

Metal-ion Controlled Reactions of 2,6-Diacetylpyridine with 1,2-Diaminoethane and 2,6-Diformylpyridine with *o*-Phenylenediamine and the Crystal and Molecular Structure of a Pentagonal Pyramidal Cadmium(II) Complex containing Unidentate *o*-Phenylenediamine

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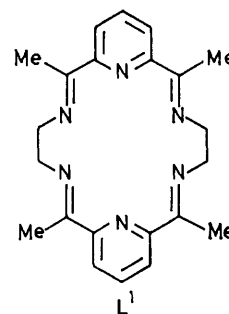
Reaction of 2,6-diacetylpyridine (dap) with an excess of 1,2-diaminoethane (en) in the presence of $\text{Ba}[\text{ClO}_4]_2$ in MeOH or EtOH at room temperature yields the complex $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ where the ligand L^2 is the open-chain condensate of two molecules of dap with three molecules of en. The i.r. spectrum of the solid complex indicates that L^2 exists in the di-imine form containing two imidazolidine rings derived from the nucleophilic addition of the two primary amine groups of the tetra-imine form across adjacent C=N linkages. The use of higher reaction temperatures affords the complex $[\text{BaL}^1(\text{ClO}_4)_2]$ of the 18-membered macrocycle L^1 derived from the [2 + 2] condensation of two molecules of dap with two molecules of en. The intermediacy of the co-ordinated open-chain ligand L^2 in the L^1 macrocycle formation is evidenced by the subsequent ring closure of $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ in the absence of added diketone; a transamination mechanism is proposed. Corresponding reactions of 2,6-diformylpyridine (dfp) with *o*-phenylenediamine (opd) in the presence of Ba^{2+} give complexes of the 18-membered macrocycle with the isolation of an intermediate. The single Ba^{2+} in $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ may be replaced by two Cu^{2+} with isomerization of L^2 to the tetra-imine form, L^3 . The isomerization is reversed on treatment of $\text{Cu}_2\text{L}^3(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ with NCS^- . The Ba^{2+} in the macrocyclic complex $[\text{BaL}^1(\text{ClO}_4)_2]$ may also be replaced by two Cu^{2+} to yield $\text{Cu}_2\text{L}^1(\text{OH})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ in which the two Cu^{2+} ions are intramolecularly bridged, and antiferromagnetically coupled, *via* the hydroxide ion. The use of $\text{Cd}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ as template affords the complexes $[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$ and $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$ where L^5 is the open-chain ligand derived from the condensation of one molecule of dap with two molecules of en, and L^6 is the corresponding ligand derived from dfp and opd. Crystals of $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$ are triclinic with $a = 9.117(9)$, $b = 10.797(8)$, $c = 16.084(11)$ Å, $\alpha = 97.89(8)$, $\beta = 81.43(9)$, $\gamma = 70.70(10)^\circ$, $Z = 2$, and space group $P\bar{1}$. 2560 Reflections above background were measured by a diffractometer and refined by full-matrix least-squares to R 0.065. The co-ordination geometry of the Cd atom is approximately pentagonal pyramidal, being bonded to the five nitrogen atoms (Cd–N 2.35–2.46 Å) of L^6 in the pentagonal plane and to one NH_2 group [Cd–N 2.341(9) Å] of the opd molecule in one axial position, the metal lying 0.42 Å above the equatorial N_5 plane. The other NH_2 group of opd is not co-ordinated. An incomplete X-ray analysis of $[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$ indicates a seven-co-ordinate polymeric structure in which the en molecules bridge adjacent Cd^{2+} ions. Treatment of $\text{CdL}^6(\text{opd})(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with Ni^{2+} in the presence of O_2 yields the complex $[\text{Ni}(\text{L}^6)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ the properties of which suggest that the terminal NH_2 groups of L^6 have added across the adjacent C=N bonds, this being followed by oxidative dehydrogenation to generate 2,6-di(2-benzimidazolyl)pyridine.

In recent papers^{1,2} we described the use of the alkaline-earth metal ions Ca^{2+} , Sr^{2+} , and Ba^{2+} as templates in the stepwise synthesis of macrocyclic Schiff-base ligands derived from the [2 + 2] condensation of 2,6-diacetylpyridine (dap) with 3,6-diazooctane-1,8-diamine¹ or diethylenetriamine.² It was shown that by the use of appropriate reaction conditions complexes of open-chain ligands derived from the condensation of one molecule of diketone with two molecules of diamine could be isolated in good yield and that several of those would subsequently undergo ring closure to the [2 + 2] macrocycle in the absence of added diketone. A transamination mechanism involving a sequence of nucleophilic additions, followed by deamination, of the NH_2 functions across co-ordinated C=N bonds was proposed. In this paper we examine analogous reactions of dap with 1,2-diaminoethane (en) and of 2,6-diformylpyridine with *o*-phenylenediamine. The formation of the 18-membered [2 + 2] macrocycles has been briefly reported previously;^{3,4} here, we describe the preparation and some reactions, including ring-closure reactions, of some open-chain complexes.

RESULTS AND DISCUSSION

Reactions between 2,6-Diacetylpyridine and 1,2-Diaminoethane.—Reaction of 2,6-diacetylpyridine (dap) with

1,2-diaminoethane (en) in the presence of a salt of Ca^{II} , Sr^{II} , Ba^{II} , or Pb^{II} in 1:1:1 molar proportions in refluxing methanol or ethanol affords complexes of the 18-membered [2 + 2] macrocycle L^1 in high yield. The structures of the complexes $[\text{SrL}^1\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and $[\text{PbL}^1$



(NCS)(SCN)] have been reported.³ In each case the co-ordination geometry is approximately hexagonal bipyramidal, the six nitrogen atoms of the macrocycle defining the equatorial hexagonal plane with the unidentate ligands in the axial positions. When the reaction is carried out at room temperature using a 5:1 molar excess of en over dap in the presence of $\text{Ba}[\text{ClO}_4]_2$, crystals of a new complex $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ are isolated in >90%

yield. Analogous complexes containing Ca^{II} or Sr^{II} were not obtained under these conditions. Instead, the products of reaction were oils of indefinite composition having broad poorly resolved i.r. spectra.

Elemental analysis (Table 1) indicates that the new

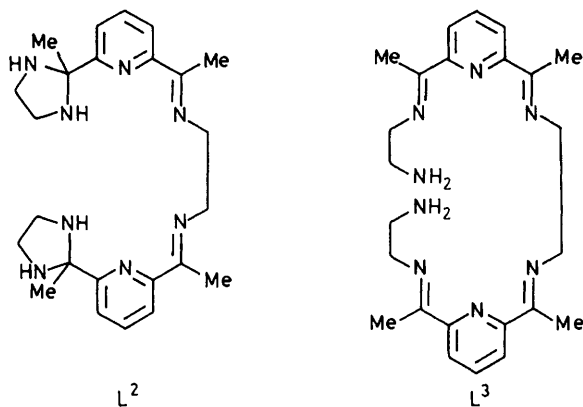
than in complexes of the tetra-imine macrocycle L^1 . Molecular models lend further support for the L^2 form of the ligand. They indicate that it is not possible to arrange for all eight nitrogen atoms of L^3 to be within acceptable bonding distances of a single central metal

