Complexes of Ligands providing Endogenous Bridges. Part 3.[1] Non-transition Metal Complexes of Macrocycles derived from 2,6-Diacetyl-4-methylphenol; the Crystal Structure of a Mononuclear Barium Complex†

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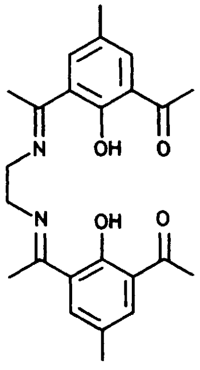
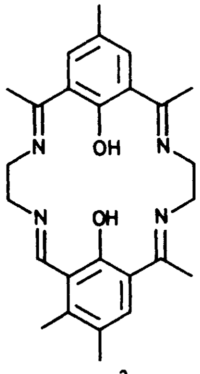
The synthesis of macrocyclic complexes derived from the condensation of 2,6-diacetyl-4-methylphenol and 1,*n*-alkanediamines in the presence of non-transition-metal templating agents is discussed. The crystal structure of a mononuclear barium perchlorate complex of the macrocycle derived from 1,3-diamino-2-propanol and the phenol is reported. The ligand is folded such that the aromatic rings are parallel to each other and the barium sits on top of the donor-atom ring. The crystals are orthorhombic, space group *Fdd*2 (C_{2v}^{19}, no. 43), with a = 37.252(28), b = 7.643(4), c = 22.631(22) Å, and Z = 8; 1 134 independent reflections with $I/\sigma(I) > 3.0$ gave R = 0.0350.

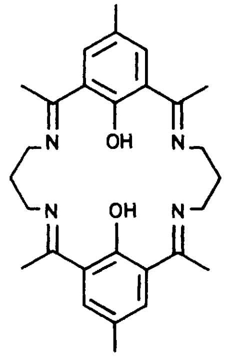
In furtherance of our programme aimed at the introduction of endogenous bridging groups into the lateral units of [2 + 2] Schiff-base macrocycles[1,2] we have investigated the synthesis of macrocycles derived from the condensation of 2,6-diacetyl-4-methylphenol and 1,*n*-alkanediamines in the presence of non-transition-metal templating agents.



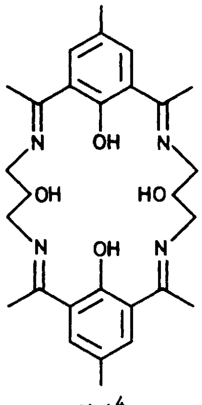
L^1



H_2L^2



H_2L^3



H_4L^4

Results and Discussion

During attempts to prepare mononuclear metal complexes from the compartmental ligand L^1 derived from the condensation of 2 mol of 2,6-diacetyl-4-methylphenol with 1 mol of 1,2-diaminoethane (en) it was found that use of lead(II) and zinc(II) salts resulted in the isolation of homobinuclear complexes $M_2L^2X_2$ (M = Pb, X = NCS; M = Zn, X = O_2CMe). These complexes could also be prepared directly from the components by using standard template techniques. They were characterised by i.r. and microanalytical data; the i.r. spectra showed no bands attributable to the carbonyl and amine functions present in the precursors and imine bands at *ca.* 1 620 cm^{-1} were detected. The spectrum of $Pb_2L^2(NCS)_2 \cdot 2H_2O$ showed a band at 2 040 cm^{-1}, indicative of *N*-bonded thiocyanate,[3] and that of $Zn_2L^2(O_2CMe)_2 \cdot 0.5H_2O$ gave bands at 1 535 and 1 420 cm^{-1} ascribable to symmetric and asymmetric modes of the acetate anion.[4] The ^1H n.m.r. spectrum of the dizinc complex was recorded in $(CD_3)_2SO$ and indicated the discrete nature of the macrocyclic species in solution: 2.36 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 4.00 (s, 4 H, CH_2CH_2), and 7.51 p.p.m. (s, 2 H, aromatic). The dilead(II) complex was too insoluble to obtain a spectrum.

