed metal ion) from eight to six. As pointed out in the preceding paper,[1] *gem*-diamine addition compounds are not generally stable. The present complexes of L^2 are thus notable exceptions. The stability of the L^2 complexes, and the thermodynamic driving force for the ring contraction, can be traced to a mismatch of the cavity size of the macrocycle in its extended L^3 form and the size of the alkaline-earth metal ion. In this respect the ring contraction inferred here is entirely analogous to the $[18] \longrightarrow [15]$ ring contraction observed [5] on replacement of alkaline-earth metal ions by the smaller transition-metal ions Mn^{2+}, Fe^{2+}, Co^{2+}, or Zn^{2+} in a related Schiff-base macrocycle. Earlier work has established that 18-membered [2 + 2] Schiff-base macrocycles derived from diacetylpyridine and related dicarbonyls have an appropriate cavity size for the sexidentate complexation in a planar conformation of large ions such as Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} (eight-co-ordinate ionic diameters in the range 2.24—2.84 Å) [6] but not for the smaller first-row transition-metal ions.* By the same reasoning it may be argued that the 24-membered macrocycle L^3 is too large to form stable mononuclear complexes with these ions. For this to occur eight-membered chelate rings are required (assuming the secondary amine groups of L^3 to be unco-ordinated) and these are neither small enough nor large enough to provide a strain-free configuration. Thus, in this respect, L^3 is less well suited to the formation of mononuclear complexes than the more flexible 30-membered macrocycles discussed in the preceding paper.

The failure of $[MgL^1]^{2+}$ to undergo the ring-closure reaction can now be understood in terms of the Mg^{2+} ion (eight-co-ordinate diameter 1.80 Å) [6] being too small for the macrocycle even in its contracted form L^2.

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* An exception is the conjugated 18-membered macrocycle derived from 2,6-diformylpyridine and *o*-phenylenediamine which has a cavity slightly too small for the Ba^{2+} ion; in this case a ' sandwich ' complex is obtained (see ref. 7).

The near identity of the i.r. spectra of the L^2 series of complexes strongly suggests that they all contain the macrocyclic ligand in the same 18-membered form L^2, at least in the solid state. The ^1H n.m.r. spectrum of $[CaL^2][NO_3]_2\cdot MeCN$, the only complex having sufficient solubility in CD_3OD, further suggests that the macrocycle retains this arrangement in solution. In addition to a multiplet at 7.9 p.p.m. (pyridine protons, relative intensity 3) and a singlet at 4.87 p.p.m. ($NH + H_2O$), the spectrum consisted of a complex multiplet between 4.0 and 2.7 p.p.m. (relative intensity 8) and two singlets at 1.94 and 1.78 p.p.m. (each of relative intensity 3). This spectrum clearly rules out structure L^3. On the other hand it appears consistent with L^2 for which two distinct CH_3 group resonances are predicted provided the rate of interconversion of equivalent L^2 structures is slower than the n.m.r. time scale. No line broadening of the CH_3 group signals was observed on heating to 55 °C.

Reversible Ring Expansion of the Co-ordinated Macrocycle L^2.—It was argued above that the extended tetraimine form (L^3) of the macrocycle is not well suited to the encapsulation of a single metal ion. However, the same restrictions do not apply to the accommodation of two metal ions. Treatment of $[SrL^2(ClO_4)_2]$, for example, with $Ag[ClO_4]$ yielded yellow crystals of $[Ag_2L^3][ClO_4]_2$. Analytical data do not, of course, discriminate between L^2 and L^3 and i.r. spectra, although different in detail, provide no clear structural information. However, the ^1H n.m.r. spectrum of the disilver(I) complex in CD_3CN establishes beyond doubt that the macrocycle is in the L^3 form. The spectrum consists of a multiplet at 8.02, a triplet at 3.86, a poorly resolved triplet at 3.14, and a singlet at 2.42 p.p.m. of relative intensity ratio 3 : 4 : 4 : 6 attributable, respectively, to the pyridine protons, the CH_2–C=N groups, the CH_2 groups adjacent to the secondary amine groups, and the methyl protons. Additionally, a broad singlet at 2.20 p.p.m. was assigned to $NH + H_2O$ protons on the basis of its downfield shift on addition of D_2O. The addition of D_2O also had the effect of sharpening the poorly resolved triplet at 3.14 p.p.m., showing that in the absence of D_2O the CH_2 protons adjacent to NH are coupled both to the NH proton and to the CH_2–C=N protons.

