A Barium Dithiocyanate Complex with an Unusual Macrocycle containing Pendant Arms, the Amine Precursor, and Related Copper(II) Diperchlorate Complexes: Synthesis and Structure *

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The ligand 1-(*p*-nitrobenzylideneaminoethyl)-2-(*p*-nitrophenyl)imidazolidine (L^1) was synthesized by condensation of *p*-nitrobenzaldehyde and diethylenetriamine. Reaction of L^1 with 2-chloromethylpyridine yielded 1-(*p*-nitrobenzylideneaminoethyl)-2-(*p*-nitrophenyl)-3-(2'- pyridylmethyl)imidazolidine (L^2), which by hydrolysis gave 7-(2'-pyridyl)-3,6-diazaheptylamine (L^3). Crystals of L^2 are monoclinic, space group $P2_1/n$, with a = 21.050(5), b = 7.935(6), c = 13.529(6) Å, and β = 94.01(3)°. The structure, determined by *X*-ray crystallography, was refined to a final *R* of 0.054 based on 2 646 observed reflections. The molecule shows the expected imidazolidine ring with normal bond lengths and angles. The behaviour in solution and the stereospecific assignments for the methylene protons of L^2 were studied by ^{1}H n.m.r. spectroscopy. The reaction of the polyamine L^3 with $Cu(ClO_4)_2$ produced $[CuL^3(ClO_4)_2]$. Crystals are orthorhombic, space group $P2_12_12_1$, with a = 14.295(6), b = 13.143(6), and c = 9.068(6) Å. The structure was determined by *X*-ray crystallography and refined to a final *R* of 0.079 based on 1 068 observed reflections. The quadridentate ligand is equatorially bonded to Cu^{2+} through the N atoms. Two axial Cu • • • O contacts with the ClO_4^- anions complete the tetragonally elongated octahedral environment around the copper ion. Reaction of L^3 with 4-chloro-2,6-diformylphenol in the presence of $Ba(SCN)_2$ gave a macrocyclic complex $[BaL^4(SCN)_2]$. Crystals are orthorhombic, space group *Pbcn*, with a = 15.759(6), b = 14.124(6), and c = 19.393(5) Å. The structure was determined by *X*-ray crystallography and refined to a final *R* of 0.075 based on 1 270 observed reflections. The neutral macrocycle is co-ordinated to the Ba^{2+} ion through four N and two O atoms. Two SCN^- ions complete the co-ordination polyhedron around the metal. The Ba^{2+} ion lies on a crystallographic two-fold axis so that the molecular symmetry is C_2.

The preparation of macrocycles and their interaction with metal ions is a fascinating area of growing interest in both basic and applied chemistry. Bioinorganic chemistry, catalysis, separation and incapsulation processes, formation of compounds with unusual properties, metal–metal interactions, transport and activation of small molecules have received considerable impetus from the employment of such ligands.[1–8] Moreover, new ligands have been designed and synthesized on the basis of the chemical properties required by the various fields of application. For example, the shape of the macrocycle is of crucial importance in order to improve selectivity towards a particular ion or a particular process, thereby reducing the possibility of undesired reactions.

Planar macrocycles have been widely studied and applied, but often do not offer good discrimination for different metal ions; three-dimensional ligands, instead, may offer good selectivity.[9,10] Macrocyclic planar complexes have been found to be more stable than the corresponding complexes with the three-dimensional ligands. Moreover the kinetics of metallation using these ligands is many orders of magnitude faster.[11–13] Thus, in particular separation processes, the kinetics of metallation is very important, favouring the use of three-dimensional ligands. Moreover such ligands can offer a spatial arrangement about a metal ion which may favour selectivity.

From the synthetic viewpoint, preparation of three-dimensional ligands is often difficult and the yields are low, whereas planar macrocycles are easier to prepare and obtainable in higher yield.

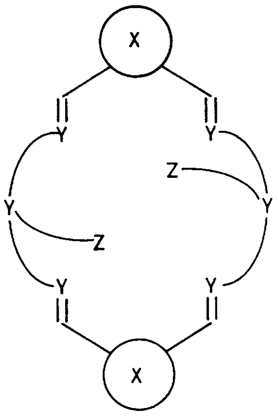

Figure 1. Schematic representation of open cryptands (X = a pyridine, furan, thiophene, pyrrole, or phenol unit; Y = N or NH of an aliphatic chain; Z = pyridine, carboxylic group, *etc.*)

A good balance of all these factors is represented by open cryptands of the type in Figure 1, where the two pendant arms Z can co-ordinate to a metal ion in its apical positions. The

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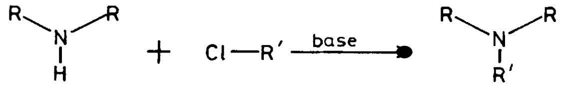
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.
Non-S.I. unit employed: eV ≈ 1.60 × 10^{-19} J.

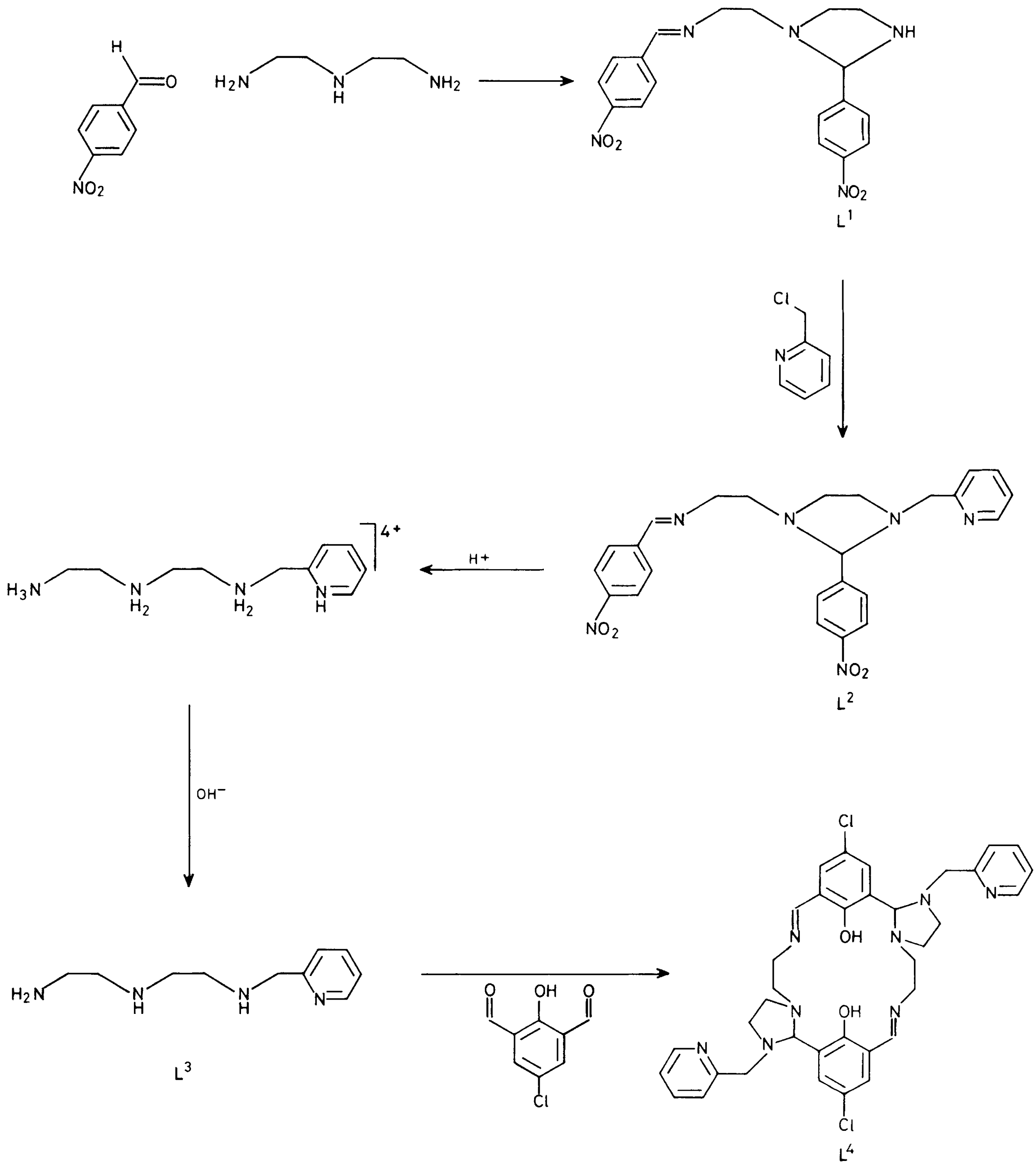
mobility of these arms may allow a highly dynamic complexation and decomplexation of several ions, as required, for example, for efficient transport.[9,10]