The observation that the lead(II) complex is binuclear is unexpected if one applies the cavity size–cation size matching criterion used frequently in selectivity studies[5] [lead(II), 1.06; zinc(II), 0.74 Å]. It is proposed that steric factors would allow one lead(II) to lie 'above' the plane of the macrocycle with the second lead(II) 'below' this plane. The observation of a single imine stretch implies that the complex is symmetrical. It was not possible to obtain suitable crystals for *X*-ray analysis, but in the complex $Cu_2L^2(BF_4)_2 \cdot 2H_2O$ the two copper(II) atoms (r = 0.96 Å) lie on either side of the donor-ligand plane of the macrocycle and are displaced from it by 0.18 Å.[6]

The use of lead(II) perchlorate as the templating agent in the reaction of 2,6-diacetyl-4-methylphenol with 1,3-diaminopropane gave a mononuclear complex, $Pb(H_2L^3)(ClO_4)_2 \cdot 2H_2O$ as a bright yellow powder. The i.r. spectrum showed no carbonyl or amine bands from the precursors but gave an imine band at 1 625 cm^{-1} and a single band at 1 080 cm^{-1} indicative of a non-co-ordinated (T_d) perchlorate anion.[7] A broad band was observed at 3 540 cm^{-1}, due to the OH stretches from the ligand and the water molecules of crystallisation. The fact that the ligand is not deprotonated is not unique and will be discussed later.

The introduction of 1,3-diamino-2-propanol as a lateral unit gives rise to two sets of potentially deprotonated hydroxyl groups: one alkoxy and one aryloxy. The reaction of 2,6-diacetyl-4-methylphenol and 1,3-diamino-2-propanol in the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. ≈ 9.27 × 10^{-24} A m^2.

presence of the templating agents Sr^{2+}, Ba^{2+}, and Pb^{2+} gave both mononuclear and homobinuclear complexes of H_4L^4. All the complexes showed evidence for cyclisation according to the i.r. spectra, *i.e.* absence of ν(C=O) and ν(NH_2) and the presence of ν(C=N). The binuclear complexes $Sr_2(H_2L^4)(ClO_4)_2{\cdot}EtOH$ and $Pb_2(H_2L^4)(SCN)_2{\cdot}4H_2O$ have very similar spectra; the imine bands are at 1 630 and 1 620 cm^{-1} respectively and there are broad bands at *ca.* 3 400 cm^{-1} related to the OH groups. The anions give rise to bands at 1 100 cm^{-1} for the perchlorate, indicating a non-co-ordinated (T_d) anion,[7] and at 2 040 cm^{-1} for the thiocyanate, indicative of *N*-bonding.[3] The mononuclear complex $Ba(H_4L^4)(ClO_4)_2$ has a slightly different spectrum; the hydroxyl stretch is now sharp at 3 450 cm^{-1} and there are two imine bands at 1 645 and 1 635 cm^{-1} suggesting that there are two environments for these functions. Two bands, at 1 115 and 1 085 cm^{-1}, are ascribable to a unidentate (C_{3v}) perchlorate anion.[7]

The crystal structure of $Ba(H_4L^4)(ClO_4)_2$ has been solved (Figure 1). The barium atom is bound to two diammetrically opposed N atoms, both phenolic O atoms, and two endogenous hydroxyl groups, and two O atoms from unidentate perchlorate anions. This is shown schematically in Figure 2(*a*), with the perchlorates omitted for clarity. The ligand is folded such that the two aromatic rings are almost parallel with each other, and the Ba^{2+} sits 'on top' of this feature with the anions on the opposite face [Figure 2(*b*)]. The two aromatic rings are extremely close to parallel, being situated on planes having a dihedral angle of 178° between them. The molecule exhibits crystallographically imposed C_2 symmetry with an axis running through the barium atom parallel to the aromatic rings. There is an intramolecular hydrogen bond between the phenolic oxygen [O(1)] and the unco-ordinated imino-nitrogen atom [N(2)].

The barium atom is 2.6 Å from the phenoxy function [O(1)], 2.9 Å from the endogenous hydroxy function [O(2)], and 2.8 Å

