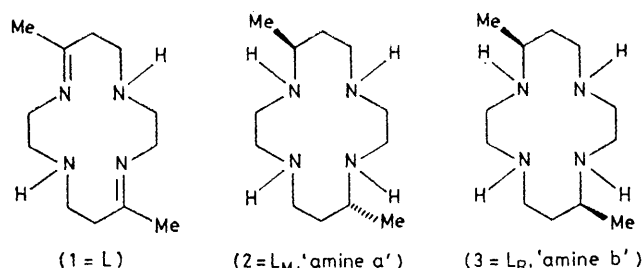


Crystal and Molecular Structure of *trans*-Diazido(*C-meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III) Azide

By Roderic J. Restivo and George Ferguson,* The Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1
Robert W. Hay and Dharam P. Piplani, Chemistry Department, University of Stirling, Stirling FK9 4LA

Crystals of the blue-violet title complex are triclinic, space group $P\bar{1}$, with $Z = 1$ in a unit cell of dimensions $a = 7.932(4)$, $b = 7.232(4)$, $c = 10.392(5)$ Å, $\alpha = 109.71(3)$, $\beta = 124.07(2)$, and $\gamma = 80.78(3)^\circ$, molecular symmetry $\bar{1}$ required for both ions. The structure has been solved by the heavy-atom method and refined by full-matrix least-squares calculations to R 0.073 for 1 291 reflections measured by diffractometer. The cation has octahedral co-ordination with the macrocycle in *C-meso* configuration and *trans* azide groups. Principle bond lengths are Co-N(azide) 1.953(11), Co-N(macrocycle) 1.986(7) and 2.016(6), and N-N(azide) 1.172(15) and 1.166(21) Å. The crystal structure contains azide ions [N-N 1.165(17) Å] and macrocyclic cations linked to form sheets parallel to (010) by N-H...N hydrogen bonds (2.96 Å) which utilise all the N-H and terminal azide groups.

A PREVIOUS paper¹ has dealt with some transition-metal complexes of the macrocyclic ligand 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene ($1 = L$) and crystallographic work on *trans*-[CoL(NCS)₂][SCN]·H₂O



has been reported.² Reduction of [NiL][ClO₄]₂ with nickel-aluminium alloy³ followed by treatment with sodium cyanide gives two isomeric tetra-amines, one of m.p. 144–145 °C, designated 'amine a' and thought to be the *C-meso* isomer (2 = L_M), the other of m.p. 109–110 °C designated 'amine b' and thought to be the *C-rac* isomer (3 = L_R).⁴ Complexes of L_M and L_R contain six chiral centres (two carbon and four nitrogen) so that 20 diastereoisomers (16 racemates and four *meso* forms) are theoretically possible. In the *C-meso* series there are six racemates and four *meso* forms and in the *C-rac* series there are 10 racemates.

It has been established that the thermodynamically most stable form of complexes of macrocyclic 14-membered secondary amine ligands in the absence of C-methyl-group interactions is (4).⁵⁻⁸ This structure, often referred to as the cyclam of *trans*-III form,⁵ minimises hydrogen-hydrogen interactions in the chelate rings and is virtually free from torsional bond strain. In the *C-meso* ligand (2 = L_M) this formulation can also place the two methyl groups in equatorial positions so that structure (5) is expected to be strongly favoured for metal complexes of (2).

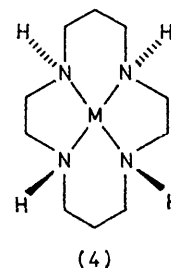
¹ R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1466.
² R. J. Restivo, J. Horney, and G. Ferguson, *J.C.S. Dalton*, 1976, 514.

³ R. A. Kolinski and B. Korybut-Daszkiwics, *Bull. Acad. polon. Sci.*, 1969, 17, 13.