A convenient way to prepare diamines with pendant arms is represented by Scheme 1.[14] The R groups are protecting groups for the primary amines; by deprotection, compounds with NH_2 groups can be obtained. The amines thus obtained can be treated with carbonyl compounds to produce Schiff bases. A template procedure with barium salts is often employed in these reactions; subsequent transmetallation reactions can yield products not obtainable otherwise.



Scheme 1. Preparation of amines with pendant arms

The polyamine 7-(2'-pyridyl)-3,6-diazaheptylamine (L^3) was obtained according to Scheme 2 and its reactivity toward metal ions was studied in the present work. Physico-chemical



Scheme 2. Preparation of the polyamine L^3

properties and crystal structures were determined for 1-(*p*-nitrobenzylideneaminoethyl)-2-(*p*-nitrophenyl)-3-(2′-pyridylmethyl)imidazolidine (L^2), for the copper complex $[CuL^3(ClO_4)_2]$, and for the barium thiocyanate complex $[BaL^4(SCN)_2]$, where L^4 is the macrocycle obtained by template condensation of L^3 with 4-chloro-2,6-diformylphenol in the presence of barium thiocyanate.

Experimental

4-Chloro-2,6-diformylphenol was prepared according to literature methods.[15] 1,5-Diamino-3-azapentane (K&K) was distilled prior to use; 2-chloromethylpyridine (Aldrich) and *p*-nitrobenzaldehyde (C.Erba) were used without further purification.

Preparations.—L^1. A methanolic solution of *p*-nitrobenzaldehyde (0.2 mol, 30.3 g) was added to a methanolic solution (200 cm^3) of 1,5-diamino-3-azapentane (0.1 mol, 10.3 g). The resulting yellow solution was refluxed for 8 h and then allowed to cool overnight. The pale yellow solid obtained was collected by filtration, washed three times with diethyl ether, and dried *in vacuo*. Yield 95%, *m/z* 369 (P^+), m.p. 102—104 °C (Found: C, 58.95; H, 5.20; N, 18.90. Calc. for $C_{18}H_{19}N_5O_4$ C, 58.55; H, 5.20; N, 18.95%).

L^2. An ethanolic solution (100 cm^3) of 2-chloromethylpyridine (0.02 mol, 3.28 g) containing Na_2CO_3 (0.02 mol, 2.12 g) was refluxed under nitrogen for 2 h until the colour had changed from white to pink. To the hot solution, an ethanolic suspension (100 cm^3) of L^1 (0.02 mol, 7.38 g) and Na_2CO_3 (0.02 mol, 2.12 g) was added maintaining a nitrogen flux. The yellow suspension was refluxed for 24 h; the white solid obtained was filtered off and treated with hot CH_2Cl_2 to dissolve the organic fraction which was collected and evaporated to dryness. The residue crystallized from absolute ethanol gave well formed yellow crystals suitable for *X*-ray analysis. Yield 65%, *m/z* 460 (P^+), m.p. 147—148 °C (Found: C, 62.65; H, 5.30; N, 18.20. Calc. for $C_{24}H_{24}N_6O_4$: C, 62.60; H, 5.25; N, 18.25%).

In the i.r. spectrum of L^1, ν(NH) lies at 3 219 cm^{-1} and ν(C=N) at 1 604 and 1 649 cm^{-1}, while for L^2 ν(C=N) is at 1 651 and 1 609 cm^{-1} and absorptions due to the NH group are absent.

L^3. Yellow crystals of L^2 were dissolved in hot acidic (HCl, pH ≈ 2) water (200 cm^3). On cooling, white crystals of *p*-nitrobenzaldehyde formed; the supernatant was extracted with $CHCl_3$ (3 × 100 cm^3) to remove the remaining *p*-nitrobenzaldehyde. The pale yellow aqueous solution was then made basic with NaOH (pH ≈ 12) and evaporated to dryness. The residue was treated with CH_2Cl_2. The undissolved white inorganic residue was filtered off and the solution was dried over Na_2SO_4 overnight, then evaporated to dryness to obtain a red hygroscopic oil. Yield 40%, *m/z* 194 (P^+) (Found: C, 61.55; H, 9.85; N, 28.10. Calc. for $C_{10}H_{18}N_4$: C, 61.85; H, 9.25; N, 28.85%).

$[CuL^3(ClO_4)_2]$. A methanolic solution of L^3 (1 mmol, 194 mg) was added to a methanol solution (50 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 370 mg). The violet solution deposited a blue solid which was recrystallized from absolute ethanol to give well formed blue crystals, suitable for *X*-ray analysis. The i.r. spectrum shows the stretchings of the NH_2 and NH groups at 3 465, 3 369, 3 268, 3 192, and 3 120 cm^{-1}, the ν(C–H) of the aromatic rings, the ν(CH_3) and the ν(CH_2) of the aliphatic chains (3 053, 3 028, 2 961, 2 924, 2 879, and 2 833 cm^{-1}) (Found: C, 26.45; H, 4.10; N, 12.25. Calc. for $C_{10}H_{18}CuN_4 \cdot 2ClO_4$: C, 26.30; H, 3.95; N, 12.25%).

$[Cu_2L^9(ClO_4)_4]$. A red methanol solution of L^3 (1 mmol, 194 mg) was added to a methanol solution (50 cm^3) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 370 mg). The suspension was heated to dissolve the blue solid formed and then 4-chloro-2,6-diformylphenol (1 mmol, 184 mg) was added. The resulting suspension was refluxed for 6 h. The complex $[CuL^3(ClO_4)_2]$ was removed by filtration and the green solution was evaporated to dryness. The residue was treated with methanol. The green solid that separated was washed with methanol and dried *in vacuo* (Found: C, 31.30; H, 3.85; N, 10.40. Calc. for $C_{28}H_{37}ClCu_2N_8O \cdot 4ClO_4$: C, 31.65; H, 3.50; N, 10.55%).

$[BaL^4(SCN)_2]$. A methanolic solution (10 cm^3) of $Ba(SCN)_2$ (1 mmol, 289 mg) was added to a methanol solution (30 cm^3) of L^3 (1 mmol, 194 mg). To the resulting pale orange solution, 4-chloro-2,6-diformylphenol (1 mmol, 184 mg) in methanol was added and the orange mixture was refluxed for 8 h. The solvent was partially removed and the solution treated with diethyl ether. The yellow precipitate obtained was filtered off, washed with ethanol, and dried *in vacuo*. The complex can be approximately formulated as $[Ba_2(L^4 - 2H)(SCN)_2]$ (see below). Yield 40% (Found: C, 41.80; H, 3.90; N, 12.10. Calc. for $C_{38}H_{36}BaCl_2N_{10}O_2S_2 \cdot H_2O$: C, 41.80; H, 3.50; N, 12.80%). From the ethanol–ether mother-liquor, small crystals of $[BaL^4(SCN)_2]$ were obtained, *m/z* 821 (P^+) (Found: C, 48.55; H, 4.25; N, 15.10. Calc. for $C_{38}H_{38}BaCl_2N_{10}O_2S_2$: C, 48.60; H, 4.10; N, 14.90%).

