Hexaco-ordination of a Diamino-substituted Tetra-azamacrocycle to Cobalt(III) and Nickel(II): Compressed Co–N Bonds?

Neil F. Curtis,[a]* Graeme J. Gainsford,[b] Trevor W. Hambley,[c] Geoffrey A. Lawrance,[d]* Keith R. Morgan,[a] and Asokamali Siriwardena[a]

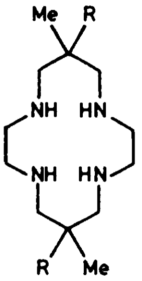
[a] *Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand*
[b] *Chemistry Division, D.S.I.R., Wellington, New Zealand*
[c] *Department of Inorganic Chemistry, The University of Sydney, Australia 2006*
[d] *Department of Chemistry, The University of Newcastle, Australia 2308*

The substituted cyclam macrocycle 6,13-diamino-6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane (L^2) can co-ordinate to metal ions as a hexadentate ligand; whereas M–N distances for the Ni$^{\text{II}}$ complex are 'normal,' those for the Co$^{\text{III}}$ complex are unusually short, and this is reflected in a very negative Co$^{\text{III/II}}$ redox couple and a significant shift of the electronic spectrum maxima to higher energy.

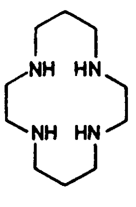
Facile syntheses of new multidentate ligands by metal-directed condensation reactions involving formaldehyde and carbon acids have attracted considerable interest, with syntheses around both inert[1,2] and labile[3—6] metal ions being investigated recently. We have initiated a study of reactions using nitroalkane carbon acids, since subsequent reduction of the nitro group yields pendant primary amines which are potentially co-ordinating. Here we report the first example of a ligand with such pendant amines which can complex metal ions as a hexadentate ligand despite significant strain being introduced as a consequence of this mode of co-ordination.

Reaction of $[\text{Cu(en)}_2]^{2+}$ or $[\text{Ni(en)}_2]^{2+}$ (en = 1,2-diaminoethane) with formaldehyde and nitroethane forms the substituted macrocycle L^1 as the M$^{\text{II}}$ complex in high yield.[4,6] Reduction of the nitro groups for the Cu$^{\text{II}}$ complex yields the diamino macrocycle L^2 or for the Ni$^{\text{II}}$ complex yields $[\text{Ni}(L^2)]^{2+}$, from which L^2 can be isolated; L^2 is a substituted cyclam (1,4,8,11-tetra-azacyclotetradecane, L^3). The chemistry has been investigated, and the structures determined, for compounds of L^2 with a variety of metal ions, including copper(II), nickel(II), and cobalt(III). For all of the latter three metal ions, the complexes are extremely resistant to acid hydrolysis.

With Cu$^{\text{II}}$, all compounds isolated have the pendant primary amine groups unco-ordinated. The macrocycle conformation, and Cu–N distances [2.021(5), 2.027(6) Å] of $[\text{Cu}(L^2)]^{2+}$ closely resemble those of $[\text{Cu(cyclam)}]^{2+}$.[4,5,7]