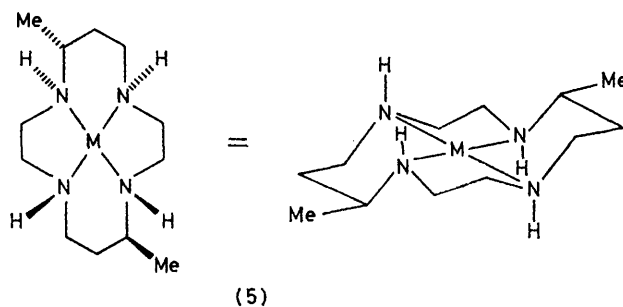
⁴ R. W. Hay and D. P. Piplani, *J.C.S. Dalton*, 1977, 1956.

⁵ B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, 4, 1102; B. Bosnich, R. Mason, P. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 1965, 97.

The complex *trans*-diazido(*C-meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradecane)cobalt(III) azide was



prepared using 'amine a', as described by Hay and Piplani,⁴ and the structure of the blue-violet crystals



was determined by a single-crystal X-ray analysis (details in the Experimental section).

In the crystal structure (Figure 1) the macrocyclic cations and azide anions are both required crystallographically to occupy sites with $\bar{1}$ symmetry from space-group considerations. Thus, immediately, the *C-meso* formulation for 'amine a' (2 = L_M) is established and by inference 'amine b' (2 = L_R) has the *C-rac* configuration. A detailed view of the cation is shown in Figure 2 which also shows the hydrogen-atom positions; these together with the details of molecular geometry (Table 1) establish that fomulation (5) is indeed correct for this metal complex of L_M.

⁶ L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, 1969, 91, 4092.

⁷ L. G. Warner and D. H. Busch, 'Coordination Chemistry: Papers Presented in Honour of J. C. Bailar, Jr.', Plenum, New York, 1969, p. 1.

⁸ D. K. Cabbiness and D. W. Margerum, *J. Amer. Chem. Soc.*, 1970, 92, 2151.

The cobalt atom has octahedral co-ordination (*cis*-N-Co-N 86.5–93.5°) with the azide ligands necessarily

Co-N(azide) geometry [Co-N 1.95(1) Å, Co-N-N 124.5–(7)°, and mean N-N 1.17(2) Å] agree well with those

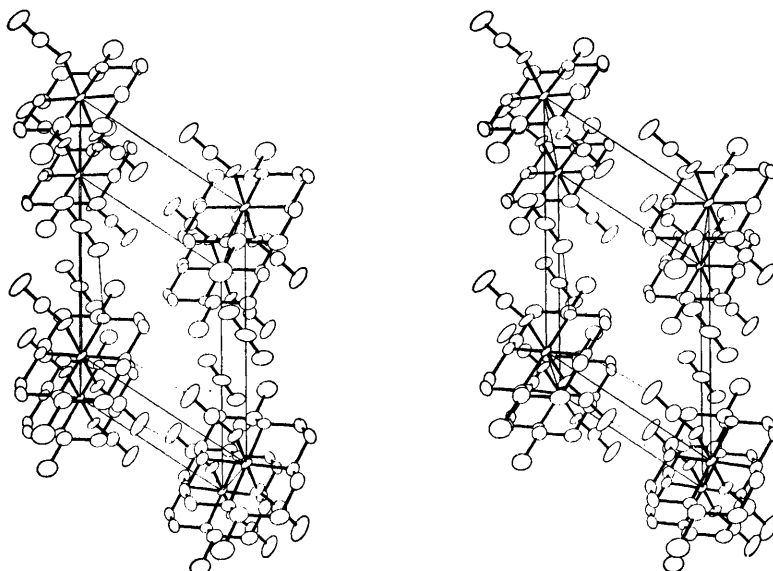


FIGURE 1 Ionic packing diagram for $[\text{CoL}_M(\text{N}_3)_2][\text{N}_3]$; H-N...N hydrogen bonds from the cation at the origin of the cell are shown by thin lines

trans; space group requirements also impose planarity on the four nitrogen atoms of the macrocycle and the cobalt atom. The Co-N(macrocycle) distances [mean 1.996(10) Å] are in accord with accepted values⁹ and the

found in penta-ammineazidocobalt(III) azide¹⁰ [Co-N 1.94 Å, Co-N-N 125°, and N-N 1.15 and 1.21 Å].