Physico-chemical Measurements.—The i.r. spectra were obtained as KBr pellets and/or Nujol mulls using a Perkin-Elmer 580B model spectrophotometer.

Metal ratios were determined by integral counting of backscattered *X*-ray fluorescence radiation from a Philips SEM 505 model scanning electron microscope equipped with an EDAX model data station. Samples suitable for scanning electron microscope analysis were prepared by suspending the microcrystalline powders in light petroleum (b.p. 30—40 °C). Some drops of the resulting suspension were placed on a graphite plate.[16]

Proton n.m.r. spectra were recorded at 400.132 MHz on a Bruker AM 400 spectrometer equipped with an Aspect 3000 computer. The solvent was $CDCl_3$ and the concentration was 0.5 mg sample per cm^3 solvent. Nuclear Overhauser effect (n.O.e.) experiments were made on degassed samples in $CDCl_3$ and were carried out using a sufficient number of transients (256) to ensure a good signal-to-noise ratio. The data were acquired using 16 K data points and a sweep width of 5000 Hz, irradiating each multiplet for 5 s. Difference spectra were obtained by subtracting a reference spectrum (with the decoupler off-resonance) collected under the same conditions.

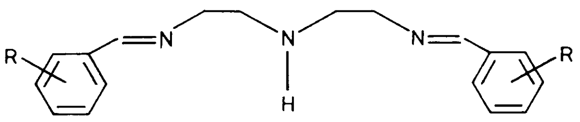
X-Ray Crystallography.—Well formed crystals of the compounds were mounted on glass fibres. Unit-cell parameters were determined from accurate settings of 25 medium-angle reflections on a Philips four-circle diffractometer using graphite-monochromatized Mo-K_α radiation. Crystal data are given in Table 1 together with data collection conditions. Two standard reflections monitored every 100 reflections indicated no significant systematic fluctuation in intensity. Because of the relatively high absorption coefficients of the barium and copper complexes, absorption corrections were applied to the intensities recorded for these compounds.[17] The structure of the ligand was solved by direct methods using the SHELXS 86 program package.[18] The structures of the complexes were solved by the heavy-atom method. Non-hydrogen atoms were refined anisotropically for the organic compound but anisotropy was introduced only for selected atoms of the two complexes, because of the less favourable ratio between the number of observed reflections and the number of parameters to be refined. No weighting scheme was used during refinements.

For the organic compound, hydrogen atoms were located by inspections of the electron-density map; for the two complexes, they were introduced in calculated positions with fixed isotropic thermal parameters of 0.06 Å^2. At convergence the maximum shifts of the refined parameters were 0.02σ for the organic

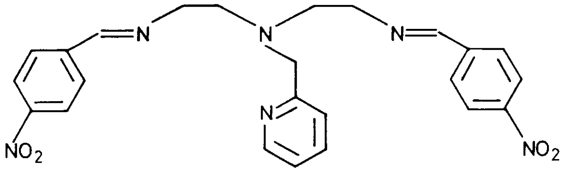
Table 1. Crystal data* for L^2, $[BaL^4(SCN)_2]$, and $[CuL^3(ClO_4)_2]$

Formula	$C_{24}H_{24}N_6O_4$	$C_{38}H_{38}BaCl_2N_{10}O_2S_2$	$C_{10}H_{18}Cl_2CuN_4O_8$
M	461	882	456.5
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$Pbcn$	$P2_12_12_1$
a/Å	21.050(5)	15.759(6)	14.295(6)
b/Å	7.935(6)	14.124(6)	13.143(6)
c/Å	13.529(6)	19.393(5)	9.068(6)
β/°	94.01(3)		
U/Å^3	2 254	4 317	1 703
F(000)	972	1 896	932
D_c/g cm^{-3}	1.36	1.36	1.78
μ/(Mo-K_α)/cm^{-1}	1.0	12.0	17.0
Max. crystal size (mm)	0.3	0.2	0.3
Reflections recorded	4 409	2 597	1 444
[$I > 3\sigma(I)$]	2 646	1 270	1 068
Correction applied	Lorentz polarization	Lorentz polarization absorption[17]	Lorentz polarization absorption[17]
Parameters varied	379	165	140
R (observed reflections)	0.0537	0.075	0.079

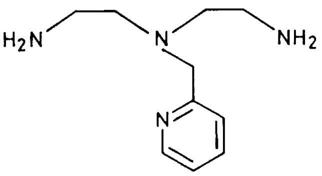
* Details in common: $Z = 4$; Mo-K_α radiation; θ scan speed 2° min^{-1}; 2θ range 2–50°.



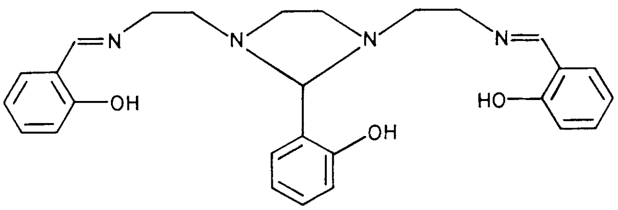
L^5



L^6



L^7



L^8

compound and 0.04 and 0.7σ for the barium and the copper complexes, respectively. Scattering factors for neutral atoms were taken from ref. 19. A correction was applied for the anomalous dispersion of Ba and Cu. Calculations were performed with the programs of ref. 18. Final atomic co-ordinates for the compounds are reported in Table 2, bond lengths and angles in Tables 3—5.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

It is known that the condensation of diethylenetriamine with substituted benzaldehydes leads to the formation of the Schiff bases L^5.[20–22] These are often oils, which can be purified and handled with difficulty; some substituents (*i.e.* NO_2) prevent the formation of oils and yield solid products. Accordingly, we treated *p*-nitrobenzaldehyde and diethylenetriamine in methanol in a 2:1 molar ratio, with the aim of obtaining the above Schiff base ($R = NO_2$), which represents the starting material for the subsequent formation of L^6 by reaction with 2-chloromethylpyridine. However, as shown in Scheme 2, the condensation produces a different Schiff base, which, by reaction with 2-chloromethylpyridine, gives L^2, the hydrolysis of which produces L^3.

The first product of this reaction sequence is L^1, instead of the bis-condensed Schiff base; thus the overall reaction scheme seems to be governed by the facile formation of the five-membered ring in L^1. The NH group at the end of the molecule then yields L^2 by reaction with 2-chloromethylpyridine. Further hydrolysis of L^2, followed by extraction (after raising the pH to about 12), produces L^3 instead of L^7.