TABLE 1
Analytical, magnetic, and electrical conductance data for the complexes

Complex	Analysis (%)						Λ^a $\text{S cm}^2 \text{ mol}^{-1}$	$\mu_{\text{eff.}}^b/\text{B.M.}$	
	Found			Calc.				293 K	93 K
	C	H	N	C	H	N			
$[\text{BaL}^1(\text{ClO}_4)_2]$	37.2	3.8	11.7	37.2	3.7	11.8	314		
$[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$	36.5	4.4	14.4	36.6	4.6	14.2	<i>c</i>		
$\text{Cu}_2\text{L}^1(\text{OH})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$	31.8	3.4	10.0	31.7	3.5	10.1	330	1.82 ^d	1.68 ^d
$[\text{Cu}_2\text{L}^2(\text{NCS})_4] \cdot \text{H}_2\text{O}$	41.7	4.3	20.4	41.4	4.5	20.7	135	2.03 ^d	2.01 ^d
$\text{Cu}_2\text{L}^3(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	29.0	3.8	10.9	29.0	3.9	11.2	279	1.89 ^d	1.80 ^d
$[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$	28.6	4.8	15.7	29.1	4.7	15.8	270		
$\text{CdL}^5(\text{ClO}_4)_2$	28.0	3.8	12.5	28.0	3.8	12.5	298		
$[\text{CdL}^6(\text{NCS})][\text{ClO}_4]$	32.7	4.3	16.1	32.5	4.1	16.2	168		
$[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$	40.9	3.4	13.5	40.9	3.4	13.3	300		
$[\text{Ni}(\text{L}^8)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$	50.3	2.8	15.4	50.8	3.1	15.6	293	3.22	
$[\text{Ni}(\text{L}^8)_2][\text{BPh}_4]_2 \cdot \text{H}_2\text{O}$	76.7	5.4	10.5	77.2	5.1	10.5	227	3.35	

^a For 10^{-3} mol dm^{-3} MeCN solutions at 25 °C. ^b Corrected for diamagnetism of ligands. ^c Insoluble. ^d Magnetic moment per metal atom.

ligand L^2 is the product of the condensation of two molecules of dap with three molecules of en. Two isomeric formulations, L^2 and L^3 , may be written for this condensate. The potentially sexidentate, di-imine, form L^2 may be regarded as being derived from the potentially octadentate, tetra-imine, form L^3 by addition of the two terminal NH_2 functions (of L^3) across adjacent azomethine bonds with accompanying formation of two five-membered imidazolidine rings. The i.r. spectrum (Table 2) of the complex $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$



favours the L^2 formulation. Thus, a single $\nu(\text{NH})$ vibration of moderate intensity is observed at 3265 cm^{-1} . If the ligand were in the L^3 form a much stronger double-peaked absorption corresponding to the antisymmetric and symmetric $\nu(\text{NH}_2)$ vibrations of the primary amine groups would be expected. Secondly, no absorption at $1590\text{--}1610 \text{ cm}^{-1}$, attributable to the $\delta(\text{NH}_2)$ bending mode, was observed, as would be expected for L^3 . Thirdly, the $\nu(\text{C}=\text{N})$ band at 1630 cm^{-1} of $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ is notably less intense (relative to other ligand vibrations, such as the pyridine-ring deformations),

ion; in particular, the two NH_2 groups will be uncoordinated or, at best, very weakly so. They will therefore be available for nucleophilic addition to adjacent $\text{C}=\text{N}$ bonds. In contrast, the models show that L^2 is well suited to co-ordinate as a sexidentate ligand particularly in an approximately planar conformation. As noted above, this is the arrangement found³ in complexes of the sexidentate macrocycle L^1 . Finally, it may be noted that there is recent precedent for the stabilization, *via* co-ordination, of amine-to-imine addition products in the chemistry of Schiff-base ligands formed from dap, or related dicarbonyls, and other diprimary amines.^{3,5} Of particular relevance is the barium(II) complex of the 18-membered $[2+2]$ macrocycle derived from dap and diethylenetriamine which also contains two imidazolidine rings formed by the nucleophilic addition of the two secondary amine groups across neighbouring azomethine bonds.³

When the complex $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ was refluxed in dry MeOH or EtOH for 15–30 min the complex $[\text{BaL}^1(\text{ClO}_4)_2]$ was obtained in high yield. To account for the ring closure, in the absence of added dicarbonyl, we propose the transamination mechanism outlined in the Scheme. The mechanism assumes that in solution the complex (1) containing the ligand in the di-imine form (L^2) is in equilibrium with the complex (2) in which the ligand is in its tetra-imine form (L^3). Because of the low solubility of (1) it was not possible to test this proposal by means of n.m.r. spectroscopy. The ring closure is seen as proceeding by an intramolecular attack of a free NH_2 group of (2) at the $\text{C}=\text{N}$ group associated with the other pyridyl moiety to give the intermediate addition product (3). The final step is a deamination with elimination of a molecule of en affording the macrocyclic product (4). The mechanism is essentially the same as the latter stages of that proposed for the formation of the $[2+2]$ macrocycles from dap and 3,6-

dioxaoctane-1,8-diamine or diethylenetriamine (see Scheme 3 of ref. 1). The difference is that in the former cases the isolable intermediate is the open-chain species formed by the condensation of one molecule of diketone with two molecules of diprimary amine, whereas in the present system the isolable intermediate is made up of two dap units and three molecules of di-primary amine. It seems likely that for an intermediate to be sufficiently stable to be isolated it is necessary for the ligand to have a certain minimum availability of donor atoms. A condensate of dap : en (1 : 2) would have a denticity of only five, probably too small to satisfy the large Ba^{2+} ion even allowing for anion co-ordination.

moment (Table 1). This visible-near-i.r. electronic spectrum consists of a single band at *ca.* $16\,000\text{ cm}^{-1}$ (Table 2). These observations are consistent with a structure comprising two non-interacting copper(II) ions each in a square plane of nitrogen donors in each half of the ligand and with one or two axially co-ordinated ClO_4^- ions or water molecules completing a square pyramidal or tetragonal co-ordination sphere. The complex is a 2 : 1 electrolyte in MeCN suggesting that two of the ClO_4^- ions remain co-ordinated in solution.

The $\text{L}^2 \rightarrow \text{L}^3$ ligand rearrangement brought about by replacement of the single Ba^{2+} in $[\text{BaL}^2(\text{ClO}_4)_2]\cdot\text{H}_2\text{O}$ by two Cu^{2+} can apparently be reversed, while still retaining

TABLE 2
Infrared (cm^{-1}) and electronic spectral data for the complexes

Complex	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\delta(\text{NH}_2)$	$\nu_{\text{asym}}(\text{NCS})$	Electronic spectra (10^3 cm^{-1})	
						Solid	Solution ^a
$[\text{BaL}^1(\text{ClO}_4)_2]$			1 630s				
$[\text{BaL}^2(\text{ClO}_4)_2]\cdot\text{H}_2\text{O}$		3 265m	1 627m				
$\text{Cu}_2\text{L}^1(\text{OH})(\text{OH}_2)(\text{ClO}_4)_3$			1 626s			17.4 (sh),	14.5 (118)
$[\text{Cu}_2\text{L}^2(\text{NCS})_4]\cdot\text{H}_2\text{O}$		3 350w, 3 250m,br	1 622m		2 080s	14.4	14.3 (200)
$\text{Cu}_2\text{L}^2(\text{ClO}_4)_4\cdot 2\text{H}_2\text{O}$	3 338s, 3 280s		1 664s	<i>ca.</i> 1 605m		14.1	16.1 (134)
$[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$	3 360s, 3 302s		1 662s	<i>ca.</i> 1 605m			
$\text{CdL}^5(\text{ClO}_4)_2$	3 360s, 3 300s		1 655s	1 600m			
$[\text{CdL}^5(\text{NCS})][\text{ClO}_4]$	3 340s, 3 280s		1 650s	<i>ca.</i> 1 600m	2 078s		
$[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$	3 330s, 3 272s		<i>ca.</i> 1 640 (sh)	<i>ca.</i> 1 600m			
$[\text{Ni}(\text{L}^8)_2][\text{ClO}_4]_2\cdot\text{H}_2\text{O}$		3 230m,br	1 620m, 1 602m, 1 588m			<i>ca.</i> 18.0 (sh), 11.8	<i>b</i>
$[\text{Ni}(\text{L}^8)_2][\text{BPh}_4]_2\cdot\text{H}_2\text{O}$		3 290m	1 612m, 1 595m, 1 582s			<i>ca.</i> 18.0 (sh), 11.9	<i>ca.</i> 18.0 (sh), 12.0 (<i>ca.</i> 50) ^c