The five-membered ring of the cation has a symmetric *gauche* conformation with torsion angle $\phi[\text{N}(1)-\text{C}(2)-\text{C}(3)-\text{N}(4)] = 56^\circ$; the C-N bond lengths in this ring are normal (mean 1.495 Å) but the CH₂-CH₂ bond [1.46(1)

TABLE 1

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) In the cation

(i) Distances

Co-N(1)	1.986(7)	N(21)-N(22)	1.172(15)
Co-N(4)	2.016(6)	N(22)-N(23)	1.166(21)
Co-N(21)	1.953(11)		
		C(2)-C(3)	1.455(14)
N(1)-C(2)	1.496(11)	C(5)-C(6)	1.538(14)
N(1)-C(7 ^I)	1.437(12)	C(5)-C(15)	1.513(14)
N(4)-C(3)	1.493(11)	C(6)-C(7)	1.509(15)
N(4)-C(5)	1.461(13)		

(ii) Angles

N(1)-Co-N(4)	86.7(3)	C(2)-N(1)-C(7 ^I)	112.1(8)
N(1)-Co-N(4 ^I)	93.3(3)	C(3)-N(4)-C(5)	112.9(7)
N(1)-Co-N(21)	86.5(4)		
		N(1)-C(2)-C(3)	108.3(8)
N(1)-Co-N(21 ^I)	93.5(4)	N(1)-C(7 ^I)-C(6 ^I)	112.8(9)
N(4)-Co-N(21)	89.8(4)	N(4)-C(3)-C(2)	108.8(7)
N(4)-Co-N(21 ^I)	90.2(4)	N(4)-C(5)-C(6)	110.2(7)
		N(4)-C(5)-C(15)	112.8(9)
Co-N(21)-N(22)	124.5(7)	C(15)-C(5)-C(6)	110.0(10)
Co-N(1)-C(2)	106.0(6)	C(5)-C(6)-C(7)	114.1(11)
Co-N(1)-C(7 ^I)	118.5(5)		
Co-N(4)-C(3)	105.3(6)		
Co-N(4)-C(5)	119.1(6)	N(21)-N(22)-N(23)	175.3(13)

(b) In the anion

N(31)-N(32) 1.165(17)

(c) Interion distances

N(1) ... N(23 ^{II})	2.96(2)	H(4) ... N(31)	2.09
H(1) ... N(23 ^{II})	2.27	N(23) ... N(23 ^{II})	3.06(2)
N(4) ... N(31)	2.97(2)		

The superscripts refer to the following equivalent positions which should be applied to the co-ordinates of the second atom: I -x, -y, -z; II 1 + x, y, z; III -1 - x, -y, -z

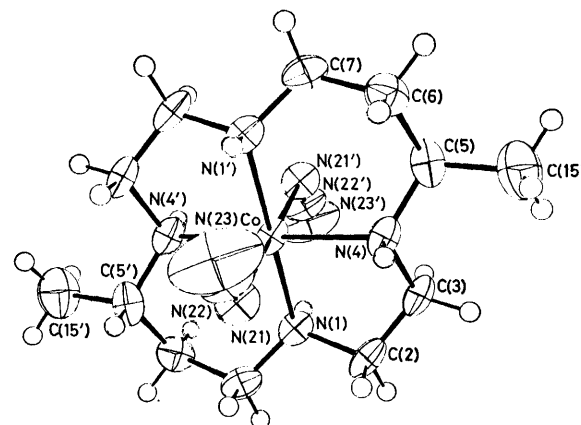


FIGURE 2 An ORTEP drawing of the $[\text{CoL}_M(\text{N}_3)_2]^+$ cation showing the atomic numbering and thermal ellipsoids at the 50% probability level. The hydrogen atoms have been included with fixed isotropic thermal parameters (B 1.0 Å²)