The formation of a five-membered ring in a Schiff-base condensation is not unknown. It was observed, for example, in the condensation of salicylaldehyde with diethylenetetramine $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; the structure of the product obtained (L^8) was confirmed by *X*-ray analysis.[23–26]

A comparison of the i.r. spectra of L^1 and L^2 shows for L^2 the presence of a multiplicity of bands in the ν(C–H) (aromatic) range (3 100—2 900 cm^{-1}) due to the presence of a pyridine ring, together with a band at 1 589 cm^{-1} [ν(C=N) (pyridine aromatic)]. In both spectra, strong absorptions due to the NO_2

Table 2. Atomic co-ordinates

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
(*a*) L^2							
O(1)	0.701 64(17)	−0.431 94(54)	1.334 13(25)	C(8)	0.566 99(22)	−0.751 13(51)	0.748 60(32)
O(2)	0.606 98(16)	−0.332 90(51)	1.314 68(26)	C(9)	0.546 59(18)	−0.615 94(50)	0.675 59(30)
O(3)	0.408 93(14)	0.031 51(40)	0.955 30(23)	C(10)	0.570 23(16)	−0.323 33(43)	0.631 26(26)
O(4)	0.342 30(13)	0.050 27(41)	0.828 41(23)	C(11)	0.676 04(19)	−0.353 34(50)	0.592 54(32)
N(1)	0.651 19(18)	−0.415 48(49)	1.284 93(28)	C(12)	0.649 45(20)	−0.523 98(51)	0.620 54(35)
N(2)	0.570 60(16)	−0.685 33(39)	0.847 77(24)	C(13)	0.622 80(17)	−0.083 57(49)	0.558 82(29)
N(3)	0.593 83(13)	−0.480 67(34)	0.675 77(22)	C(14)	0.681 85(16)	0.025 53(44)	0.561 09(26)
N(4)	0.629 91(13)	−0.228 04(35)	0.625 47(20)	C(15)	0.724 31(18)	0.036 46(48)	0.642 16(29)
N(5)	0.393 05(15)	0.009 41(39)	0.868 36(26)	C(16)	0.776 92(19)	0.142 04(52)	0.638 42(31)
N(6)	0.688 28(15)	0.112 17(40)	0.477 75(22)	C(17)	0.783 66(19)	0.232 02(50)	0.553 41(33)
C(1)	0.643 07(17)	−0.488 20(50)	1.186 67(28)	C(18)	0.739 46(20)	0.214 98(52)	0.476 63(32)
C(2)	0.591 27(19)	−0.446 60(54)	1.125 76(31)	C(19)	0.438 79(15)	−0.080 09(42)	0.807 17(26)
C(3)	0.585 06(18)	−0.513 85(53)	1.033 42(32)	C(20)	0.495 64(17)	−0.130 61(49)	0.852 03(27)
C(4)	0.629 51(17)	−0.631 11(47)	1.001 33(28)	C(21)	0.538 63(16)	−0.211 77(48)	0.793 57(27)
C(5)	0.681 09(19)	−0.669 43(54)	1.065 44(33)	C(22)	0.523 83(15)	−0.234 71(41)	0.694 87(24)
C(6)	0.689 21(19)	−0.601 44(57)	1.157 57(33)	C(23)	0.465 63(17)	−0.182 96(50)	0.652 65(28)
C(7)	0.620 85(20)	−0.701 51(49)	0.901 49(31)	C(24)	0.421 89(17)	−0.101 84(50)	0.709 78(29)
(*b*) [BaL^4(SCN)$_2$]							
Ba	1.0000	0.187 6(1)	0.2500	C(6)	1.001 5(6)	0.555 1(9)	0.418 6(7)
S(1)	0.729 5(5)	0.203 7(5)	0.422 2(4)	C(7)	0.879 0(14)	0.486 8(17)	0.365 7(13)
O(1)	0.980 0(7)	0.331 6(8)	0.329 9(8)	C(8)	0.753 3(14)	0.429 0(16)	0.302 8(12)
Cl(1)	1.130 5(5)	0.644 8(4)	0.485 7(4)	C(9)	0.759 1(13)	0.423 3(16)	0.227 0(11)
N(1)	0.840 0(12)	0.424 4(13)	0.327 3(10)	C(10)	1.166 4(13)	0.323 8(15)	0.365 4(13)
N(2)	1.198 9(11)	0.332 1(11)	0.296 3(11)	C(11)	1.211 1(14)	0.175 9(16)	0.331 9(13)
N(3)	1.135 9(11)	0.224 6(11)	0.362 1(10)	C(12)	1.257 6(15)	0.248 8(15)	0.288 0(12)
N(4)	1.045 5(13)	0.054 4(12)	0.368 8(11)	C(13)	1.109 5(14)	0.184 2(16)	0.428 4(12)
N(5)	0.855 6(17)	0.146 4(18)	0.335 9(15)	C(14)	1.090 1(16)	0.082 0(17)	0.422 9(15)
C(1)	0.966 3(6)	0.479 6(9)	0.382 1(7)	C(15)	1.115 8(17)	0.017 7(19)	0.473 0(14)
C(2)	1.015 9(6)	0.400 8(9)	0.366 0(7)	C(16)	1.096 1(18)	−0.076 9(19)	0.466 8(16)
C(3)	1.100 7(6)	0.397 5(9)	0.386 4(7)	C(17)	1.048 7(17)	−0.106 6(19)	0.413 8(15)
C(4)	1.135 9(6)	0.473 0(9)	0.423 0(7)	C(18)	1.022 8(17)	−0.038 9(19)	0.363 0(15)
C(5)	1.086 3(6)	0.551 8(9)	0.439 1(7)	C(19)	0.802 2(18)	0.168 4(19)	0.372 7(20)
(*c*) [CuL^3(ClO$_4$)$_2$]							
Cu	0.157 2(1)	0.190 5(1)	0.195 3(3)	C(2)	−0.002 9(15)	0.060 9(18)	−0.153 1(28)
Cl(1)	0.174 2(3)	−0.084 6(3)	0.204 9(7)	C(3)	−0.087 0(16)	0.045 3(18)	−0.083 6(30)
O(1)	0.163 1(10)	−0.006 6(9)	0.311 8(20)	C(4)	−0.095 6(15)	0.072 5(16)	0.055 6(28)
O(2)	0.249 1(12)	−0.057 9(13)	0.112 0(22)	C(5)	−0.022 7(12)	0.122 9(14)	0.126 9(25)
O(3)	0.090 0(12)	−0.097 7(13)	0.127 7(21)	C(6)	−0.026 3(13)	0.152 6(14)	0.282 1(27)
O(4)	0.195 5(11)	−0.177 8(12)	0.277 8(21)	N(2)	0.046 7(11)	0.226 8(11)	0.315 2(24)
Cl(2)	0.125 9(3)	0.413 8(3)	−0.009 7(7)	C(7)	0.078 6(15)	0.243 5(19)	0.472 9(31)
O(5)	0.165 0(13)	0.511 2(12)	−0.037 2(21)	C(8)	0.178 1(13)	0.289 0(14)	0.470 1(27)
O(6)	0.171 3(14)	0.371 1(15)	0.109 3(25)	N(3)	0.231 9(10)	0.222 9(11)	0.377 4(21)
O(7)	0.150 1(20)	0.349 7(20)	−0.122 3(32)	C(9)	0.321 5(13)	0.255 4(15)	0.327 0(28)
O(8)	0.032 0(15)	0.415 7(16)	0.013 0(28)	C(10)	0.357 5(13)	0.184 5(15)	0.209 7(27)
N(1)	0.059 3(10)	0.136 9(12)	0.066 6(20)	N(4)	0.282 1(11)	0.170 0(11)	0.100 4(23)
C(1)	0.067 1(15)	0.109 8(21)	−0.074 4(39)				

groups are readily detectable; for L^1 the asymmetric stretching of the NO$_2$ group lies at 1 516 cm^{-1}, the symmetric stretching at 1 316 cm^{-1}; for L^2 the corresponding bands can be assigned at 1 541, 1 518, and 1 349 cm^{-1} respectively.

The crystal structure of L^2 was determined by *X*-ray analysis. The molecular conformation of this compound, a perspective view of which is shown in Figure 2, is self-explanatory and its structural details are generally as expected. The mean C–C bond length is 1.38 Å in the phenylene rings [C(1) to C(6) and C(19) to C(24)] and 1.37 Å in the pyridine ring, where the N–C bond distances are 1.34 and 1.35 Å (N–C 1.36 Å in free pyridine). The diaza ring has a quasi-planar envelope structure which is characteristic for non-aromatic penta-atomic rings, with C(10) displaced by 0.64° from the plane of the other four atoms. The mean N(*sp*^{3})–C(*sp*^{3}) bond length is 1.46 Å in this ring (C–N 1.47 Å in NMe$_3$). The C(7) to N(2) link of the chain is essentially a double bond of length 1.25 Å, while the adjacent C(8)–N(2) bond is of the same length (1.44 Å) as that of the single C–N bond of MeNC.