^a In MeCN; values of $\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ are given in parentheses. ^b Insoluble. ^c Measured in acetonitrile-dimethyl sulphoxide (9 : 1).

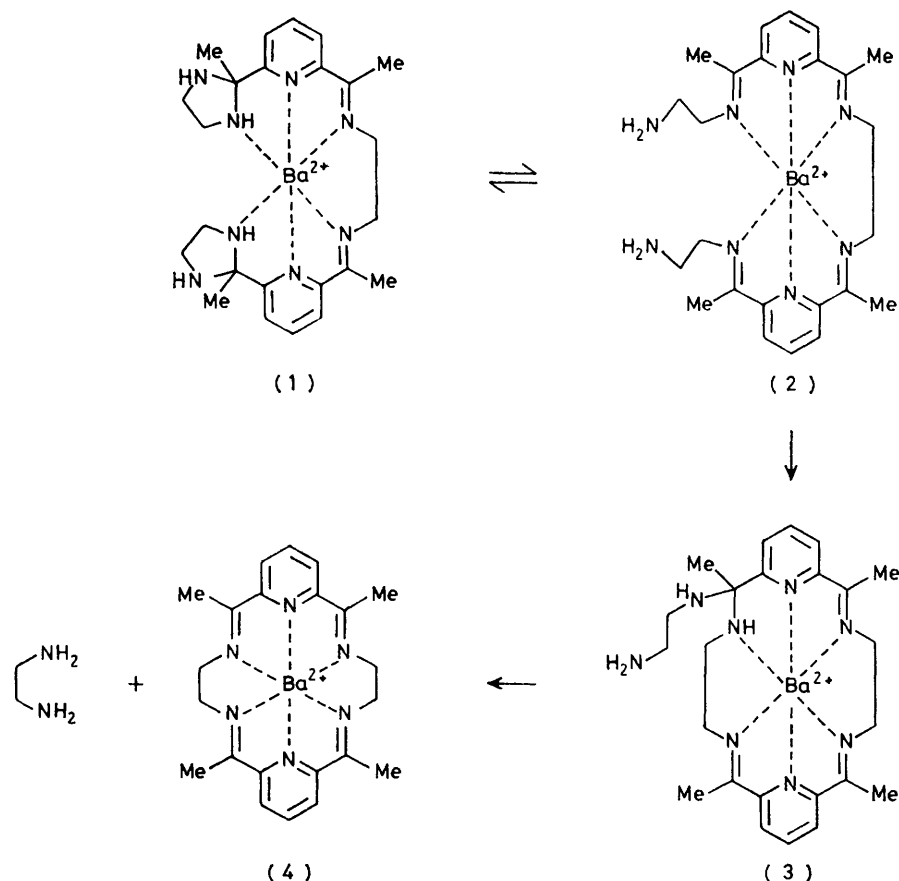
Transmetallation with Copper(II).—It was argued above that the tetra-imine ligand L^3 is not well suited to the complexation of a single metal ion, this being the reason for the rearrangement to the di-imine form L^2 . In contrast, however, L^3 might well be the preferred form for complexation to two metal ions. To test this prediction the complex $[\text{BaL}^2(\text{ClO}_4)_2]\cdot\text{H}_2\text{O}$ was treated with an excess of $\text{Cu}[\text{ClO}_4]_2\cdot 6\text{H}_2\text{O}$ in MeOH. The binuclear complex $\text{Cu}_2\text{L}^3(\text{ClO}_4)_4\cdot 2\text{H}_2\text{O}$ was obtained in good yield. In contrast to the mononuclear barium(II) complex, the i.r. spectrum of the binuclear copper(II) complex exhibits a pair of strong absorption bands at 3 338 and 3 280 cm^{-1} which we assign to the ν_{asym} and ν_{sym} vibrations of NH_2 , along with a band of moderate intensity at 1 605 cm^{-1} attributable to $\delta(\text{NH}_2)$. The strong $\nu(\text{C}=\text{N})$ vibration occurs at 1 664 cm^{-1} . These results suggest that the ligand has rearranged from the L^2 to the L^3 form during the transmetallation reaction. Splitting of the ν_3 and ν_4 ClO_4^- vibrations indicates co-ordination of at least one of the anions. In addition, one or both of the water molecules may be bonded to the metal ions. The complex is magnetically normal with only a small temperature dependence of the magnetic

the two copper(II) ions, simply by exchange of the ClO_4^- anions by NCS^- . In the i.r. spectrum of the complex $[\text{Cu}_2\text{L}^2(\text{NCS})_4]\cdot\text{H}_2\text{O}$ the strong doublet at *ca.* 3 400 cm^{-1} characteristic of $\nu(\text{NH}_2)$ is absent. Instead, a weak sharp band at 3 350 cm^{-1} along with a broader band at 3 250 cm^{-1} , attributable to free and hydrogen-bonded secondary NH , are observed. The $\delta(\text{NH}_2)$ vibration at *ca.* 1 605 cm^{-1} is also absent and the single $\nu(\text{C}=\text{N})$ band at 1 625 cm^{-1} is of reduced intensity. The NCS^- ν_{asym} mode occurs as an unsplit band at 2 080 cm^{-1} suggesting that all four NCS^- groups are terminally *N*-bonded. The electronic spectrum (Table 2) is at least consistent with a square-pyramidal geometry. We suggest that the reason for the $\text{L}^3 \rightarrow \text{L}^2$ rearrangement in this case has its origin in the desire of the copper(II) ion for an equatorial field of four good co-ordinating groups. The planar trimethine group provides three of these ligand atoms. Where the anions have weak co-ordinating properties, as in the tetraperchlorate, the fourth equatorial position is taken up by the terminal NH_2 groups with the ligand in the L^3 form, the perchlorate ions occupying one or more axial positions. On the other hand, in the tetraisothiocyanate it is the strongly co-ordinating NCS^- ions which occupy

the fourth equatorial co-ordination sites. The NH_2 functions are then free to add to adjacent $\text{C}=\text{N}$ bonds thereby converting L^3 into L^2 .

