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THE STRUCTURE OF TRANS-DICHLORO(1,4,8,11-TETRAAZACYCLOTETRADECANE)NICKEL(III) PERCHLORATE

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The Ni in the title compound, $[Ni^{III}Cl_2L](ClO_4)$, has an octahedral geometry of trans-$NiCl_2N_4$ type and is in the trivalent state. The Ni-N and Ni-Cl distances average 1.970(4) and 2.452(4) Å, respectively.

Trivalent nickel complexes with tetraaza macrocyclic ligands having saturated nitrogen donors have been reported, and their chemical and physical properties have been investigated.[2,3)] However, no structural study has been reported so far. In general, the title and analogous tetraazamacrocyclic Ni(III) complexes are exceptionally stable in solid state,[2,3)] but they decompose gradually in solution and it is difficult to grow the crystals.

Crystals of $[Ni^{III}Cl_2L](ClO_4)$ suitable for the X-ray work were obtained by a very slow reaction between an aqueous solution of oxidized $[Ni^{II}L](ClO_4)_2$ by $(NH_4)_2S_2O_8$ and an excess of concentrated HCl.[4)] The crystal data are : orthorhombic, $P2_12_12_1$, a = 13.228(2), b = 19.804(3), c = 6.468(1) Å, U = 1694.4(6) Å^3, Z = 4, D_c = 1.68, D_m = 1.68 g cm^{-3}, μ(Mo Kα) = 1.63 mm^{-1}, R = 0.031 and R_w = 0.039 for 2023 independent reflections ($2\theta_{Mo\ K\alpha} < 60°$ and $|Fo| > 3\sigma(|Fo|)$).[5)]

The Ni atom is surrounded octahedrally by a square-planar array of four nitrogens and two Cl atoms occupying the axial positions (Figure). The macrocyclic ligand adopts the most stable conformation[6)] : the two six-membered rings take the chair form and the two five-membered rings adopt the gauche conformation. The total stereochemistry is the same as that of the corresponding Ni(II) analog, trans-$[Ni^{II}Cl_2L]$.[7)] However, the coordination bond lengths of trans-$[Ni^{III}Cl_2L]^+$ are significantly shorter than those in the Ni(II) analog in which the average Ni^{II}-N and Ni^{II}-Cl distances are 2.058 and 2.492 Å, respectively (see Table). The Ni and the four nitrognes are coplanar within 0.004 Å. The Ni-Cl(1) and Ni-Cl(2) bonds are tilted 3.6 and 2.9° from the normal to the NiN_4 plane, respectively. The Cl atoms move away from hydrogens attached to carbon and toward those bonded to nitrogen, as are in the Ni(II) analog.[7)]

There have been some arguments on the authenticity of the Ni(III) state. It has been reported that some of so-called Ni(III) complexes are more properly described as a Ni(II) stabilized ligand radical, a mixed-valence complex of Ni(II) and Ni(IV), or a partially oxidized Ni(II) complex.[8)] The Ni in the present compound is in the trivalent state in view of the structural parameters around the Ni and the normal bond lengths and angles within the organic ligand.

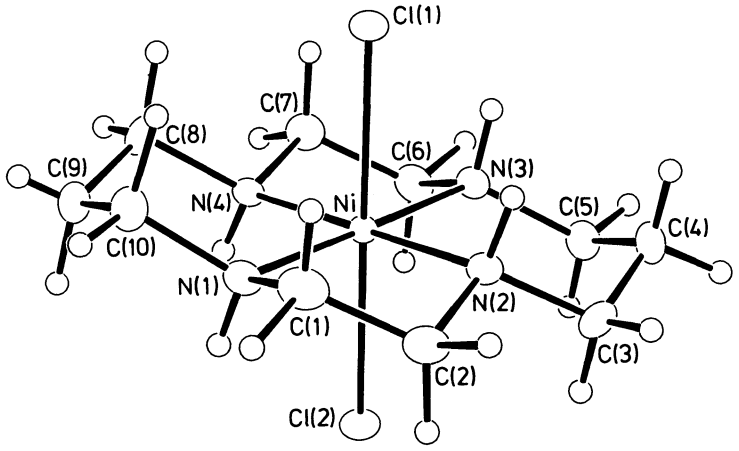

Figure A perspective view of trans-$[Ni^{III}Cl_2L]^+$.

Table Bond lengths (Å) and angles (°) around the Ni(III).

Ni-Cl(1)	2.456(1)
Ni-Cl(2)	2.447(1)
Ni-N(1)	1.979(3)
Ni-N(2)	1.965(4)
Ni-N(3)	1.973(4)
Ni-N(4)	1.963(4)
Cl(1)-Ni-Cl(2)	179.2(1)
Cl(1)-Ni-N(1)	92.3(1)
Cl(1)-Ni-N(4)	92.3(1)
Cl(1)-Ni-N(2)	87.5(1)
Cl(1)-Ni-N(3)	87.4(1)
Cl(2)-N--N(1)	87.9(1)
Cl(2)-Ni-N(4)	88.5(1)
Cl(2)-Ni-N(2)	91.7(1)
Cl(2)-Ni-N(3)	92.5(1)
N(1)-Ni-N(2)	86.5(2)
N(3)-Ni-N(4)	85.9(2)
N(1)-Ni-N(4)	93.2(1)
N(2)-Ni-N(3)	94.4(2)
N(1)-Ni-N(3)	179.0(1)
N(2)-Ni-N(4)	179.7(2)

References

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4) An excess of concentrated HCl was continuously added to a solution of oxidized $[Ni^{II}L](ClO_4)_2$ at a rate of ca. 0.2 cm^3 h^{-1} through a very thin capillary (see the preparative method for trans-$[Ni^{III}Cl_2(Me_2L)](ClO_4)$ reported in Ref. 2), where Me_2L stands for the dimethyl derivative of the present ligand).
5) Diffraction data were measured on a Rigaku AFC-5 diffractometer. A brown needle elongated along the c axis with approximate dimensions 0.11 x 0.09 x 0.38 mm was used for the intensity measurement. Weighting scheme employed was $w = [\sigma_{count}^2 + (0.015|Fo|)^2]^{-1}$. Absorption correction was applied. All the calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with a universal crystallographic computation program system, UNICS III.[9]
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