Information on the behaviour of L^2 in solution can be inferred from the ^{1}H n.m.r. spectrum (Figure 3) which shows a complexity in the methylene region consistent with non-equivalence of the CH$_2$ groups. The assignments for the aromatic protons are based on those in the literature[27] while the aliphatic pattern has been assigned by decoupling (Table 6) and n.O.e. experiments (Table 7).

Decoupling data show that the multiplets at 3.47 and 3.31 are coupled to each other and to the signal at 2.73. In the same way the multiplets at 3.69 and 3.57 are coupled to each other and to the multiplets at 2.81 and 2.68. The doublet at 3.76 is coupled only to the doublet at 3.56.

The complexity of the signals arising from the prochirality

Table 3. Bond lengths (Å) [estimated standard deviations (e.s.d.s) <0.01 Å] and selected bond angles (°) (e.s.d.s <0.4°) for L^2

N(1)–O(1)	1.22	N(5)–O(3)	1.21
N(1)–O(2)	1.23	N(5)–O(4)	1.21
N(1)–C(1)	1.45	N(5)–C(19)	1.49
C(1)–C(2)	1.36	C(19)–C(20)	1.36
C(2)–C(3)	1.36	C(20)–C(21)	1.40
C(3)–C(4)	1.41	C(21)–C(22)	1.36
C(4)–C(5)	1.38	C(22)–C(23)	1.38
C(5)–C(6)	1.36	C(23)–C(24)	1.40
C(6)–C(1)	1.40	C(24)–C(19)	1.35
C(4)–C(7)	1.46	C(22)–C(10)	1.52
C(7)–N(2)	1.25	N(4)–C(13)	1.46
N(2)–C(8)	1.44	C(13)–C(17)	1.51
C(8)–C(9)	1.50	C(14)–C(15)	1.37
C(9)–N(3)	1.46	C(15)–C(16)	1.39
N(3)–C(10)	1.46	C(16)–C(17)	1.37
C(10)–N(4)	1.47	C(17)–C(18)	1.35
N(4)–C(11)	1.48	C(18)–N(6)	1.35
C(11)–N(12)	1.52	N(6)–C(14)	1.34
C(12)–N(3)	1.47		
O(1)–N(1)–O(2)	121.9	C(10)–N(4)–C(11)	104.5
O(3)–N(5)–O(4)	124.8	N(4)–C(11)–C(12)	105.2
C(4)–C(7)–N(2)	123.0	C(11)–C(12)–N(3)	103.7
C(7)–N(2)–C(8)	119.6	C(10)–N(4)–C(13)	112.6
N(2)–C(8)–C(9)	110.4	C(11)–N(4)–C(13)	112.5
C(8)–C(9)–N(3)	111.1	N(4)–C(13)–C(14)	112.8
C(9)–N(3)–C(10)	114.6	C(13)–C(14)–N(6)	114.1
C(9)–N(3)–C(12)	113.1	C(13)–C(14)–C(15)	122.8
C(10)–N(3)–C(12)	104.5	C(14)–N(6)–C(18)	116.6
N(3)–C(10)–C(22)	112.1	N(6)–C(14)–C(15)	123.0
N(4)–C(10)–C(22)	112.2	N(6)–C(18)–C(17)	123.9
N(3)–C(10)–N(4)	101.2		

Table 4. Selected bond lengths (Å) and angles (°) for $[BaL^4(SCN)_2]$ with e.s.d.s in parentheses referring to the last significant digit

Ba–O(1)	2.58(1)	N(2)–C(10)	1.44(3)
Ba–N(3)	3.10(2)	N(2)–C(12)	1.51(3)
Ba–N(4)	3.06(2)	N(2)–C(9^I)	1.52(3)
Ba–N(5)	2.88(3)	C(10)–C(3)	1.52(2)
N(4)–C(14)	1.32(3)	C(1)–C(7)	1.42(2)
N(4)–C(18)	1.37(3)	C(7)–N(1)	1.31(3)
C(14)–C(15)	1.39(3)	N(1)–C(8)	1.45(3)
C(14)–C(13)	1.48(3)	C(8)–C(9)	1.47(3)
C(13)–N(3)	1.47(3)	N(5)–C(19)	1.15(3)
N(3)–C(11)	1.49(3)	C(19)–S	1.58(3)
N(3)–C(10)	1.48(3)	Cl–C(5)	1.74(1)
C(11)–C(12)	1.52(3)	C(2)–O(1)	1.33(2)
O(1)–BaO(1^I)	75.8(7)	C(14)–C(13)–N(3)	112(2)
O(1)–Ba–N(3)	61.9(4)	C(13)–N(3)–C(11)	115(2)
O(1)–Ba–N(4)	93.5(5)	C(13)–N(3)–C(11)	113(2)
O(1)–Ba–N(5)	73.5(6)	C(10)–N(3)–C(11)	101(2)
N(3)–Ba–N(4)	54.0(5)	N(1)–C(8)–C(9)	106(2)
N(3)–Ba–N(5)	100.0(7)	N(3)–C(11)–C(12)	107(2)
N(4)–Ba–N(5)	68.0(7)	C(11)–C(12)–N(2)	100(2)
Ba–O(1)–C(2)	148(1)	C(12)–N(2)–C(10)	105(2)
Ba–N(3)–C(10)	114(1)	N(3)–C(10)–N(2)	99(2)
Ba–N(3)–C(11)	101(1)	C(10)–N(2)–C(9^I)	119(2)
Ba–N(3)–C(13)	111(1)	C(12)–N(2)–C(9^I)	111(2)
Ba–N(4)–C(14)	123(2)	N(2)–C(10)–C(3)	116(2)
Ba–N(4)–C(18)	118(2)	N(3)–C(10)–C(3)	116(2)
Ba–N(5)–C(19)	152(2)	C(1)–C(7)–N(1)	122(2)
C(14)–N(4)–C(18)	119(2)	C(7)–N(1)–C(8)	127(2)
N(5)–C(19)–S	177(3)		

The carbon atoms of the C(1)—C(6) ring were refined as rigid bodies (C–C 1.395 , C–H 1.08 Å). $^I = 2 - x, y, \frac{1}{2} - z$.

Table 5. Selected bond lengths (Å) and angles (°) for $[CuL^3(ClO_4)_2]$ with e.s.d.s in parentheses referring to the last significant digit