Unlike $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ the dicopper(II) complex does not undergo ring closure on heating its solutions either in the absence or in the presence of dap. This may be due to the co-ordination of the NH_2 groups of L^3 rendering them unavailable for nucleophilic attack. However,

L^4 prepared from dap and 1,3-diaminopropane.⁶ Infra-red and electronic spectra (see selected data in Table 2) are fully consistent with this proposed structure. Support for the occurrence of a hydroxo-bridge is provided by magnetic susceptibility measurements in the range 100–300 K. The magnetic moment falls from a value of 1.82 B.M.* at 293 K to 1.68 B.M. at 113 K. The Curie-Weiss plot is linear and gives a Weiss constant



SCHEME

treatment of $[\text{BaL}^1(\text{ClO}_4)_2]$ with $\text{Cu}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ gave the binuclear complex $\text{Cu}_2\text{L}^1(\text{OH})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ of the 18-membered macrocycle L^1 in which there is a hydroxo-bridge between the two copper(II) ions (see later). Molecular models, as well as the earlier structure determinations of $[\text{SrL}^1\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ and $[\text{PbL}^1(\text{NCS})(\text{SCN})]$, clearly show that the cavity size of L^1 , in its planar conformation, is too small to accommodate the $\text{Cu}-\text{O}(\text{H})-\text{Cu}$ unit. However, this can be achieved if the macrocycle is folded about the axis bisecting the two $-\text{CH}_2-\text{CH}_2$ linkages so that the two trimethylene moieties are approximately perpendicular to each other. In this macrocycle conformation each ' CuN_3O_2 ' square pyramid shares a corner (presumed to be the oxygen atom of OH^- rather than of H_2O) and an apex (presumed to be the oxygen atom of H_2O). This is the arrangement found, by X -ray analysis, in the analogous complex $\text{Cu}_2\text{L}^4(\text{OH})(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ containing the closely related 20-membered ring

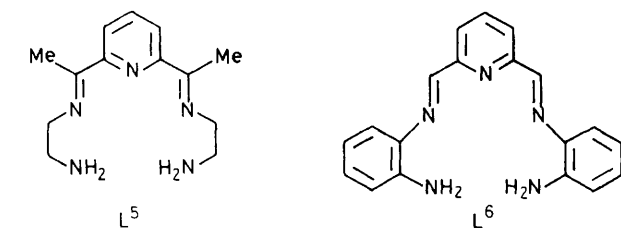
θ of -36° . While accurate evaluation of the coupling constant must await measurements at lower temperatures it is clear that there is weak antiferromagnetic superexchange between the copper(II) ions. The coupling is clearly small compared to other binuclear copper(II) complexes containing mono- or di-hydroxo-bridges.⁷⁻⁹ It is recognized that the magnitude (and sign) of the coupling constant is dependent on the ground state (d_{z^2} or $d_{x^2-y^2}$) of the copper(II) ions, on the position of the bridging group(s) (axial or equatorial), and on the $\text{Cu}-\text{O}-\text{Cu}$ bridge angle.^{7,8}

In reactions between 2,6-diformylpyridine (dfp) and *o*-phenylenediamine (opd) in the presence of $\text{Ba}[\text{ClO}_4]_2$ the product was invariably the barium(II) complex of the $[2+2]$ macrocycle described earlier;⁴ no intermediate open-chain species could be isolated.

Reactions in the Presence of Cd^{II} .—The effect of Cd^{II}

* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m².

$[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ on reactions between dap and en and between dfp and opd was briefly investigated using a range of molar ratios of reactants and a range of reaction temperatures. In no case was a macrocyclic product obtained. In both reaction systems the products were $[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$ and $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$, respectively, where L^5 and L^6 are the open-chain Schiff-base ligands formed *via* the condensation of one molecule of dicarbonyl with two molecules of di-primary amine. The occurrence of the ligands L^5 and L^6 in these complexes was inferred from their i.r. spectra and confirmed, in the case of $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$, by an X-ray structure determination (see below). Thus, the i.r. spectra showed the expected features, discussed earlier, for the $\nu(\text{NH}_2)$, $\delta(\text{NH}_2)$, and $\nu(\text{C}=\text{N})$ modes (Table 2). At first it was speculated that the en and opd molecules in the complexes might be covalently bound to the Schiff-base ligand (L^5 or L^6) rather than co-ordinated to the Cd^{II} . In the light of results discussed above for both barium(II) and copper(II) complexes it seemed possible that one primary amine group might have added across one $\text{C}=\text{N}$ bond with the other co-ordinated to the metal ion, although there was no clear i.r. indication for this. The problem was solved by a single-crystal structure determination of $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$.



Structure of $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$.—The structure of the $[\text{CdL}^6(\text{opd})]^{2+}$ cation is illustrated in Figures 1 and 2, together with the atomic numbering scheme. The

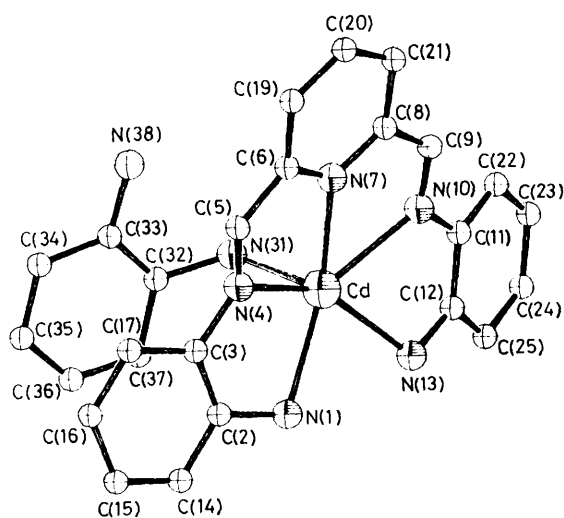


FIGURE 1 Structure of the $[\text{CdL}^6(\text{opd})]^{2+}$ cation together with the atom-numbering scheme

metal atom is bonded to the five nitrogen atoms of the L^6 ligand which forms a pentagonal girdle (mean deviation of a contributing atom from the N_5 plane, 0.10 \AA ; Table 5). The metal atom lies 0.42 \AA above this plane and is bonded in this axial position to a nitrogen atom [N(31)] of the opd molecule. A perchlorate oxygen atom [O(14)] is sited at 2.84 \AA [$\text{O}(14) \cdots \text{Cd}-\text{N}(31) 166.2^\circ$]

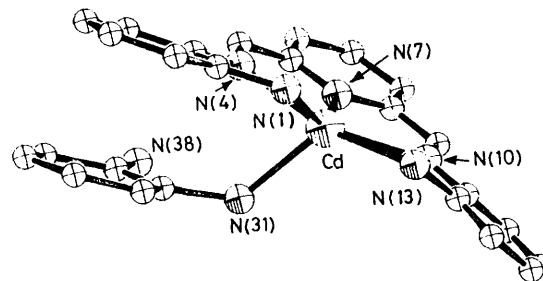


FIGURE 2 Structure of the $[\text{CdL}^6(\text{opd})]^{2+}$ cation showing the relationship between the plane of the axially co-ordinated opd molecule and that of the quinquedentate ligand L^6

from the metal in the other axial position but this cannot be considered as other than a very weak interaction. The structure is therefore best considered as a pentagonal pyramid. This geometry is very rare in six-coordinate complexes; previous examples are those in which the pentagonal girdle is provided by the five donor atoms of a macrocycle.^{10,11} In the present case the near planarity of the non-cyclic ligand L^6 is ensured by the extended conjugation. In the pentagonal pyramid it is expected that the metal atom should be displaced out of the equatorial plane in the direction of the axial atom, and this is observed in all the cases referred to.