Å] is shorter than expected. In the six-membered ring a regular chair conformation is found with the methyl group equatorial and with the ring torsion angles (Figure 3) showing the expected symmetry; N-C and C-C torsion angles (55–69°) are not far removed from 60°. The C-C distances in the ring have the expected values [mean 1.52(1) Å] but the C-N bonds [mean 1.45(1) Å] are slightly shorter than expected.

⁹ *Special Publ.*, The Chemical Society, London, 1965, no. 18.

In the crystal structure (Figure 1) the azide anions occupy centres of symmetry between the cations in the z direction; the anion N-N bond length [1.17(2) Å] agrees exactly with those found in other structures.¹⁰ The interion distances (Table 1) reveal that the ions are linked to form infinite sheets parallel to (010) by N-H...N hydrogen bonds which utilise all the available N-H groups and terminal azide nitrogen atoms. Parallel to the x direction, cations are linked to form an infinite chain by pairs of centrosymmetrically related N-H...N [2.96(2) Å] hydrogen bonds between the N(1)-H moiety of one cation and the terminal azide nitrogen N(23) of one related by a unit-cell translation in the x direction. These chains are cross-linked in the z direction by the

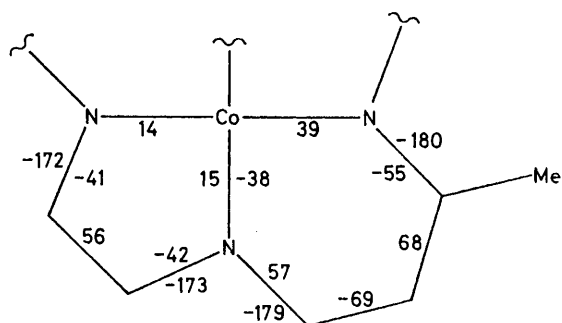


FIGURE 3 Torsion angles ($^{\circ}$) for the $[\text{CoL}_M(\text{N}_3)_2]^+$ cation

azide anions utilising the remaining macrocycle N-H group [N(4)-H...N(31) 2.97(2) Å] to form infinite sheets.

EXPERIMENTAL

Blue-violet needle-shaped crystals of $[\text{CoL}_M(\text{N}_3)_2][\text{N}_3]$ suitable for X-ray analysis were obtained by slow evaporation from methanol-ethanol. A crystal *ca.* $0.09 \times 0.09 \times 0.23$ mm was chosen for the analysis.

Crystal Data.— $\text{C}_{12}\text{H}_{28}\text{CoN}_{13}$, $M = 413.4$, Triclinic, $a = 7.932(4)$, $b = 7.232(4)$, $c = 10.392(5)$ Å, $\alpha = 109.71(3)$, $\beta = 124.07(2)$, $\gamma = 80.78(3)^{\circ}$, $U = 464.6$ Å³, $D_m = 1.41(1)$, $Z = 1$, $D_c = 1.44$ g cm⁻³, $F(000) = 228$, Mo- K_{α} radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo-}K_{\alpha}) = 9.9$ cm⁻¹. No systematic absences; space group $P1$ (C_1^1 , no. 1) or $P\bar{1}$ (C_1^1 , No. 2) from the analysis. Molecular symmetry: centre for both cation and anion.