Cu–N(1)	1.95(2)	C(10)–N(4)	1.48(3)
Cu–N(2)	1.98(2)	Cl(1)–O(1)	1.42(2)
Cu–N(3)	2.01(2)	Cl(1)–O(2)	1.41(2)
Cu–N(4)	2.00(2)	Cl(1)–O(3)	1.40(2)
Cu • • • O(1)	2.80(1)	Cl(1)–O(4)	1.42(2)
Cu • • • O(6)	2.51(2)	Cl(2)–O(5)	1.42(2)
C(5)–N(1)	1.31(2)	Cl(2)–O(6)	1.38(2)
C(5)–C(6)	1.46(3)	Cl(2)–O(7)	1.37(2)
C(6)–N(2)	1.46(2)	Cl(2)–O(8)	1.36(2)
N(2)–C(7)	1.52(3)	N(1)–C(1)	1.33(4)
C(7)–C(8)	1.54(3)	C(1)–C(2)	1.39(4)
C(8)–N(3)	1.43(2)	C(2)–C(3)	1.37(3)
N(3)–C(9)	1.42(2)	C(3)–C(4)	1.32(3)
C(9)–C(10)	1.50(3)	C(4)–C(5)	1.39(3)
N(1)–Cu–N(3)	161.2(7)	Cu–N(3)–C(8)	109(1)
N(2)–Cu–N(4)	169.3(7)	Cu–N(3)–C(9)	106(1)
N(1)–Cu–N(4)	109.5(8)	Cu–N(4)–C(10)	110(1)
N(1)–Cu–N(2)	81.0(7)	N(2)–C(6)–C(5)	111(2)
N(2)–Cu–N(3)	85.5(8)	N(2)–C(7)–C(8)	108(2)
N(3)–Cu–N(4)	84.7(8)	C(6)–N(2)–C(7)	120(2)
O(1) • • • Cu • • • O(6)	172.5(6)	C(7)–C(8)–N(3)	106(2)
Cu–N(1)–C(1)	127(1)	C(8)–N(3)–C(9)	119(1)
Cu–N(1)–C(5)	116(1)	N(3)–C(9)–C(10)	110(2)
Cu–N(2)–C(6)	107(1)	C(9)–C(10)–N(4)	108(1)
Cu–N(2)–C(7)	108(1)		

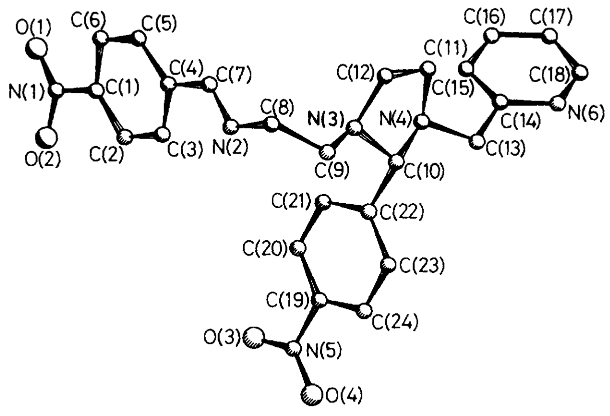


Figure 2. Perspective view of the crystal structure of L^2

shown by some methylene protons[28] necessitated a careful study. In particular, n.O.e. measurements were carried out completely to assign the signals and suggest a possible structure in solution. The speaks at 3.69 due to H^{15a} and at 3.57 due to H^{15b} show strong interactions with H^9. The same interaction of H^{15a} and H^{15b} is observed when H^9 is irradiated. An interaction involving H^{14a} and H^{14b} is also observed when H^{15a} and H^{15b} are irradiated; more precisely, H^{15a} causes an effect on H^{14b} while H^{15b} causes a similar effect on H^{14a} and no effect is detected for H^{15b} and H^{14b}. This suggests that H^{15b} and H^{14b} are rather far from each other. By irradiation of the two H^{13} protons, the same strong interaction is detected for H^{12a} and H^{12b}; in agreement with this, irradiation of H^{12a} and H^{12b} results in interactions with H^5 and H^{13}.

Some additional structural information can be inferred from n.O.e. data for the aromatic protons. Irradiation of the H^5 and H^3 protons produces the same interaction with H^1 and H^{10}. A strong interaction with H^5 is detected when H^1 is irradiated and H^3 and H^9 interact in the same way when H^8 is irradiated. These data suggest that the three aromatic rings are close together in solution, while they are apart in the solid.

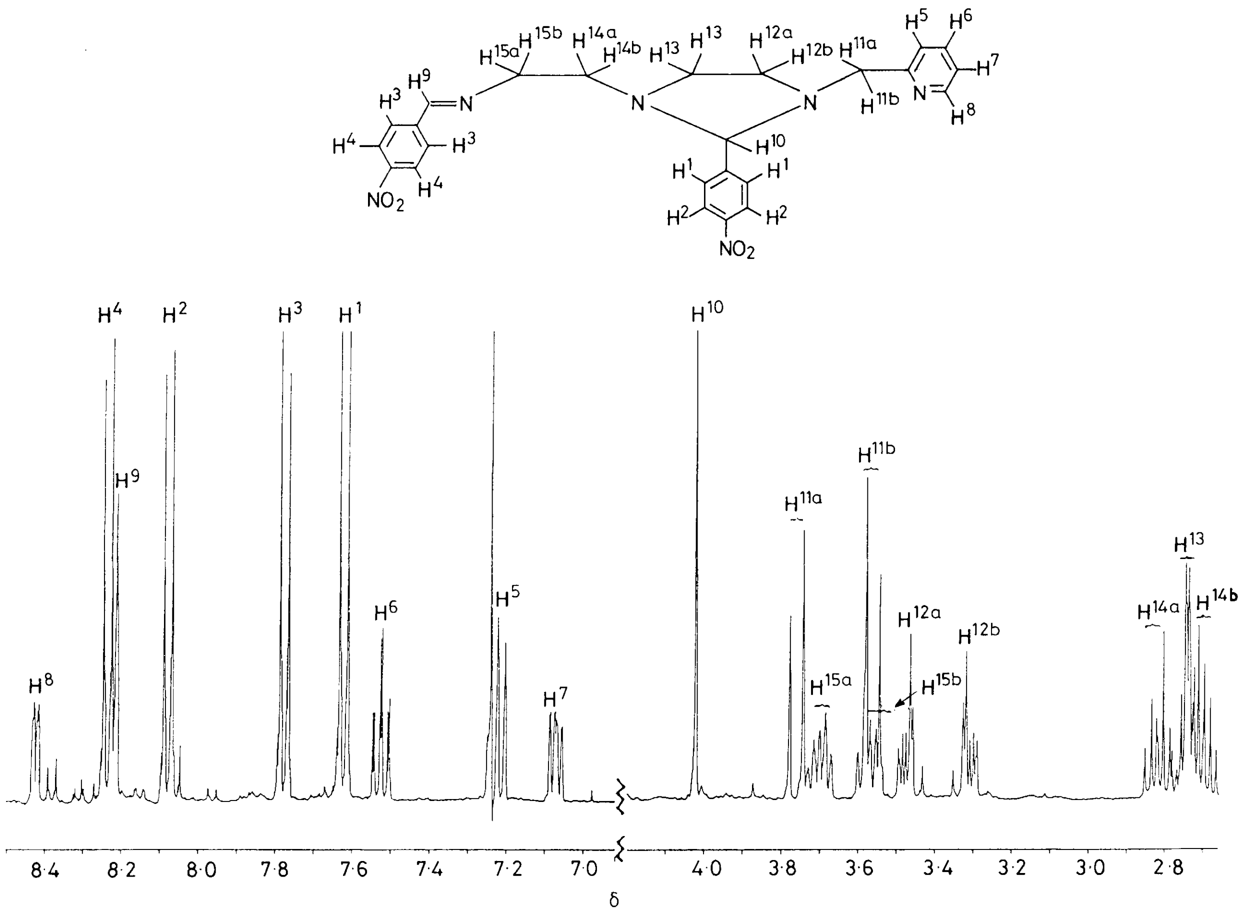


Figure 3. Proton n.m.r. spectrum of L^2 in $CDCl_3$

As reported above, L^2 easily forms, by acid hydrolysis, the protonated form of L^3 which is converted into the free amine by raising the pH to ≃12. The i.r. spectrum of L^3 shows broad peaks at 3 351 and 3 292 cm^{-1} associated with the stretchings of the NH_2 and NH groups, but no band due to NO_2 groups.