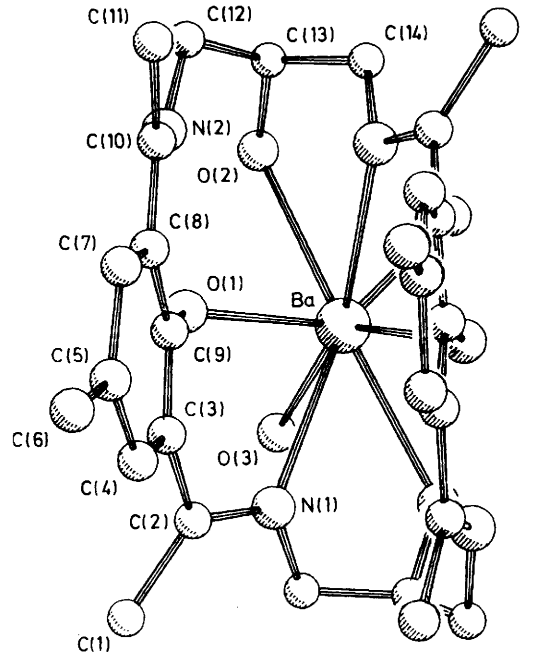

Figure 1. The molecular structure of $Ba(H_4L^4)(ClO_4)_2$ with atom labelling. The molecule possesses crystallographically imposed C_2 symmetry. For clarity, only the co-ordinating oxygen atom of each of the perchlorate ligands is shown

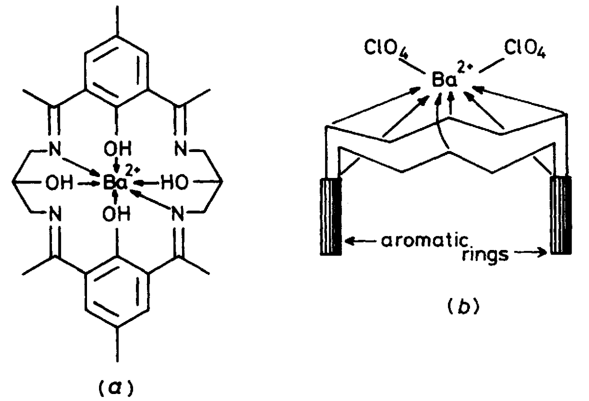

Figure 2. Schematic representations of (*a*) barium–macrocycle bond formation and (*b*) conformation of the complex

Table 1. Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for $Ba(H_4L^4)(ClO_4)_2$. Primed atoms are related to the others by C_2 symmetry (-*x*, *y*, *z*)

Ba–O(1)	2.576(7)	Cl(1)–O(5)	1.369(14)	C(2)–C(3)	1.487(14)	C(8)–C(9)	1.409(12)
Ba–O(2)	2.898(7)	Cl(1)–O(6)	1.329(17)	C(3)–C(4)	1.379(14)	C(8)–C(10)	1.460(13)
Ba–O(3)	2.839(13)	O(1)–C(9)	1.320(11)	C(3)–C(9)	1.418(13)	C(10)–C(11)	1.504(15)
Ba ··· O(4)	3.399(10)	O(2)–C(13)	1.436(12)	C(4)–C(5)	1.384(14)	N(2)–C(10)	1.267(13)
Ba–N(1)	3.014(8)	N(1)–C(14′)	1.456(14)	C(5)–C(6)	1.532(16)	N(2)–C(12)	1.462(14)
Cl(1)–O(3)	1.398(13)	N(1)–C(2)	1.289(13)	C(5)–C(7)	1.390(14)	C(12)–C(13)	1.508(15)
Cl(1)–O(4)	1.430(10)	C(1)–C(2)	1.505(18)	C(7)–C(8)	1.405(13)	C(13)–C(14)	1.490(16)
O(1)–Ba–O(1′)	96.61(21)	O(3)–Ba–N(1′)	159.76(30)	N(1)–C(2)–C(1)	123.8(10)	C(9)–C(8)–C(10)	120.4(8)
O(1)–Ba–O(2)	71.04(20)	N(1)–Ba–N(1′)	114.72(22)	N(1)–C(2)–C(3)	118.5(9)	O(1)–C(9)–C(3)	119.5(8)
O(1)–Ba–O(2′)	119.63(20)	Ba–O(1)–C(9)	126.7(5)	C(1)–C(2)–C(3)	117.7(9)	O(1)–C(9)–C(8)	121.8(8)
O(1)–Ba–O(3)	96.98(30)	Ba–O(2)–C(13)	123.1(6)	C(2)–C(3)–C(4)	118.7(9)	C(3)–C(9)–C(8)	118.7(8)
O(1)–Ba–O(3′)	137.93(30)	Ba–O(3)–Cl(1)	117.6(7)	C(2)–C(3)–C(9)	122.4(9)	C(8)–C(10)–C(11)	120.0(9)
O(1)–Ba–N(1)	62.24(21)	O(3)–Cl(1)–O(4)	107.8(7)	C(9)–C(3)–C(4)	118.8(9)	N(2)–C(10)–C(8)	117.6(9)
O(1)–Ba–N(1′)	75.41(21)	O(3)–Cl(1)–O(5)	106.1(8)	C(3)–C(4)–C(5)	123.6(9)	N(2)–C(10)–C(11)	122.4(9)
O(2)–Ba–O(2′)	165.37(19)	O(3)–Cl(1)–O(6)	108.3(9)	C(4)–C(5)–C(6)	122.7(9)	C(10)–N(2)–C(12)	129.0(9)
O(2)–Ba–O(3)	102.45(29)	O(4)–Cl(1)–O(5)	115.1(7)	C(4)–C(5)–C(7)	117.3(9)	N(2)–C(12)–C(13)	108.6(9)
O(2)–Ba–O(3′)	67.61(29)	O(4)–Cl(1)–O(6)	109.3(9)	C(6)–C(5)–C(7)	120.0(9)	O(2)–C(13)–C(12)	110.9(8)
O(2)–Ba–N(1)	132.51(21)	O(5)–Cl(1)–O(6)	110.0(10)	C(5)–C(7)–C(8)	121.5(9)	O(2)–C(13)–C(14)	108.4(8)
O(2)–Ba–N(1′)	57.42(21)	Ba–N(1)–C(14′)	108.5(6)	C(7)–C(8)–C(9)	119.8(8)	C(12)–C(13)–C(14)	113.9(9)
O(3)–Ba–O(3′)	99.03(37)	Ba–N(1)–C(2)	126.7(8)	C(7)–C(8)–C(10)	119.8(8)	C(13)–C(14)–N(1′)	112.8(9)
O(3)–Ba–N(1)	76.24(30)	C(14′)–N(1)–C(2)	118.7(10)				
	O(1) ··· N(2)	2.497(10)	N(2) ··· H(O1)	1.67	O(1)–H(O1) ··· N(2)	143	