The L^2 to L^3 ring expansion on exchange of co-ordinated alkaline-earth metal ion by two silver(I) ions was found to be reversible. Treatment of $[Ag_2L^3][ClO_4]_2$ with $BaBr_2$ in methanol gave AgBr along with the complex $[BaL^2(ClO_4)_2]$ shown to be identical in properties to an authentic sample prepared *via* the template method.

Treatment of the alkaline-earth metal complexes containing L^2 with $Cu[ClO_4]_2\cdot 6H_2O$ similarly yielded a binuclear complex $Cu_2L^3(ClO_4)_4$ which on the basis of the close similarity of the i.r. spectrum to that of the disilver(I) complex is considered to contain the tetraimine macrocycle L^3. A minor difference between the two spectra relates to the ClO_4^- absorptions, these being somewhat broadened in the case of the copper(II) complex suggesting weak co-ordination to the metal. A probable co-ordination geometry for both binuclear complexes is that in which each metal ion lies in the square plane (possibly tetrahedrally distorted) made up of the three trimethine nitrogen atoms and one secondary amine nitrogen of one half of the macrocycle, with additional weak axial ligation of one or more ClO_4^- ions in the case of the dicopper(II) complex. This is the arrangement found [8] in a disilver(I) complex of a closely related 28-membered [2 + 2] macrocycle, although molecular models indicate some strain in the present 24-membered case. The electronic spectrum of $Cu_2L^3(ClO_4)_4$ consists of a single band at 15 800 cm^{-1} in both solid state and in solution ($\varepsilon_M = 330$ dm^3 mol^{-1} cm^{-1}) and is at least consistent with a tetragonally based structure. The complex is magnetically normal having a moment of 1.86 B.M.* at 293 K with little or no temperature dependence in the range 93—293 K. It is readily hydrolysed to the complex $[Cu(dap)(dien)][ClO_4]_2$ containing one molecule each of 2,6-diacetylpyridine (dap) and diethylenetriamine (dien).

EXPERIMENTAL

Preparation of Complexes.—The L^1 series of complexes were prepared by allowing 2,6-diacetylpyridine (0.01 mol), diethylenetriamine, and a salt (usually perchlorate, occasionally nitrate) in 1 : 2 : 1 molar ratio to react in dry methanol (100 cm^3) at room temperature. Crystals of the products separated in 30—40% yield on standing. Improved yields (up to 80%) were obtained by the use of an excess of diethylenetriamine.

The L^2 series of complexes of Ca^{II}, Sr^{II}, and Ba^{II} were obtained by a similar procedure except that only 1 : 1 : 1 molar proportions of reactants (0.01 mol scale in 200 cm^3 dry solvent) were used and the solutions were refluxed for periods of 1—4 h. The crystalline products separated on cooling and standing. Yields were 60% for $[CaL^2(NO_3)_2]\cdot MeCN$, 62% for $[SrL^2(NO_3)_2]\cdot 2H_2O$, 70% for $[SrL^2(ClO_4)_2]$, and 50% for $[BaL^2(ClO_4)_2]$.

Ring-closure Reactions of the L^1 *Complexes.*—2,6-Diacetylpyridine (0.001 mol) was added to MeOH or MeCN solutions of the Ca^{II}, Sr^{II}, or Ba^{II} complexes of L^1 in 1.1 : 1.0 molar proportion and the solution refluxed for 1 h or allowed to stand overnight at room temperature. Yields were in the range 55—65%.

The same products were obtained without appreciable penalty in yield in the absence of diketone. In several of these experiments solutions of the metal salt were pre-dried by refluxing in dried MeOH containing 2,2-dimethoxypropane, again without loss in yield.

Transmetallations.—The complex $[Ag_2L^3][ClO_4]_2$ was obtained by addition of a MeOH solution of $Ag[ClO_4]$ to a MeOH solution of $[ML^2(NO_3)_2]\cdot 2H_2O$ ($M = Ca^{II}$ or Sr^{II}) in 2 : 1 molar proportion. As the mixture was refluxed over a 30 min period, the fluorescent yellow colour deepened and small yellow crystals separated in 80% yield on cooling.

$Cu_2L^3X_4$ ($X = ClO_4$ *or* NO_3).—To a solution of $[ML^2X_2]\cdot xH_2O$ ($M = Ca^{II}$, Sr^{II}, or Ba^{II}) in dry MeOH at reflux temperature was added a solution of CuX_2 in methanol in two-fold excess. For $X = ClO_4$ fine blue crystals separated almost immediately. The more soluble nitrate separated on cooling in 75% yield. Both complexes are susceptible to hydrolysis.