The violet complex $[CuL^3(ClO_4)_2]$ can be obtained from the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ and L^3 in methanol. The same compound has been also obtained from the reaction of 4-chloro-2,6-diformylphenol and the amine L^3 in the presence of copper(II) perchlorate in alcoholic solution. For ionic ClO_4^- groups only one band is expected in the range 1 095—1 080 cm^{-1} (antisymmetric stretching ν_3) and only one band at 620 cm^{-1} (antisymmetric bending ν_4).[29] The multiplicity of perchlorate absorptions for this complex (strong peaks at 1 145, 1 116, and 1 088 cm^{-1}, together with a shoulder at 1 046 and at 635 and 628 cm^{-1}) suggests that the ClO_4^- groups are not completely ionic and that interaction with the central metal ion takes place.

The *X*-ray structure of $[CuL^3(ClO_4)_2]$ (Figure 4) shows that the quadridentate ligand is equatorially co-ordinated to the metal ion through the nitrogen donor atoms. The mean-plane calculation shows that the four atoms are not exactly coplanar, being alternately displaced by *ca.* ±0.13 Å from the plane in a slightly staggered structure. In addition, the metal ion makes two axial Cu ··· O contacts with oxygen atoms from the two ClO_4^- anions; these contacts are relatively long compared with normal Cu–O covalent bonds but not so long as to be neglected. The Cu ··· O distances are not equivalent (2.51 and 2.80 Å) but their values are typical of those found for copper(II) complexes with tetragonally elongated octahedral environments.[30,31] The directions of these bonds are almost collinear with the normal to the least-squares plane passing through the four N-donor atoms of the equatorial co-ordination sphere, the distortion angles being 1.4 [Cu–O(1)] and 6.1° [Cu–O(6)]. The four Cu–N bond lengths are between 1.95 and 2.01 Å, with a mean of 1.985 Å which compares favourably with the sum of the corresponding atomic radii (Cu, 1.35; N, 0.65 Å).[32] Chelation of the ligand implies the formation of three penta-atomic non-

Table 6. Proton n.m.r. data for L^2

Chemical shift	Integral	Assignment	Coupling constant
8.42	1 (d)	H^8	$J(H^8H^7)$ 6
8.24	2 (d)	H^4	$J(H^4H^3)$ 8
8.21	1 (s)	H^9	
8.09	2 (d)	H^2	$J(H^2H^1)$ 8
7.78	2 (d)	H^3	$J(H^3H^4)$ 8
7.62	2 (d)	H^1	$J(H^1H^2)$ 8
7.51	1 (t)	H^6	$J(H^6H^{5-7})$ 8, $J(H^6H^8)$ 2
7.23	1 (t)	H^5	$J(H^5H^6)$ 8
7.07	1 (t)	H^7	$J(H^7H^{6-8})$ 6
4.01	1 (s)	H^{10}	
3.76	1 (d)	H^{11a}	$J(H^{11a}H^{11b})$ 14
3.69	1 (m)	H^{15a}	$J(H^{15a}H^{15b})$ 14
3.57	1 (m)	H^{15b}	
3.56	1 (d)	H^{11b}	
3.47	1 (m)	H^{12a}	$J(H^{12a}H^{12b})$ 7, $J(H^{12}H^{13})$ 12
3.31	1 (m)	H^{12b}	
2.81	1 (m)	H^{14a}	$J(H^{14}H^{15})$ 6
2.73	2 (m)	H^{13}	
2.68	1 (m)	H^{14b}	$J(H^{14a}H^{14b})$ 14

Table 7. Proton nuclear Overhauser enhancement data (%) for L^2

Proton observed	Protons irradiated														
	H^1	H^3	H^5	H^8	H^9	H^{10}	H^{11a}	H^{11b}	H^{12a}	H^{12b}	H^{13}	H^{14a}	H^{14b}	H^{15a}	H^{15b}
H^1		−3.0	1.2		1.0	9.0	1.20		0.3	0.8		1.4		0.6	0.2
H^2	18.5	1.5				−1.7									0.2
H^3				2.0	14.0			−0.20				0.3	0.5	0.3	0.3
H^4	3.5	16.5													
H^5						−0.9	2.6	0.6	0.3	4.0				1.0	0.9
H^6			12.0												
H^7			−3.4	8.0											
H^8															
H^9		16.5		−6.0			1.8	7.3	1.2					6.1	8.1
H^{10}	7.0	1.0	0.4		0.3		2.8	3.1			7.1	5.0	6.3	1.4	4.2
H^{11a}	0.8		0.7			2.8		20.5	1.9						28.0
H^{11b}						3.4	10.0		−4.3		4.7	1.0	2.7	20.0	
H^{12a}								−1.0		2.0	19.5	10.0	10.0		
H^{12b}								−1.5	1.5		21.5	7.0	15.0		
H^{13}						2.0		2.5	11.3	13.0					3.5
H^{14a}	0.2					2.0		1.3					16.8	0.5	2.2
H^{14b}						2.0						15.0		1.3	
H^{15a}					3.2			14.5	1.2		2.6	1.9	2.6		17.0
H^{15b}					3.2		6.0					3.0		8.1	

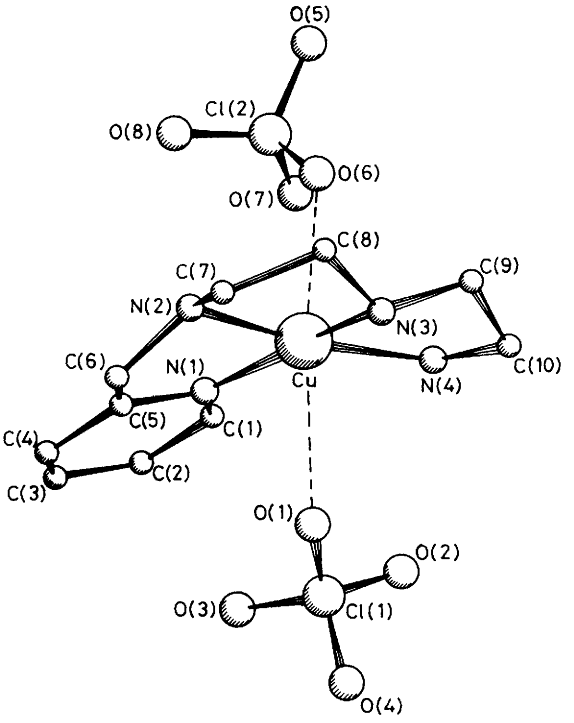
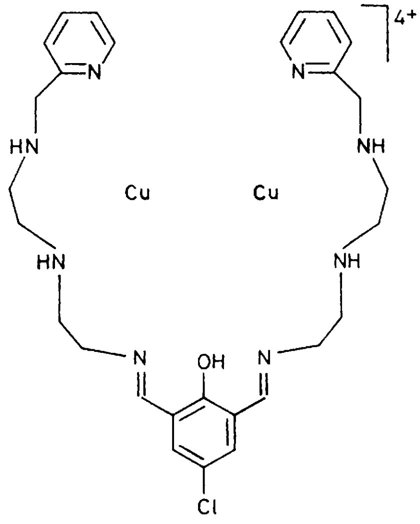


Figure 4. Structure of [CuL^3(ClO$_4$)$_2$]

planar metallocycles with comparable N–Cu–N angles (81—86°). The mean of the N(sp^3)–C(sp^3) bond lengths is 1.46 Å.

For the green complex collected as the final product in the condensation of 4-chloro-2,6-diformylphenol and L^3 in the presence of copper(II) perchlorate the configuration [Cu$_2$L^9]$^{4+}$ can be tentatively suggested on the basis of i.r. spectra and elemental analysis. Broad absorptions in the ranges 3 435—3 421 and 3 218—3 155 cm^{-1} can be associated with the ν(NH) of the ligand and the ν(O–H) of phenol; the ν(C=N) bands lie at 1 662 and 1 651 cm^{-1} while bands at 1 146, 1 114, and 1 090 cm^{-1} and those at 635 and 628 cm^{-1} are associated with non-completely ionic perchlorates.



