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Crystal Structures of a Five-co-ordinate Copper(II) and a Six-co-ordinate Cobalt(III) Complex Containing Flexible Quinquedentate Macrocyclic Ligands

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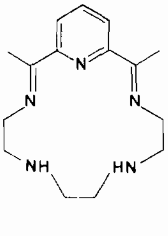
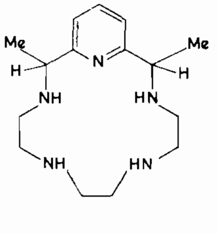
Several different quinquedentate macrocyclic nitrogen ligands have been found to coordinate to transition metal ions [1]. The resulting metal complexes can be five, six or seven co-ordinate dependent to some extent upon the nature of the anions but predominantly upon the size of metal and the size and flexibility of the macrocycle. Complexes of the rigid 15-membered cyclic ligand L^1 are invariably seven-co-ordinate with the ligand in the planar girdle and two monodentate ligands in the axial positions of a pentagonal bipyramid: thus for example $FeL^1(NCS)_2$ [2].



L^1



L^2

However this macrocycle can be hydrogenated to give L^2, 2,13-Dimethyl-3,6,9,12,18-pentaazabicyclo[12,3,1]octadeca-1(18),14,16 triene, a much more flexible ligand. Indeed five, six and seven-co-ordinate complexes of the type ML^2, ML^2X, and ML^2X_2, X = monodentate ligand, have been prepared [3]. In the different complexes, the quinquedentate ligand will have different conformations. Accordingly we have begun to determine the structures of these complexes to establish their geometry and to check on the flexibility of the ligand. Here we report crystal structure determinations of the first two types of compound, namely $[CuL^2][PF_6]_2$ and $[CoL^2Cl][ClO_4]_2$.

The two compounds were prepared following the published methods [3].

Crystal data: $[CuL^2][PF_6]_2$, M = 620.8, a = 12.931(8), b = 16.604(12), c = 11.441(9) Å, U = 2456.3 Å^3, Z =4, orthorhombic, space group $P2_12_12_1$. $[CoL^2Cl][ClO_4]_2$, M = 560.6, a = 14.145(12), b = 9.030(6), c = 16.743(11) Å, β = 90.9(3)°, U = 2138.3 Å^3, Z = 4, monoclinic, space group $P2_1/c$. 1608, 1336 independent reflections were collected on a G.E. XRD 5 diffractometer and have been refined to R 0.078, 0.086 respectively by full-matrix least squares.

TABLE. Distances (Å), Angles (°).

	in $[CuL^2]^{2+}$	in $[CoL^2]^{2+}$
M–N(3)	2.04(1)	1.99(1)
M–N(6)	1.90(1)	1.80(1)
M–N(9)	2.02(1)	1.94(1)
M–N(12)	2.10(1)	1.90(1)
M–N(15)	2.10(1)	1.91(1)
M–Cl	–	2.170(5)
N(3)–M–N(6)	81.6(8)	85.8(4)
N(3)–M–N(9)	163.2(8)	168.3(6)
N(3)–M–N(12)	103.9(8)	104.6(6)
N(3)–M–N(15)	85.7(8)	85.4(5)
N(6)–M–N(9)	81.8(6)	82.7(6)
N(6)–M–N(12)	124.4(6)	168.8(6)
N(6)–M–N(15)	150.9(6)	86.3(6)
N(9)–M–N(12)	83.7(6)	87.0(6)
N(9)–M–N(15)	110.2(6)	96.4(6)
N(12)–M–N(15)	84.0(6)	90.5(6)
Cl–M–N(3)	–	89.6(4)
Cl–M–N(6)	–	98.1(4)
Cl–M–N(9)	–	89.5(5)
Cl–M–N(12)	–	86.1(4)
Cl–M–N(15)	–	173.0(5)

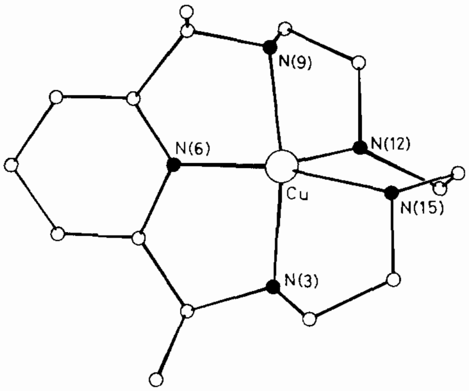


Figure 1. $[CuL^2]^{2+}$.

The two structures (Figures 1, 2) contain five-co-ordinate $[CuL^2]^{2+}$ and six-co-ordinate $[CoL^2Cl]^{2+}$ cations respectively well separated from the counter ions. The molecular dimensions (Table) show that the quinquedentate ligand L^2 has adapted to the two different geometries without undue strain. In both cations the M, N(3), N(6), N(9) atoms are approximately planar with the different conformations arising from the positions of N(12) and N(15). In both structures the M–N(6) bond lengths are the

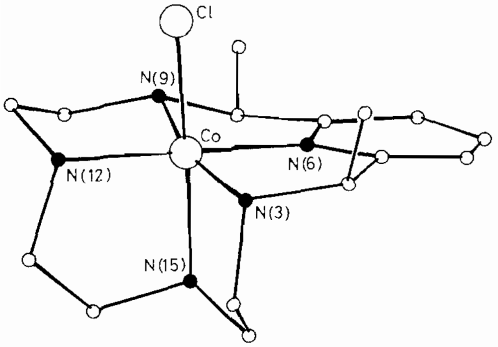


Figure 2. $[CoL^2Cl]^{2+}$.

shortest; this being a regular feature of such complexes [2].

The geometry of the $[CuL^2]^{2+}$ cation is best described as distorted trigonal bipyramidal with N(3), N(9) as axial atoms. This contrasts with the geometry of another $[CuL]^{2+}$ cation with L a 20-membered macrocyclic ligand in which the co-ordination sphere is more of a square pyramid [4]. The geometry of the $[CoL^2Cl]^{2+}$ cation is a relatively undistorted octahedron.

References

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