L^1; R = NO_2
L^2; R = NH_2



L^3

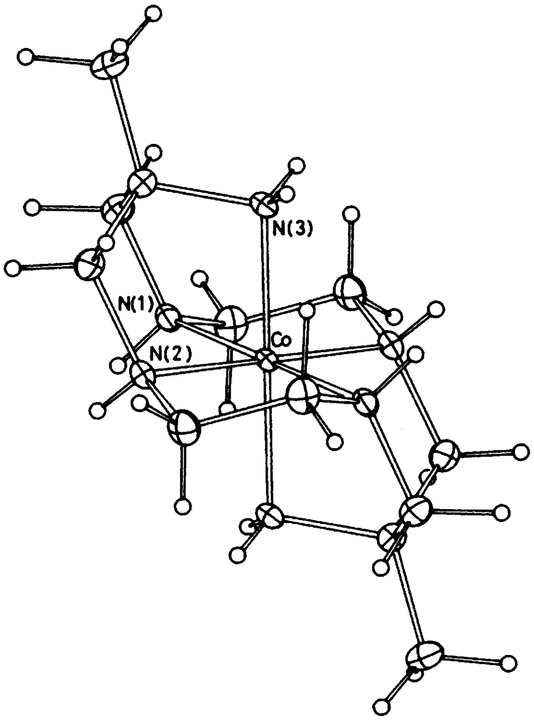


Figure 1. ORTEP drawing of the $[Co(L^2)]^{3+}$ cation. Selected bond lengths and angles are Co–N(1) 1.937(2), Co–N(2) 1.936(2), Co–N(3) 1.946(2) Å; N(2)–Co–N(1) 88.8(1), N(3)–Co–N(2) 85.0(1), and N(1)–Co–N(3) 85.5(1)°. For the Ni^{II} analogue, selected values are Ni–N(1) 2.075(3), Ni–N(2) 2.069(3), Ni–N(3) 2.126(3) Å; N(2)–Ni–N(1) 92.3(1), N(3)–Ni–N(2) 80.3(1), and N(1)–Ni–N(3) 83.4(1)°.

Apparently the Jahn–Teller tetragonal elongation common with this ion makes solids with these primary amine groups co-ordinated energetically disfavoured relative to arrangements in which these groups engage in other types of lattice interactions. With metal ions where this axial distortion will not be significant, hexaco-ordination should be possible.

For Ni^{II}, complex cations of L^2 isolated from neutral or basic solution have the primary amine groups co-ordinated axially (or displaced by competing ligands such as thiocyanate). From acid solution, compounds with the primary amine groups protonated are isolated, with square planar geometry or octahedral in species such as the *trans*-diaqua cation. The $[Ni(L^2)](ClO_4)_2\cdot H_2O$ complex was characterized by an *X*-ray crystal structure analysis.† Reaction of L^2 with $Co^{2+}{}_{aq.}$ in air, or with $[Co(CO_3)_3]^{3-}$ in aqueous HCl, results in the formation of the green *trans*-$[Co(L^2)Cl_2]^+$, which is converted in base into yellow $[Co(L^2)]^{3+}$. The crystal structure analysis of the Co^{III} complex defines hexaco-ordination;† an ORTEP drawing of the cation appears in Figure 1. The structures of the hexaco-ordinate Ni^{II} and Co^{III} complex cations are similar; the fourteen-membered macrocycles adopt configurations similar to those of cyclam complexes in planar co-ordination,[8] except that the six-membered chelate rings are folded back into boat conformations which permit pendant amino groups to co-ordinate axially.

For $[Co(L^2)]^{3+}$ the Co–N distances are similar for the equatorial (macrocycle) and axial (pendant) nitrogens at 1.938(1) and 1.946(2) Å respectively. These distances are shorter than reported values for cyclam complexes [ranging from 1.987(7) to 2.016(6) Å][9] or for non-cyclic amines, typified by the mean value for 27 structures of $[Co(en)_3]^{3+}$ salts at 1.964 Å.‡ Thus, in spite of strain in the macrocycle indicated by distorted bond angles [*e.g.* Co–$N_{ax.}$–C 99.6(1)° and C–$N_{eq.}$–C 117(1)°] and unfavourable torsion angles (*e.g.* Co–N–C–C at 12.0 and 6.5°), the Co–N distances are short. We believe they are the shortest values reported for a precisely determined Co^{III} hexa-amine structure.