Crystallographic Measurements.—Preliminary cell data were obtained from precession and Weissenberg photographs; accurate unit-cell data were obtained from a least-squares refinement of diffractometer setting angles of 12 strong general-order reflections. A Hilger and Watts Y290 computer-controlled diffractometer equipped with graphite-monochromatised Mo- K_{α} radiation was used for data collection with a small needle crystal in a manner similar to that described previously.¹¹ 1291 Intensity maxima were collected and corrected for Lorentz and polarisation effects (but not for absorption which was negligible). The 924 reflections with $I > 3\sigma(I)$ were used for the solution and refinement of the structure. All the calculations were carried

out on an IBM 370/155 computer using our local modifications of the 'X-Ray '72' system.¹²

Structure Analysis.—The cobalt atom is required from space-group considerations to lie at the origin; the positions of the remaining non-hydrogen atoms in the structure were readily found by application of the heavy-atom method. Full-matrix least-squares refinement with unit weights using isotropic thermal parameters for all the atoms converged with R 0.16. Full-matrix least-squares refinement was then carried out allowing for anisotropic thermal motion of all the atoms, and with a weighting scheme $w^2 = 1/[\sigma^2(F) + pF^2]^2$ where the final p parameter was 5×10^{-4} ; at convergence, when R 0.087, a final difference-Fourier synthesis revealed electron-density concentrations in chemically reasonable positions for all the hydrogen atoms and showed no other chemically recognisable features. In a further two cycles of full-matrix least-squares calculations allowance was made for hydrogen-atom contributions in chemically expected positions with C-H = N-H = 0.96 Å and isotropic U values of 0.063 Å², but the hydrogen parameters were not refined. The scattering factors from ref.

TABLE 2

Atomic positional parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for H) with estimated standard deviations in parentheses for $[\text{CoL}_M(\text{N}_3)_2][\text{N}_3]$

Atom	x	y	z
Co	0	0	0
N(1)	2 511(9)	-1 534(11)	647(8)
N(4)	1 385(10)	1 605(11)	2 368(8)
N(21)	-988(11)	-1 896(11)	420(9)
N(22)	-2 325(11)	-1 628(12)	630(10)
N(23)	-3 588(16)	-1 443(20)	907(16)
N(31)	1 047(16)	186(23)	4 592(13)
N(32)	0	0	5 000
C(2)	3 673(12)	-1 027(15)	2 463(10)
C(3)	3 569(12)	1 079(15)	3 129(10)
C(5)	1 117(14)	3 725(15)	2 790(11)
C(6)	-1 163(15)	4 161(14)	1 961(12)
C(7)	-2 310(13)	3 621(15)	129(12)
C(15)	2 211(18)	4 712(18)	4 611(14)
H(1)	320	-96	35
H(21)	309	-174	277
H(22)	507	-143	289
H(31)	428	147	430
H(32)	425	178	288
H(4)	079	105	277
H(5)	170	430	240
H(61)	-179	344	223
H(62)	-132	554	240
H(71)	-158	422	-14
H(72)	-364	417	-29
H(151)	207	612	490
H(152)	363	448	513
H(153)	167	420	505

13 for the neutral species and ref. 14 for hydrogen atoms were used throughout the refinement and anomalous-dispersion corrections were included for the cobalt atom.¹⁵ At convergence, the final value of $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ was 0.073, that of $R' = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o^2)]^{1/2}$ was 0.089. The estimated standard deviation of an observation of unit weight was 1.8.

¹² J. M. Stewart, Technical Report TR 192, University of Maryland Computer Science Center, College Park, Maryland, 1972.

¹³ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

¹⁴ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1964, **42**, 3175.

¹⁵ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

¹⁰ G. J. Palenik, *Acta Cryst.*, 1964, **17**, 360.

¹¹ See, for example, G. Ferguson, P. A. Gunn, W. C. Marsh, R. McCrindle, R. Restivo, J. D. Connolly, J. W. B. Fulke, and M. S. Henderson, *J.C.S. Perkin I*, 1975, 491.

Details of interatomic distances are in Table 1 and coordinates are in Table 2. The anisotropic thermal parameters and observed and calculated structure factors are

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

listed in Supplementary Publication No. SUP 22279 (14 pp.).*

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