from the perchlorate anion [O(3)]. The imine N is 3.0 Å from the barium and these distances indicate electrostatic interactions. The C–N bond length for the bound imine group [N(1)–C(2)] is 1.29 Å compared with 1.27 Å for the unbound imine; this presumably arises from loss of electron density towards Ba^{2+}. Principal bonds and angles are given in Table 1. The stoicheiometry of the complex is similar to that of $Pb(H_2L^3)(ClO_4)_2{\cdot}2H_2O$ which also retains the fully protonated ligand; it is speculated that the structure of the lead complex would be similar to that described above.

It was previously mentioned that cavity size and cation size play an important role in metal-ion selectivity. In the series of macrocyclic complexes derived from 2,6-diacetyl-4-methylphenol and 1,3-diamino-2-propanol it is noted that binuclear complexes are available for Sr^{2+} (r = 1.13 Å) and Pb^{2+} (r = 1.06 Å) but a mononuclear complex arises with Ba^{2+} (r = 1.29 Å). There appears to be a critical ion radius below which binuclear products are obtained with this ligand H_4L^4, *i.e. r ca.* 1.20 Å.[8]

The binuclear copper(II) complex $Cu_2(H_2L^4)(ClO_4)_2$ (Cu, r = 0.96 Å) is also readily prepared by template procedures. The corresponding complex $Cu_2L^3(ClO_4)_2$ has been reported previously[9] and by analogy it is likely that the phenolic protons are those deprotonated in the complex of H_2L^4. The magnetic moment of $Cu_2(H_2L^4)(ClO_4)_2$ was found to be 1.20 B.M. per Cu atom, as compared with 0.66 B.M. per Cu atom for $Cu_2L^3(ClO_4)_2$. The reduced value is due to antiferromagnetic coupling mediated by the endogenously bridging phenolic groups. It is likely that in $Cu_2(H_2L^4)(ClO_4)_2$ the higher value arises from either severe steric changes caused by the presence of the lateral hydroxy units, or by involvement of these groups with the copper(II), either inter- or intra-molecularly, and so perturbing the mediation by the phenolic units. It has not yet been possible to grow crystals of $Cu_2(H_2L^4)(ClO_4)_2$ suitable for structural analysis.