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

Conversion of $[Ag_2L^3][ClO_4]_2$ *into* $[BaL^2(ClO_4)_2]$.—A solution of the silver(I) complex in dry MeOH was refluxed with 1.5 equivalents of $BaBr_2$. The greyish precipitate of (mainly) AgBr was removed by filtration and the product crystallized out in *ca.* 40% yield on standing. It was shown to be identical in properties to those of an authentic sample.

Crystal Data.—$[BaL^2(ClO_4)_2]$, $C_{26}H_{36}BaCl_2N_8O_8$, $M = 768.5$, Monoclinic, $a = 19.427(12)$, $b = 9.320(8)$, $c = 9.768(11)$ Å, $\beta = 116.1(1)°$, $U = 1\,588.5$ Å^3, $D_m = 1.64$, $Z = 2$, $D_c = 1.61$ g cm^{-3}, μ(Mo-K_α) = 15.1 cm^{-1}, λ(Mo-K_α) = 0.7107 Å, $F(000) = 776$, space group $P2_1/a$ from systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$.

A crystal of approximate size 0.4 × 0.4 × 0.1 mm was set up to rotate around the b axis on a Stoe Stadi-2 diffractometer and 4 420 reflections with $2\theta < 60°$ were measured *via* w scans of width $[1.0 + 1.5(\sin\theta)/(\tan\mu)]°$ and a scan speed of 60 s deg^{-1}. Data were corrected for Lorentz-polarization factors but not for absorption or extinction. 2 312 Reflections with $I > 3\sigma(I)$ were used in subsequent calculations.

The barium atom was placed at the origin and subsequent Fourier maps were calculated to locate all other atoms. All atoms, except those of hydrogen, were refined anisotropically. The hydrogen atoms were placed in the appropriate trigonal or tetrahedral position but their parameters were not refined. The methyl hydrogen atoms could not be located. The weighting scheme was chosen to give equivalent values of $w\Delta^2$ over ranges of F_o and $(\sin\theta)/\lambda$, and was equal to $1/[\sigma(F) + 0.002\ F^2]$ where $\sigma(F)$ was obtained from counting statistics. In the final cycle of refinement no shift was $>0.10\sigma$ and R was 0.075. The final difference-Fourier map showed no significant electron density. The calculations were done using the SHELX 76 package [9] at the University of Manchester Computer Centre. Scattering factors were taken from International Tables.[10] The atomic co-ordinates are given in Table 3, molecular dimensions in Table 4. The Supplementary Publication No. SUP 23078 (15 pp.) * contains anisotropic thermal parameters, hydrogen-atom parameters, and observed and calculated structure factors.

TABLE 3

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

Atom	X	Y	Z
Ba(1)	0(0)	0(0)	0(0)
Cl(1)	1 362(2)	−2 575(3)	−202(3)
O(1)	1 207(6)	−1 125(9)	−721(11)
O(2)	1 169(8)	−3 512(13)	−1 488(16)
O(3)	2 141(6)	−2 720(18)	817(14)
O(4)	898(7)	−2 811(12)	570(15)
C(1)	871(7)	3 019(13)	−1 148(13)
C(2)	1 391(9)	2 681(19)	383(13)
N(3)	1 171(4)	2 137(9)	1 477(9)
C(4)	814(9)	3 476(16)	1 917(19)
C(5)	1 432(14)	4 153(23)	3 192(18)
N(6)	2 150(7)	3 101(13)	3 755(11)
C(7)	1 758(9)	1 832(19)	3 008(13)
C(8)	1 417(6)	1 093(13)	3 956(11)
N(9)	886(5)	34(10)	3 276(9)
C(10)	681(5)	−821(11)	4 145(10)
C(11)	124(5)	−2 005(9)	3 372(10)
N(12)	−306(5)	−1 907(8)	1 934(8)
C(13)	2 422(11)	933(36)	2 901(22)
C(14)	1 714(6)	1 345(12)	5 538(11)
C(15)	1 501(7)	444(13)	6 414(12)
C(16)	990(6)	−623(13)	5 710(11)
C(17)	98(9)	−3 239(14)	4 345(15)

TABLE 4

Molecular dimensions [distances (Å), angles (°)] with estimated standard deviations in parentheses

Ba(1)–O(1)	2.923(10)	Ba(1)–N(9)	2.891(8)
Ba(1)–O(4)	3.060(11)	Ba(1)–N(12)	2.841(7)
Ba(1)–N(3)	2.887(8)		