The Cd-N bond distances are in the range $2.35\text{--}2.46 \text{ \AA}$, with the axial bond [Cd-N(31)] being the shortest at $2.341(9) \text{ \AA}$. As is usually found in Schiff-base complexes derived from dap the metal-N(pyridine) bond [$2.35(1) \text{ \AA}$] is the shortest of the equatorial set.¹²

The most novel feature of the structure is the unidentate co-ordination of the opd molecule which is best suited to chelation to a single metal ion. This co-ordination mode is, of course, impossible in the present case since two mutually *cis* co-ordination sites are not available on the planar 'CdL⁶' moiety. An intermolecular bridging function for opd would seem possible although the rigid framework of this molecule renders this less feasible than with flexible diamines such as en. Figure 2 shows that the phenyl ring of the opd molecule is disposed nearly parallel to the plane of the Schiff-base ligand L^6 . There are contacts of the order of $3.5\text{--}3.7 \text{ \AA}$ with C(2), C(3), C(14), C(15), C(16), and C(17), of one of the phenyl rings of L^6 . The planes of the two phenyl rings intersect at an angle of 5.9° . Thus, it is probable that there is a weak supplementary bonding interaction between opd and L^6 having its origin in the delocalized π systems of the two molecular planes.

As shown in Table 3, each of the four unsaturated six-membered rings are planar within experimental error. The three rings in L^6 intersect the N_5 plane at angles

ranging from 11.5 to 13.7°. The bending back of the phenyl rings of L⁶ increases the displacement of the metal atom from the planes to 0.77, 0.85 Å. The angles between the CdN₂ planes and the appropriate phenyl-ring planes are 21.6 and 22.1°. (The pyridine ring is coplanar with the metal atom.)

TABLE 3

Least-squares planes for [CdL⁶(opd)][ClO₄]₂. Distances of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with an asterisk

Plane (1): N(1) -0.09, N(4) 0.15, N(7) -0.15, N(10) 0.08, N(13) 0.01, Cd* 0.42

Plane (2): C(2), C(3), C(14), C(15), C(16), C(17), deviations less than 0.015, N(1)* 0.01, N(4)* 0.03, Cd* 0.77

Plane (3): C(6), N(7), C(8), C(19), C(20), C(21), deviations less than 0.01, Cd* 0.02

Plane (4): C(11), C(12), C(22), C(23), C(24), C(25), deviations less than 0.015, N(10)* -0.09, N(13)* 0.01, Cd* -0.85

Plane (5): C(33), C(34), C(35), C(36), C(37), C(32), deviations less than 0.015, N(31)* -0.13, N(38)* -0.07

Plane (6): N(1), N(4), Cd

Plane (7): N(10), N(13), Cd

Angles (°) between planes: (1)-(2) 11.5, (1)-(3) 13.7, (1)-(4) 12.8, (1)-(5) 16.8, (2)-(3) 17.6, (2)-(4) 24.3, (2)-(5) 5.9, (3)-(4) 18.3, (3)-(5) 19.0, (4)-(5) 29.3, (2)-(6) 21.6, (4)-(7) 22.1

There are some short intermolecular contacts, the most notable (2.85 Å) being N(31) ··· O(23) (-x, -y, 1 - z). This interaction has the correct geometry for a hydrogen bond H(31) ··· O(23) of 1.80 Å so it is somewhat surprising that this perchlorate ion is disordered and that O(23) has an occupancy of only 0.5. There are no other hydrogen bonds.

In the analogous complex [CdL⁵(en)][ClO₄]₂ an intermolecular bridging function between metal ions for en does not suffer the same steric restrictions as does the rigid opd molecule. We have attempted a single-crystal X-ray structure determination of this complex but with limited success.* However, it was clear that the structure is polymeric with each cadmium(II) ion bonded to the five nitrogen atoms of the ligand L⁵ in an equatorial plane and axially linked to adjacent metal ions *via* en bridges giving each metal ion a seven-co-ordinate pentagonal-bipyramidal geometry.

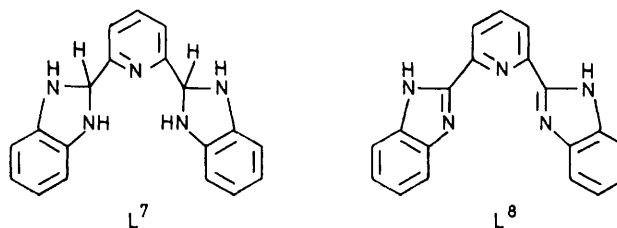
Treatment of [CdL⁵(en)][ClO₄]₂ with a four-fold excess of Na[CNS] afforded the complex [CdL⁵(NCS)][ClO₄]₂ in which the NCS⁻ ion has replaced the en molecule. The ν_{asym} mode of NCS⁻ occurs at 2 078 cm⁻¹ suggesting terminal N-bonded co-ordination and the ClO₄⁻ ν_3 and ν_4 modes are unsplit suggesting that the ClO₄⁻ ion is unco-ordinated. Thus it appears that this complex is six-co-ordinate. Treatment of the isothiocyanato-complex with an excess of Ag[ClO₄] afforded, after removal of precipitated Ag[NCS], the new complex CdL⁵(ClO₄)₂. Here, the i.r. spectrum showed appreciable broadening of

* [CdL⁵(en)][ClO₄]₂: Monoclinic, $a = 7.78(1)$, $b = 15.23(1)$, $c = 20.80(1)$ Å, $\beta = 93.9(1)^\circ$, space group $P2_1$, $Z = 4$. The two metal atoms in the asymmetric unit have approximate coordinates 0, 0, z and $\frac{1}{2}$, 0, $z + \frac{1}{2}$, and the false symmetry elements and the high correlations between parameters make refinement below R 0.15 impossible.

the ν_3 and splitting of the ν_4 ClO₄⁻ vibrations. These observations indicate ready replacement of the co-ordinated axial ligand(s) on the cadmium(II) ion while the equatorial pentagonal Schiff-base ligand is retained, as well as variable (six or seven) co-ordination number.

In the solid complexes [CdL⁵(en)][ClO₄]₂ and [CdL⁶(opd)][ClO₄]₂ the attachment of the en or opd molecule to the metal rather than, covalently, to an imino-carbon atom of the L⁵ or L⁶ ligand has been noted. However, evidence for nucleophilic attack by NH₂ at the azomethine bond is provided by the conversion of CdL⁵(ClO₄)₂ or [CdL⁵(en)][ClO₄]₂ into the binuclear complex Cu₂L³(ClO₄)₄·2H₂O, on reaction with Cu[ClO₄]₂·6H₂O, shown to be identical in properties to an authentic sample prepared from [BaL²(ClO₄)₂]·H₂O as described above. A transamination mechanism, similar to that illustrated in the Scheme, is proposed wherein a detached NH₂ function of one solvated [CdL⁶]²⁺ ion in solution adds across one C=N group of a second complex ion, this being followed by a deaminative elimination of one molecule of en.

Oxidative Dehydrogenation in a Nickel(II) Complex.—Rather different behaviour was observed in the transmetallation reaction between [CdL⁶(opd)][ClO₄]₂ and Ni[ClO₄]₂·6H₂O. No clean products were isolated following reflux for 2 h of the reactants in MeOH. However, the red solution darkened on standing in air over a period of *ca.* 2 d whereupon brown crystals of a complex [Ni(L⁸)₂][ClO₄]₂·H₂O separated out. This complex was not obtained if air was excluded.