Experimental

The physical measurements were made as reported in ref. 2. 2,6-Diacetyl-4-methylphenol was prepared by a slight modification of the method of Mandal and Nag.[9]

Complexes of Ligand H_2L^2.—(*i*) $Zn_2L^2(O_2CMe)_2{\cdot}0.5H_2O$. The acyclic ligand L^1[10] (1 mmol) was dissolved in refluxing ethanol (100 cm^3). To this was added dropwise an ethanolic solution of zinc acetate (1 mmol in 50 cm^3). The resulting solution was refluxed for 30 min, then cooled to room temperature and reduced in volume to 50 cm^3. The yellow-brown solid which formed was collected, washed with diethyl ether, and dried *in vacuo*. Yield 40% (Found: C, 52.3; H, 5.4; N, 8.1. $C_{30}H_{36}N_4O_6Zn_2{\cdot}0.5H_2O$ requires C, 52.0; H, 5.3; N, 8.2%).

(*ii*) $Pb_2L^2(SCN)_2{\cdot}2H_2O$. Acyclic ligand L^1 (1 mmol) was dissolved in refluxing ethanol (100 cm^3). To this was added an ethanolic solution of lead thiocyanate (1 mmol in 50 cm^3). The resulting solution was stirred at 50 °C causing the precipitation of a yellow powder. This was collected, washed with ethanol and diethyl ether, and dried *in vacuo*. Yield 35% (Found: C, 33.3; H, 3.2; N, 8.3. $C_{28}H_{30}N_6O_2Pb_2S_2{\cdot}2H_2O$ requires C, 33.7; H, 3.4; N, 8.4%).

Complexes of Ligand H_2L^3.—$Pb(H_2L^3)(ClO_4)_2{\cdot}2H_2O$. Lead perchlorate (1 mmol) and 1,3-diaminopropane (2 mmol) were dissolved in methanol (100 cm^3) and heated to 40 °C. To this solution was added 2,6-diacetyl-4-methylphenol (2 mmol dissolved in 50 cm^3 methanol) in a dropwise fashion. The solution was kept at 40 °C for 2 h and the resulting yellow precipitate collected, washed with cold methanol, and dried *in vacuo*. Yield 42% (Found: C, 36.8; H, 4.3; Cl, 8.3; N, 6.1. $C_{28}H_{36}Cl_2N_4O_{10}Pb{\cdot}2H_2O$ requires C, 37.2; H, 4.5; Cl, 7.9; N, 6.2%).

Complexes of Ligand H_4L^4.—(*i*) $Ba(H_4L^4)(ClO_4)_2$. Barium perchlorate (1 mmol), 1,3-diamino-2-propanol (2 mmol), and 2,6-diacetyl-4-methylphenol (2 mmol) were dissolved in methanol (150 cm^3) and stirred at room temperature for 24 h. Upon standing yellow crystals were deposited; these were collected and the supernatant reduced to 40 cm^3. A yellow powder deposited, having an i.r. spectrum identical to that of the crystals, and was collected, washed with diethyl ether, and dried *in vacuo*. Yield 38% (Found: C, 40.7; H, 4.4; Cl, 9.0; N, 6.8. $C_{28}H_{36}BaCl_2N_4O_{12}$ requires C, 40.6; H, 4.4; Cl, 8.6; N, 6.8%).

(*ii*) $Sr_2(H_2L^4)(ClO_4)_2{\cdot}EtOH$. Strontium perchlorate (1 mmol) and 2,6-diacetyl-4-methylphenol (1 mmol) were dissolved in ethanol (50 cm^3) and stirred at room temperature. A solution of 1,3-diamino-2-propanol (1 mmol) in ethanol (50 cm^3) was added slowly and the resulting solution was stirred at room temperature for 18 h. The yellow precipitate was collected, washed with cold ethanol, and dried *in vacuo*. Yield 17% (Found: C, 39.2; H, 4.4; Cl, 6.8; N, 5.8. $C_{28}H_{34}Cl_2N_4O_{12}Sr_2{\cdot}EtOH$ requires C, 39.5; H, 4.4; Cl, 7.8; N, 6.1%).

(*iii*) $Pb_2(H_2L^4)(SCN)_2{\cdot}4H_2O$. Lead thiocyanate (1 mmol) and 2,6-diacetyl-4-methylphenol (1 mmol) were added to methanol (100 cm^3) and heated to 40 °C. To this was added dropwise a solution of 1,3-diamino-2-propanol (1 mmol) in methanol (50 cm^3). The resulting solution was left stirring at 40 °C for 30 h. Upon cooling the volume was reduced to 40 cm^3 and the deposited yellow powder was collected, washed with diethyl ether, and dried *in vacuo*. Yield 46% (Found: C, 32.4; H, 3.7; N, 7.6. $C_{30}H_{32}N_6O_4Pb_2S_2{\cdot}4H_2O$ requires C, 32.9; H, 3.9; N, 7.7%).