The $[Ni(L^2)]^{2+}$ cation shows a greater tetragonal distortion, with mean Ni–N distances of 2.070(3) (equatorial) and 2.126(3) Å (axial), respectively. The equatorial distances are similar to those of complexes of type *trans*-$[Ni(cyclam)X_2]$, 2.05—2.08 Å, which typically have tetragonal distortions with long axial bonds.[10] The axial bond lengths for the L^2 complex are similar to Ni–N distances for $[Ni(en)_3]^{2+}$ cations (averaging 2.13 Å).[11]

The short Co–N bonds could be forced by the conformation of the macrocycle required for hexadentate co-ordination (*i.e.* showing evidence for metal ion 'compression'). Alternatively, the short M–N distances could indicate that intra-ligand repulsive interactions for this hexadentate ligand are less than the combined inter- plus intra-ligand interactions for other hexa-amine systems, thus permitting the adoption of more nearly optimal M–N distances (*i.e.* the M–N distances in other systems are 'stretched'). Neither mechanism appears to be operative for the larger Ni^{II} ion, since nickel–donor atom distances are similar for $[Ni(L^2)]^{2+}$, *trans*-$[Ni(L_2)(NCS)_2]$, which has the six-membered chelated rings in the normal chair conformation,[12] and *trans*-$[Ni(cyclam)(NCS)_2]$.[10]

The shorter Co–N bonds in $[Co(L^2)]^{3+}$ are reflected in some of the physical properties. The $Co^{III/II}$ redox couple is observed at very negative potential, with $E_{\frac{1}{2}}$ −0.83 V *vs.* Ag/AgCl [hanging mercury drop electrode (h.m.d.e.), cyclic, ΔE 68 mV, i_{pc}/i_{pa} 1.0, scan rate 50 mV/sec in neutral aqueous 0.1 mol dm^{-3} $NaClO_4$]. By way of comparison, the couples for $[Co(en)_3]^{3+}$ and $[Co(sar)]^{3+}$ (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]eicosane) have been reported at −0.37 V and −0.64 V [*vs.* standard calomel electrode (s.c.e.)] respectively; for a range of substituted macrobicyclic hexa-amines, the $[Co(sar)]^{3+}$ molecule has one of the most negative redox potentials.[13] Further, the maxima in the electronic spectrum determined in neutral aqueous solution are shifted significantly towards higher energy, with maxima at 451 nm (ε 40 dm^3 mol^{-1} cm^{-1}) and 327 nm (ε 42). For $[Co(en)_3]^{3+}$, the maxima occur at 468 nm and 340 nm, while for $[Co(sar)]^{3+}$, they are at 471 nm and 343 nm. Molar extinction coefficients are also lower than those reported for 'normal' $CoN_6{}^{3+}$ complexes. An example with longer than average Co–N bonds is known, and in that case electronic maxima are shifted to lower energy and have larger molar extinction coefficients, suggesting a correlation between $\lambda_{max.}$ and average Co–N

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† *Crystal data:* $C_{12}H_{32}NiCl_2N_6O_9$, $[Ni(L^2)](ClO_4)_2\cdot H_2O$, M = 534.0, monoclinic, space group $P2_1/c$, a 9.3573(14), b 14.4888(22), c 15.836(12) Å, β 96.977(44)°, D_m 1.63 g cm^{-3}, U 2130(17) $Å^3$, Z = 4, μ(Mo-K_α) 12.19 cm^{-1}, λ(Mo-K_α) 0.71069 Å. Reflections were measured using a Nicolet R3M diffractometer at −140 °C. The structure was refined to an R of 0.062 using 5708F ($I > 5\sigma(I)$). The cation has approximately $\bar{1}$ symmetry.

$C_{12}H_{30}CoCl_3N_6O_4$, $[Co(L_2)]Cl_2(ClO_4)$, M = 587.7, monoclinic, space group $C2/c$, a 15.616(4), b 7.497(1), c 17.922(9) Å, β 108.63(1)°, D_x 1.629 g cm^{-3}, U 1988(1) $Å^3$, Z = 4, μ(Mo-K_α) 12.75 cm^{-1}, λ(Mo-K_α) 0.71069 Å. Reflections were measured on an Enraf–Nonius CAD4-F four-circle diffractometer. The structure was solved by heavy atom methods and refined to an R of 0.029 on 1526F ($I > 2.5\sigma(I)$).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Averaged from Cambridge Crystallographic Data Base files.

bond lengths in CoN_6^{3+} complexes.[14] Consequences of co-ordinating L^2 to other metal ions are being pursued.

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