We believe the ligand has the structure L⁸ and that it may be formed by an oxidative dehydrogenation of the precursor ligand L⁷ which in turn is derived from L⁶ by covalent nucleophilic addition of the two terminal NH₂ groups across the two azomethine linkages. Evidence for the formulation of the ligand in the nickel(II) complex as L⁸ comes from (i) the necessity for O₂ exposure during its preparation, (ii) i.r. spectra, and (iii) electronic spectra (Table 2). Significant features of the i.r. spectrum are a single broad band at 3 290 cm⁻¹ attributable to hydrogen-bonded NH and a set of three bands between 1 610 and 1 570 cm⁻¹ attributable to coupled C=N and C=C vibrations of the imino-group and the pyridine and phenyl rings; no absorption above *ca.* 1 590 cm⁻¹ is expected for L⁷. Some splitting in the ν_3 vibration at *ca.* 1 090 cm⁻¹ was observed which may be due to a hydrogen-bonding interaction with the secondary NH groups in the lattice. In the BPh₄⁻ salt the $\nu(\text{NH})$ band is significantly sharper. Both complexes are 2 : 1 electrolytes in MeCN.

The electronic spectrum of $[\text{Ni}(\text{L}^8)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$ in both the solid state and in MeCN solution exhibits a band at $11\,800\text{ cm}^{-1}$ and another at *ca.* $18\,000\text{ cm}^{-1}$ occurring as a shoulder on the low-energy side of a much more intense charge-transfer band which dominates the spectrum above *ca.* $20\,000\text{ cm}^{-1}$. The bands at $11\,800$ and $18\,000\text{ cm}^{-1}$ are assigned to transitions from the ${}^3A_{2g}$ ground state to the ${}^3T_{2g}$ and ${}^3T_{1g}$ excited levels respectively, in the approximation of O_h symmetry. The expected ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition is completely obscured. The intense absorption at higher energy is most probably a metal-to-ligand charge transfer arising from an interaction of metal t_{2g} electrons with vacant p_{π}^* orbitals of the extensively conjugated ligand L^8 . The spectrum is in this respect very similar to those of octahedral nickel(II) complexes of other ligands containing the trimethine unit¹³ whereas nickel(II) complexes of pyridyl ligands containing saturated nitrogenous chelating side chains, as in L^7 , do not show intense charge-transfer absorption in the visible region.¹⁴ Finally, support for the ligand having the planar structure L^8 rather than L^7 comes from inspection of molecular models which indicate appreciable interligand steric interaction between the two non-planar L^7 ligands in $[\text{Ni}(\text{L}^7)_2]^{2+}$.

Conclusions.—The reactions described demonstrate the control exercised by metal ions of different type on the synthesis of polydentate, cyclic, and acyclic Schiff-base ligands. It is shown how, for the case of Ba^{2+} -controlled reactions, the use of mild reaction conditions leads to the isolation of a complex of an open-chain polydentate ligand which may reasonably be considered an intermediate in the macrocycle formation. The results extend earlier studies^{1,2} on related systems which demonstrated that the ring-closure step occurs *via* a transamination mechanism. It seems probable that the isolation of a particular intermediate is due as much to thermodynamic factors (and low solubility) as to kinetic factors. Considered collectively, the results presented here and elsewhere^{1,2,5} indicate that the stability of a particular intermediate or macrocyclic product depends on several factors which include the denticity of the ligand, the nature of the metal ion, and the interplay between the geometrical preferences of the metal ion on the one hand and those of the ligand on the other. The importance of the nature of the metal ion in the present systems is shown by the fact that while Ba^{2+} acts as a template for L^1 macrocycle formation, Cu^{II} and Cd^{II} do not. Yet macrocyclic complexes of these metal ions can be obtained as stable entities *via* transmetallation once the macrocycle is formed on Ba^{II} . The special effectiveness of the large alkaline-earth metal ions in leading to macrocycle formation is probably associated with the relatively weak co-ordinate bonds which they form with nitrogen donors which frees the terminal NH_2 groups for nucleophilic attack at C=N centres.

The occurrence of nucleophilic additions of NH_2 groups to co-ordinated C=N centres is apparent also in the ready and reversible $\text{L}^2 \rightleftharpoons \text{L}^3$ ligand rearrangement on replacement of one metal ion by another or one anion

by another. Here, a major controlling factor appears to be the attainment by the metal ion of the best available co-ordination polyhedron.

Finally, the results also demonstrate the accommodation by the ligand L^8 , *via* intramolecular nucleophilic NH_2 to C=N addition followed by dehydrogenation, to the stereochemical preference (octahedral) of Ni^{II} .

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine, 1,2-diaminoethane, *o*-phenylenediamine and the metal salts were used as supplied commercially without purification.

$[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$. 2,6-Diacetylpyridine (5 mmol) and $\text{Ba}[\text{ClO}_4]_2$ (2.5 mmol) were dissolved in EtOH (125 cm^3) and added over a period of 30 min to a stirred solution of en (25 mmol) in EtOH (150 cm^3) at room temperature. After completion of the addition the mixture was stirred for another hour, filtered, and concentrated by rotary evaporation to yield the product as a microcrystalline white solid in 93% yield, calculated on dap. The use of a smaller excess of en over dap generally resulted in impure products at room temperature, while only sticky oils of indefinite composition were obtained in the absence of $\text{Ba}[\text{ClO}_4]_2$, at any temperature.

$[\text{BaL}^1(\text{ClO}_4)_2]$. This complex was obtained in 75% yield on refluxing $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ (0.5 g) in dry MeOH (200 cm^3) containing 2,2-dimethoxypropane (5 cm^3) for 3 h, followed by standing overnight. The product separated as white crystals.

It was alternatively prepared in 80% yield by reaction of dap (0.02 mol) with en (0.02 mol) in the presence of $\text{Ba}[\text{ClO}_4]_2$ (0.01 mol) in refluxing MeOH for *ca.* 2 h. Separation of the product was observed to begin after reflux for 1 h. After cooling, the crystals were filtered off. Concentration of the filtrate yielded a further crop of crystals.

$\text{Cu}_2\text{L}^1(\text{OH})(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$. Compounds $[\text{BaL}^1(\text{ClO}_4)_2]$ (1 mmol) and $\text{Cu}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ (6 mmol) were refluxed in 200 cm^3 MeOH or EtOH for 3 h and the solution set aside overnight. Dark blue crystals of the product were separated and washed with cold MeOH. Concentration of the filtrate yielded a further batch of crystals. Yield 75%.

$\text{Cu}_2\text{L}^3(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$. A four-fold molar excess of $\text{Cu}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ was added to a suspension of $[\text{BaL}^2(\text{ClO}_4)_2] \cdot \text{H}_2\text{O}$ (0.5 g) in MeOH (150 cm^3) and the mixture stirred at room temperature for 10 h during which time the barium(II) complex gradually dissolved. The product separated on concentration in 60% yield. This complex was also obtained by treatment of a solution of $[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$ or $\text{CdL}^5(\text{ClO}_4)_2$ with an excess of $\text{Cu}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ in MeOH, followed by reflux for 30 min. Yields 40–60%.

$[\text{Cu}_2\text{L}^2(\text{NCS})_4] \cdot \text{H}_2\text{O}$. A suspension of $\text{Cu}_2\text{L}^3(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (0.4 g) in MeOH (200 cm^3) was treated with $\text{Na}[\text{NCS}]$ (0.16 g). On warming, the blue solid changed to green within minutes. Stirring and heating was continued for 30 min. The green product was isolated in 80% yield.