[Cu$_2$ L^9]$^{4+}$

The same template reaction in the presence of barium(II) thiocyanate leads to the formation of a complex that may be formulated as [Ba$_2$(L^4 − 2H)(SCN)$_2$]. Crystals suitable for *X*-ray investigation were collected from the mother-liquor and were characterized by *X*-ray fluorescence spectroscopy. By integration of back-scattered *X*-rays using a scanning electron microprobe the S:Cl:Ba ratios were approximated and the sample homogeneity confirmed. Figure 5 shows an *X*-ray fluorescence spectrum of the crystals; the S:Cl:Ba ratios are approximately 2:2:1. Quantitative analysis taking into account autoabsorption phenomena [ZAF corrections; ZAF is a correction program for the atomic number (Z), absorption (A), and fluorescence (F)] also gives the same 2:2:1 ratio within the limits of the standard errors. Punctual analyses on different crystals or different parts of the same crystal always gave the same result. Similar investigations of powders of [Ba$_2$(L^4 − 2H)(SCN)$_2$] show a lack of homogeneity, both morphological and analytical. The S:Cl:Ba ratio found by this method (3:3:2) does not agree with that (1:1:1) found on the basis of elemental analysis. It is however interesting that the i.r. spectrum of the powder is almost identical to that of the crystals. The fast-atom-bombardment (f.a.b.) mass spectra are also almost identical. A strong peak at *m*/*z* 821 due to $P^+ - H$ related to the

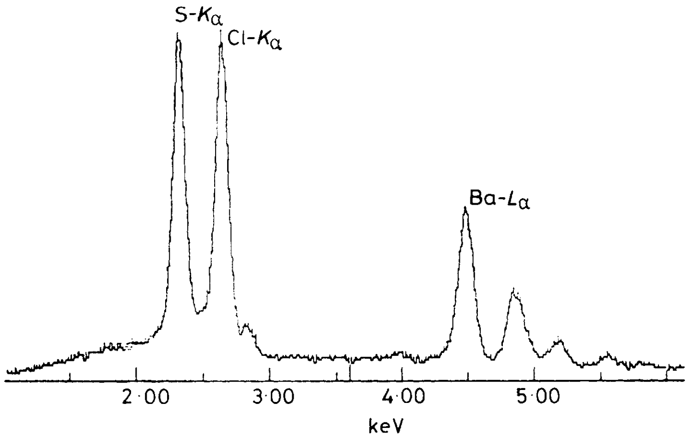


Figure 5. X-Ray fluorescence spectrum of [BaL^4(SCN)$_2$] crystals

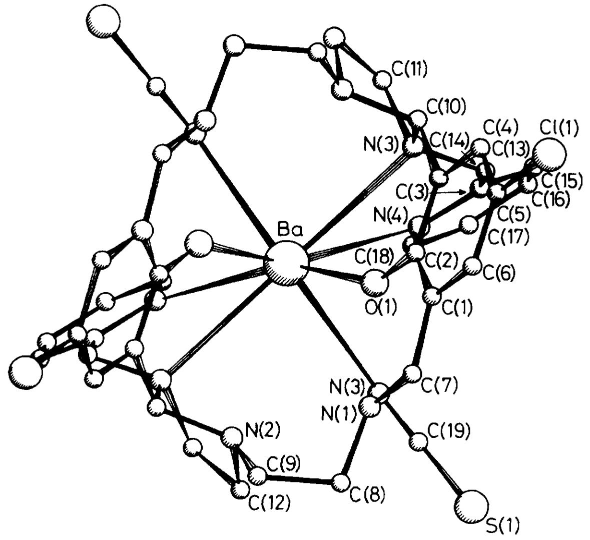


Figure 6. Structure of [BaL^4(SCN)$_2$]

mononuclear species is detectable in the mass spectra of both samples.

The SCN$^-$ group may co-ordinate to a metal through either the nitrogen or the sulphur atom, or both. An empirical criterion developed to determine the bonding type is the position of the CN stretching frequencies, which generally occur near 2 050 cm^{-1} for N-bonded and near 2 100 cm^{-1} in S-bonded complexes. For [BaL^4(SCN)$_2$] a single sharp ν(C=N) band is present at 2 055 cm^{-1}; ν(C=S) can be tentatively assigned at 847 and 810 cm^{-1} and ν(NCS) at 469 cm^{-1}. All these observations are in accord with N-bonded thiocyanate groups.[29] The ν(C=N) bands lie at 1 660 and 1 649 cm^{-1}.

Crystals of [BaL^4(SCN)$_2$] obtained from the mother-liquor are orthorhombic, space group *Pbcn*. This space group has eight equivalent general positions; however, the Ba^{2+} ions lie on special positions on the two-fold axes at $0,y,\frac{1}{4};0,\bar{y},\frac{3}{4}; \frac{1}{2},\frac{1}{2}+y,\frac{1}{4};\frac{1}{2},\frac{1}{2}-y,\frac{3}{4}$. Thus, in agreement with the value of the crystal density, there are only four molecules of the compound in the unit cell, with molecular symmetry C_2, and the asymmetric unit is one half of the entire molecule. As shown in Figures 6 and 7, the neutral ligand L^4 behaves as a sexidentate ligand, being directly bonded to Ba^{2+} through O(1), N(3), N(4), and the symmetric O(1$^{\text{I}}$), N(3$^{\text{I}}$), and N(4$^{\text{I}}$) donor atoms. Two SCN$^-$ ions complete the co-ordination polyhedron around the

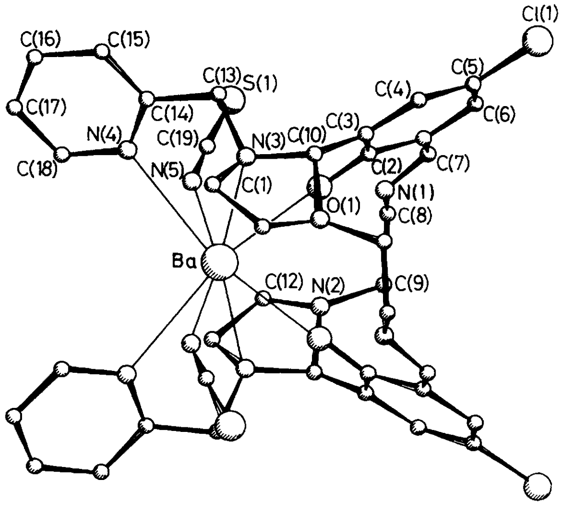


Figure 7. Structure of [BaL^4(SCN)$_2$] (alternative view)

metal, which can be approximately described as a distorted square antiprism. The upper square face [N(3), N(4), N(5), O(1)] is rotated by a mean of 17° with respect to the corresponding lower square face [N(3$^{\text{I}}$), N(4$^{\text{I}}$), N(5$^{\text{I}}$), O(1$^{\text{I}}$)]. Moreover, mean-plane calculations indicate that the two faces are not parallel, being inclined by 17° with respect to one another.

With regard to the barium–donor atom distances we note that: (*i*) all Ba–N bonds are appreciably longer than the Ba–O bonds; (*ii*) the Ba–N bonds with the neutral ligand (mean 3.08 Å) are comparable with one another and significantly longer than the corresponding distances (2.88 Å) from the SCN$^-$ anion.

The penta-atomic non-aromatic heterocycle has the usual envelope conformation, with the C(10) atom 0.73 Å from the mean plane defined by the other four atoms (the deviation of these atoms from the plane is only 0.2 Å). The mean of the N(sp^3)–C(sp^3) bond lengths in this ring is 1.48 Å. The double bond in the chain is essentially localized at C(7)=N(1) with a length of 1.31 Å, while the adjacent single C(8)–N(1) bond is 1.45 Å (a value of 1.44 Å is found for the similar bond in L^2). Other structural details in the molecule are normal.

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