(*iv*) $Cu_2(H_2L^4)(ClO_4)_2$. Copper(II) perchlorate (2 mmol) and 1,3-diamino-2-propanol (2 mmol) were dissolved in methanol (100 cm^3). The blue solution was carefully heated to reflux and 2,6-diacetyl-4-methylphenol (2 mmol) in hot methanol (50 cm^3) was slowly added. The solution became green and reflux was continued for 4 h; after cooling the solution was reduced in

Table 2. Atomic positions with e.s.d.s for $Ba(H_4L^4)(ClO_4)_2$

Atom	*X/a*	*Y/b*	*Z/c*
Ba	0.000 00	0.000 00	0.000 00
Cl(1)	−0.063 80(7)	−0.254 6(4)	−0.091 10(12)
O(1)	−0.015 13(15)	−0.240 6(10)	0.075 71(27)
O(2)	0.048 95(19)	−0.290 7(10)	−0.016 30(28)
O(3)	−0.055 69(35)	−0.078 3(15)	−0.081 4(6)
O(4)	−0.034 30(24)	−0.356 4(13)	−0.069 9(4)
O(5)	−0.070 60(42)	−0.270 2(20)	−0.150 3(5)
O(6)	−0.093 06(29)	−0.294 0(27)	−0.060 3(8)
N(1)	−0.067 59(21)	0.041 9(11)	0.071 8(4)
N(2)	0.043 27(21)	−0.383 1(11)	0.100 5(3)
C(1)	−0.117 72(27)	−0.105 0(20)	0.122 9(8)
C(2)	−0.078 81(24)	−0.060 5(14)	0.113 2(5)
C(3)	−0.051 95(25)	−0.139 6(13)	0.153 8(4)
C(4)	−0.058 06(24)	−0.132 1(14)	0.213 8(5)
C(5)	−0.034 08(22)	−0.193 4(12)	0.255 7(5)
C(6)	−0.041 60(30)	−0.184 6(18)	0.322 1(5)
C(7)	−0.001 75(26)	−0.261 4(16)	0.235 3(3)
C(8)	0.005 55(22)	−0.277 1(12)	0.174 7(4)
C(9)	−0.020 00(22)	−0.219 7(12)	0.133 1(4)
C(10)	0.039 61(25)	−0.351 8(12)	0.155 2(5)
C(11)	0.069 22(27)	−0.383 2(16)	0.199 1(5)
C(12)	0.075 40(26)	−0.437 1(16)	0.068 2(5)
C(13)	0.081 24(27)	−0.311 9(14)	0.017 6(4)
C(14)	0.093 92(30)	−0.135 4(16)	0.036 3(5)

Atoms Cl(1) and O(3)–O(6) constitute the unidentate perchlorate ligand.

volume to 40 cm^3 and allowed slowly to evaporate further. The resulting green powder was collected, washed with diethyl ether, and dried. Yield 22% (Found: C, 40.6; H, 4.3; Cl, 8.8; N, 7.2. $C_{28}H_{34}Cl_2Cu_2N_4O_{12}$ requires C, 41.2; H, 4.2; Cl, 8.7; N, 6.9%).

Crystallography.—Crystal data. $C_{28}H_{36}BaCl_2N_4O_{12}$, M = 828.813, crystallises from methanol as pale yellow triangular plates, dimensions 0.30 × 0.23 × 0.03 mm, orthorhombic, $a = 37.252(28)$, $b = 7.643(4)$, $c = 22.631(22)$ Å, $U = 6\,444(8)$ Å^3, $D_m = 1.78$, $Z = 8$, $D_c = 1.709$ g cm^{-3}, space group *Fdd*2 (C_{2v}^{19}, no. 43); Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 14.64 cm^{-1}, $F(000) = 3\,344$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan technique. The 1 134 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, for absorption, and for 5% crystal decay during data collection. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and inserted in calculated positions ($B = 7.0$ Å^2). Refinement converged at $R = 0.0350$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of barium and chlorine. Table 2 lists atomic positional parameters. Unit weights were used throughout the refinement; scattering factors were taken from ref. 11; computer programs were those of the Sheffield *X*-ray system.

Acknowledgements

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