$[\text{CdL}^5(\text{en})][\text{ClO}_4]_2$. A solution of dap (0.30 g) and $\text{Cd}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ (0.33 g) in MeOH (150 cm^3) was slowly added to a solution of en (0.55 g) in MeOH (50 cm^3). The mixture was stirred at room temperature for 2 h. The product crystallized out in *ca.* 78% yield on concentration.

$[\text{CdL}^5(\text{NCS})][\text{ClO}_4]$. Treatment of the above complex in MeOH—EtOH (3 : 1) with an excess of $\text{Na}[\text{NCS}]$ gave the product in 60% yield.

$\text{CdL}^6(\text{ClO}_4)_2$. Treatment of the isothiocyanato-complex in MeOH solution with one equivalent of $\text{Ag}[\text{ClO}_4]$ in MeOH at reflux temperature gave a grey precipitate of $\text{Ag}[\text{SCN}]$. Concentration of the filtrate afforded white crystals of the product in 69% yield.

$[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$. The compounds dfp (0.02 mol), opd (0.06 mol), and $\text{Cd}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ (0.02 mol) in MeOH (500 cm^3) were refluxed for 30 min. The slightly cloudy orange solution was filtered and concentrated by rotary evaporation to afford large orange crystals of the product in 60% yield.

$[\text{Ni}(\text{L}^8)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$. To a solution of $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$ (0.7 g) in Pr^iOH (200 cm^3) was added a 6 molar excess of $\text{Ni}[\text{ClO}_4]_2 \cdot 6\text{H}_2\text{O}$ in MeOH (50 cm^3). The solution quickly changed from orange to red. The mixture was refluxed for 2 h, filtered, and concentrated to ca. 100 cm^3 by rotary evaporation. No solid separated at this stage. The solution slowly darkened on standing in air over a period of 2 d after which time 0.30 g brown crystals were recovered. The tetraphenylborate salt was obtained by metathesis.

Crystal Data.— $\text{C}_{25}\text{H}_{25}\text{CdCl}_2\text{N}_7\text{O}_8$, $M = 734.5$, Triclinic, $a = 9.117(9)$, $b = 10.797(8)$, $c = 16.084(11)$ Å, $\alpha = 97.89(8)$, $\beta = 81.43(9)$, $\gamma = 70.70(10)^\circ$, $U = 1447.8$ Å³, $D_m = 1.66$,

TABLE 4

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Cd(1)	3 302(11)	609(1)	2 760(0)
N(1)	1 243(11)	— 70(11)	2 271(6)
C(2)	1 838(13)	— 1 248(12)	1 596(7)
C(3)	3 323(13)	— 1 659(11)	1 107(7)
N(4)	4 234(10)	— 858(9)	1 332(6)
C(5)	5 461(13)	— 887(12)	854(7)
C(6)	6 230(12)	49(12)	1 154(7)
N(7)	5 531(10)	851(9)	1 953(5)
C(8)	6 076(13)	1 779(12)	2 275(8)
C(9)	5 187(14)	2 580(11)	3 126(8)
N(10)	4 019(10)	2 349(9)	3 485(6)
C(11)	3 116(13)	3 031(11)	4 317(7)
C(12)	1 657(14)	2 909(11)	4 528(7)
N(13)	1 148(11)	2 159(11)	3 895(7)
C(14)	896(15)	— 2 005(14)	1 441(8)
C(15)	1 418(17)	— 3 135(15)	792(9)
C(16)	2 971(19)	— 3 546(13)	306(10)
C(17)	3 929(15)	— 2 810(12)	462(8)
C(19)	7 536(13)	175(14)	694(8)
C(20)	8 132(14)	1 124(14)	1 016(9)
C(21)	7 410(13)	1 937(14)	1 808(9)
C(22)	3 630(17)	3 739(13)	4 948(9)
C(23)	2 710(23)	4 300(15)	5 732(10)
C(24)	1 287(23)	4 154(16)	5 939(9)
C(25)	736(17)	3 455(13)	5 350(9)
N(31)	4 558(11)	— 1 015(9)	3 506(6)
C(33)	5 969(14)	— 3 141(12)	2 463(8)
C(34)	5 962(16)	— 4 347(12)	2 026(8)
C(35)	4 656(18)	— 4 695(14)	2 178(10)
C(36)	3 369(19)	— 3 891(15)	2 798(11)
C(37)	3 361(15)	— 2 712(13)	3 236(9)
C(32)	4 668(13)	— 2 309(11)	3 088(7)
N(38)	7 294(12)	— 2 762(13)	2 255(7)
Cl(1)	1 310(3)	3 250(3)	1 497(2)
O(11)	1 139(23)	2 127(18)	1 117(13)
O(12)	2 782(15)	3 216(15)	1 092(11)
O(13)	246(22)	4 389(19)	1 599(18)
O(14)	1 437(43)	2 974(27)	2 254(13)
Cl(2)	— 1 985(3)	201(3)	4 086(2)
O(21)	— 2 072(30)	1 539(27)	4 169(17)
O(22)	— 2 264(21)	— 274(18)	3 244(11)
O(23)	— 3 111(33)	137(27)	4 714(17)
O(24)	— 346(23)	— 608(20)	4 084(13)
O(25)	— 1 396(28)	— 148(24)	4 817(16)
O(26)	— 1 489(32)	— 867(28)	3 353(17)
O(27)	— 3 696(24)	556(20)	4 429(14)
O(28)	— 1 878(23)	1 409(20)	3 838(14)

$Z = 2$, $D_c = 1.68$ g cm^{-3} , $\mu = 9.98$ cm^{-1} , $F(000) = 740$, space group $P\bar{1}$ from the successful structure determination.

A crystal of approximate size $0.2 \times 0.5 \times 0.5$ mm was set up to rotate around a on a Stoe Stadi-2 diffractometer. 3 637 Reflections with maximum 2θ of 45° (with $\text{Mo-K}\alpha$ radiation, $\lambda = 0.7107$ Å) were measured by ω scan (speed $0.03^\circ \text{ s}^{-1}$ with peak width $1.5 + 0.5 \sin \theta / \tan \mu$). 2 560 Reflections with $I > 3\sigma(I)$ were used in the subsequent refinement. Absorption and extinction corrections were not applied.

Structure Determination.—The metal atom was located from a Patterson map. Subsequent Fourier maps were

TABLE 5

Molecular dimensions for $[\text{CdL}^6(\text{opd})][\text{ClO}_4]_2$, distances (Å), angles ($^\circ$) with estimated standard deviations in parentheses