O(1)–Ba(1)–O(4)	44.21(24)
O(1)–Ba(1)–N(3)	80.14(26)
O(1)–Ba(1)–N(9)	96.90(27)
O(1)–Ba(1)–N(12)	111.14(22)
O(1)–Ba(1)–O(1*)	135.79(36)
O(1)–Ba(1)–N(3*)	99.87(36)
O(1)–Ba(1)–N(9*)	83.08(28)
O(1)–Ba(1)–N(12*)	68.87(26)
O(4)–Ba(1)–N(3)	103.82(27)
O(4)–Ba(1)–N(9)	78.10(31)
O(4)–Ba(1)–N(12)	67.21(36)
O(4)–Ba(1)–N(3*)	76.18(26)
O(4)–Ba(1)–N(9*)	101.90(31)
O(4)–Ba(1)–N(12*)	112.79(36)
N(3)–Ba(1)–N(9)	58.98(22)
N(3)–Ba(1)–N(12)	116.66(22)
N(3)–Ba(1)–N(9*)	121.01(26)
N(3)–Ba(1)–N(12*)	63.33(22)
N(9)–Ba(1)–N(12)	57.84(22)
N(9)–Ba(1)–N(12*)	122.17(24)

N(12*)–C(1)	1.464(10)	C(8)–N(9)	1.370(13)
C(1)–C(2)	1.423(16)	C(8)–C(14)	1.411(13)
C(2)–N(3)	1.408(12)	N(9)–C(10)	1.346(12)
N(3)–C(4)	1.577(17)	C(10)–C(11)	1.497(13)
N(3)–C(7)	1.456(14)	C(10)–C(16)	1.387(13)
C(4)–C(5)	1.441(23)	C(11)–N(12)	1.284(11)
C(5)–N(6)	1.593(22)	C(11)–C(17)	1.507(13)
N(6)–C(7)	1.422(17)	C(14)–C(15)	1.385(15)
C(7)–C(8)	1.519(16)	C(15)–C(16)	1.359(17)
C(7)–C(13)	1.580(25)		

Ba(1)–N(12*)–C(1)	115.1(6)	C(8)–C(7)–C(13)	112.8(15)
N(12*)–C(1)–C(2)	114.6(8)	C(7)–C(8)–N(9)	117.9(9)
C(1)–C(2)–N(3)	124.4(11)	C(7)–C(8)–C(14)	120.9(9)
Ba(1)–N(3)–C(2)	107.7(6)	N(9)–C(8)–C(14)	120.6(9)
Ba(1)–N(3)–C(4)	109.8(6)	Ba(1)–N(9)–C(8)	120.0(6)
C(2)–N(3)–C(4)	103.8(11)	Ba(1)–N(9)–C(10)	119.6(5)
Ba(1)–N(3)–C(7)	117.9(6)	C(8)–N(9)–C(10)	119.3(8)
C(2)–N(3)–C(7)	119.2(9)	N(9)–C(10)–C(11)	117.9(8)
C(4)–N(3)–C(7)	96.5(11)	N(9)–C(10)–C(16)	120.8(9)
N(3)–C(4)–C(5)	106.5(12)	C(11)–C(10)–C(16)	121.4(8)
C(4)–C(5)–N(6)	107.4(14)	C(10)–C(11)–N(12)	118.6(7)
C(5)–N(6)–C(7)	98.3(13)	C(10)–C(11)–C(17)	117.5(8)
N(3)–C(7)–N(6)	111.5(12)	N(12)–C(11)–C(17)	123.9(9)
N(3)–C(7)–C(8)	111.1(10)	Ba(1)–N(12)–C(11)	123.1(6)
N(6)–C(7)–C(8)	110.1(12)	C(8)–C(14)–C(15)	119.1(9)
N(3)–C(7)–C(13)	109.2(13)	C(14)–C(15)–C(16)	118.7(9)
N(6)–C(7)–C(13)	101.9(15)	C(10)–C(16)–C(15)	121.4(9)

Cl(1)–O(1)	1.428(9)	Cl(1)–O(3)	1.404(11)
Cl(1)–O(2)	1.438(12)	Cl(1)–O(4)	1.424(9)

O(1)–Cl(1)–O(2)	109.3(7)	O(2)–Cl(1)–O(4)	112.7(7)
O(1)–Cl(1)–O(3)	109.7(8)	O(3)–Cl(1)–O(4)	110.2(7)
O(3)–Cl(1)–O(3)	110.3(8)	Ba(1)–O(1)–Cl(1)	108.7(4)
O(1)–Cl(1)–O(4)	104.5(6)	Ba(1)–O(4)–Cl(1)	102.4(5)

* Atom in a symmetry-related position $-x, -y, -z$ compared to x, y, z in Table 3.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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