(a) Metal co-ordination spheres			
Cd(1)—N(1)	2.423(12)	Cd(1)—N(10)	2.399(10)
Cd(1)—N(7)	2.457(8)	Cd(1)—N(13)	2.430(9)
Cd(1)—N(7)	2.355(9)	Cd(1)—N(31)	2.341(9)
N(1)—Cd(1)—N(4)	67.4(3)	N(7)—Cd(1)—N(13)	131.6(3)
N(1)—Cd(1)—N(7)	129.4(3)	N(10)—Cd(1)—N(13)	67.5(3)
N(4)—Cd(1)—N(7)	67.2(3)	N(1)—Cd(1)—N(31)	105.7(3)
N(1)—Cd(1)—N(10)	148.0(3)	N(4)—Cd(1)—N(31)	96.3(3)
N(4)—Cd(1)—N(10)	134.6(3)	N(7)—Cd(1)—N(31)	100.2(3)
N(7)—Cd(1)—N(10)	67.7(3)	N(10)—Cd(1)—N(31)	95.4(3)
N(1)—Cd(1)—N(13)	84.7(3)	N(13)—Cd(1)—N(31)	101.1(3)
N(4)—Cd(1)—N(13)	150.3(3)		
(b) Ligand dimensions			
N(1)—C(2)	1.441(14)	C(12)—C(25)	1.389(17)
C(2)—C(3)	1.356(15)	C(14)—C(15)	1.387(19)
C(2)—C(14)	1.393(22)	C(15)—C(16)	1.404(21)
C(3)—N(4)	1.430(18)	C(16)—C(17)	1.387(24)
C(3)—C(17)	1.397(15)	C(19)—C(20)	1.386(22)
N(4)—C(5)	1.248(15)	C(20)—C(21)	1.374(18)
C(5)—C(6)	1.476(19)	C(22)—C(23)	1.342(19)
C(6)—N(7)	1.377(13)	C(23)—C(24)	1.36(3)
C(6)—C(19)	1.361(18)	C(24)—C(25)	1.384(25)
N(7)—C(8)	1.335(18)	N(31)—C(32)	1.430(15)
C(8)—C(9)	1.470(15)	C(33)—C(34)	1.395(19)
C(8)—C(21)	1.404(19)	C(33)—N(38)	1.408(19)
C(9)—N(10)	1.249(17)	C(34)—C(35)	1.361(24)
N(10)—C(11)	1.418(13)	C(35)—C(36)	1.366(18)
C(11)—C(12)	1.377(19)	C(36)—C(37)	1.365(22)
C(11)—C(22)	1.414(20)	C(37)—C(32)	1.398(21)
C(12)—N(13)	1.438(18)	C(32)—C(33)	1.384(13)
Cd(1)—N(1)—C(2)	114.0(6)	C(11)—C(12)—N(13)	118.7(9)
N(1)—C(2)—C(3)	121.4(12)	C(11)—C(12)—C(25)	120.0(12)
N(1)—C(2)—C(14)	120.2(9)	N(13)—C(12)—C(25)	121.2(12)
C(3)—C(2)—C(14)	118.4(10)	Cd(1)—N(13)—C(12)	114.1(6)
C(2)—C(3)—N(4)	114.8(9)	C(2)—C(14)—C(15)	122.0(11)
C(2)—C(3)—C(17)	122.1(13)	C(14)—C(15)—C(16)	118.2(15)
N(4)—C(3)—C(17)	123.1(10)	C(15)—C(16)—C(17)	120.3(12)
Cd(1)—N(4)—C(3)	116.6(6)	C(3)—C(17)—C(16)	118.9(11)
Cd(1)—N(4)—C(5)	119.6(8)	C(6)—C(19)—C(20)	120.5(10)
C(3)—N(4)—C(5)	123.8(9)	C(19)—C(20)—C(21)	119.9(13)
N(4)—C(5)—C(6)	117.7(9)	C(8)—C(21)—C(20)	118.6(13)
C(5)—C(6)—N(7)	115.9(9)	C(11)—C(22)—C(23)	120.9(15)
C(5)—C(6)—C(19)	124.8(10)	C(22)—C(23)—C(24)	120.0(17)
N(7)—C(6)—C(19)	119.3(12)	C(23)—C(24)—C(25)	121.4(13)
Cd(1)—N(7)—C(6)	119.4(8)	C(12)—C(25)—C(24)	119.0(14)
Cd(1)—N(7)—C(8)	119.3(6)	Cd(1)—N(31)—C(32)	110.0(7)
C(6)—N(7)—C(8)	121.3(10)	C(34)—C(33)—C(32)	120.2(12)
N(7)—C(8)—C(9)	115.1(11)	C(34)—C(33)—N(38)	119.6(9)
N(7)—C(8)—C(21)	120.4(10)	C(32)—C(33)—N(38)	120.2(11)
C(9)—C(8)—C(21)	124.5(12)	C(33)—C(34)—C(35)	120.7(10)
C(8)—C(9)—N(10)	119.1(12)	C(34)—C(35)—C(36)	119.7(14)
Cd(1)—N(10)—C(9)	118.8(7)	C(35)—C(36)—C(37)	120.2(16)
Cd(1)—N(10)—C(11)	117.6(8)	C(36)—C(37)—C(32)	121.7(11)
C(9)—N(10)—C(11)	123.5(11)	N(31)—C(32)—C(33)	122.5(11)
N(10)—C(11)—C(12)	115.7(11)	N(31)—C(32)—C(37)	119.8(8)
N(10)—C(11)—C(22)	125.6(11)	C(33)—C(32)—C(37)	117.4(11)
C(12)—C(11)—C(22)	118.6(10)		

TABLE 5 (continued)

(c) Perchlorate dimensions			
Cl(1)-O(11)	1.348(21)	Cl(1)-O(13)	1.261(17)
Cl(1)-O(12)	1.389(15)	Cl(1)-O(14)	1.305(24)
O(11)-Cl(1)-O(12)	106.2(10)	O(11)-Cl(1)-O(14)	99.6(17)
O(11)-Cl(1)-O(13)	122.0(14)	O(12)-Cl(1)-O(14)	107.6(19)
O(12)-Cl(1)-O(13)	112.1(12)	O(13)-Cl(1)-O(14)	107.9(17)
Cl(2)-O(21)	1.41(3)	Cl(2)-O(23)	1.355(29)
Cl(2)-O(22)	1.459(19)	Cl(2)-O(24)	1.460(19)
O(21)-Cl(2)-O(22)	110.4(14)	O(21)-Cl(2)-O(24)	106.9(14)
O(21)-Cl(2)-O(23)	108.4(15)	O(22)-Cl(2)-O(24)	105.5(10)
O(22)-Cl(2)-O(23)	109.5(15)	O(23)-Cl(2)-O(24)	116.1(14)
Cl(2)-O(25)	1.410(28)	Cl(2)-O(27)	1.475(21)
Cl(2)-O(26)	1.430(26)	Cl(2)-O(28)	1.444(24)
O(25)-Cl(2)-O(26)	115.2(14)	O(25)-Cl(2)-O(28)	117.2(15)
O(25)-Cl(2)-O(27)	99.2(13)	O(26)-Cl(2)-O(28)	110.7(15)
O(26)-Cl(2)-O(27)	109.0(15)	O(27)-Cl(2)-O(28)	103.8(11)

used to locate the other atoms in the molecule. The perchlorates as usual proved troublesome. The oxygen atoms around Cl(1) were refined anisotropically and showed high thermal motion, but no serious disorder. Around Cl(2) two tetrahedra were refined as rigid groups with occupancies of 0.5 and these eight oxygen atoms were given isotropic thermal parameters. The Cd, Cl, N, and C atoms were refined anisotropically. Hydrogen atoms were placed in trigonal or tetrahedral positions and given thermal parameters equivalent to those of the atom to which they were bonded. The structure was refined by full-matrix least-squares to R 0.065. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.001F^2]$ where $\sigma(F)$ was taken from counting statistics. This gave similar values for $w\Delta^2$ over ranges of F_0 and $(\sin \theta)/\lambda$. In the final cycle of refinement no shift was $>0.2\sigma$. A final difference Fourier gave no significant peaks.

Calculations were carried out using SHELX-76¹⁵ at the

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

University of Manchester Computer Centre. Scattering factors were taken from International Tables.¹⁶ Final positional parameters are given in Table 4. Bond lengths and angles are in Table 5. Thermal parameters, hydrogen-atom positions, and observed and calculated structure factors are contained in Supplementary Publication No. SUP 23192 (18 pp.).*

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