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# Template Synthesis and Molecular Structure of the Nickel(II) Perchlorate–Chloride Complex with Tris(((aminoisopropyl)amino)methyl)amine

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## Abstract

The template condensation reaction of $NiCL_2\cdot 6H_2O$ with ammonia, formaldhehyde and 1,2-propylenediamine has been studied. The new Ni(II)–tris(((aminoisopropyl)amino)methyl)amine complex was formed in the reaction. The compound has been investigated by elemental analysis, magnetic measurements, IR and UV–Vis spectra. Results suggested a semisepulchrate-type structure. This is confirmed by X-ray structure determination. At 295 K the crystals are regular space group $P2_13$, $a = b = c =$ 12.870(3) Å, $V = 2131(3)$ Å$^3$, $Z = 4$, $D_{calc} = 1.46$ g cm$^{-3}$, $D_{meas} = 1.47$ g cm$^{-3}$.

## Introduction

In addition to the cryptates, which are synthesized apart from metal ions and then used to form complexes, there are other types of multicyclic ligands called 'encapsulating ligands', which are synthesized around the metal ion.

Very stable Co(II), Pt(II) and Ni(II) complexes, called sepulchrates [1–3], belong to this class of compounds. Their characteristic structure is composed from two $N(CH_2)_3$ caps and three diamine chelate rings. The encapsulating structure efficiently protects the central metal ion. As a matter of fact the sepulchrate ligands are not able to release the once coordinated metal ion [4]. The template process leading to the sepulchrate also results in the formation of so called 'semisepulchrates' [5]. The semisepulchrate contains only one $N(CH_2)_3$ cap and its structure seems to be more flexible. Semisepulchrates have been less extensively investigated from both the synthetic and spectroscopical points of view compared to their sepulchrate counterparts. In particular X-ray molecular and crystal structures have not yet been analysed. A comparison of the semisepulchrate and the sepulchrate should establish the role of the second $N(CH_2)_3$ cap in the determination of their chemical properties. In the present paper the crystallographic data for a new Ni(II) perchlorate–chloride complex with tris((((aminoisopropyl)amino)methyl)amine as well as preparation and spectroscopic investigations are reported.

## Experimental

### *Preparation*

The complex of Ni(II)–tris(((aminoisopropyl)amino)methyl)amine was synthesized by refluxing 1,2-propylenediamine, formaldehyde, ammonia and nickel chloride (3:6:2:1 mol ratio) in a 1:1 methanol–water mixture with 10 g $Li_2CO_3$ for 48 h. Then the solid deposit was filtered off and the pH of the filtrate adjusted to ~6 with concentrated $HClO_4$. The solution was left at room temperature for 5 h. The pink crystals were filtered off, washed with methanol and recrystallized from hot water. *Anal.* Calc. for $NiC_{12}H_{33}N_7Cl_2O_4$: C, 30.72; H, 7.04; N, 20.95; Cl, 15.14; Ni, 12.52. Found: C, 30.40; H, 7.10; N, 20.63; Cl, 14.81; Ni, 12.52.

### *Physical Measurements*

IR spectra were measured on a Specord-75 IR Spectrophotometer in KBr pellets over the 4000–400 cm$^{-1}$ range. Electronic absorption spectra were recorded with a Hitachi 356 spectrophotometer in water solution over the 200–800 nm range. The magnetic susceptibility was determined by the Faraday method over the 80–300 K range.

### *X-ray Data Collection*

A violet crystal of dimensions 0.5 × 0.5 × 0.2 mm was used for preliminary investigations using the Weissenberg technique and for data collection. The systematic absences *h*00 with *h* odd, 0*k*0 with *k* odd, 00*l* with *l* odd and absence of the fourfold axis on

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$0kl$ Weissenberg photography give $P2_13$ as the possible space group. The intensity data were collected at room temperature on a Stoe-Simens AED diffractometer with graphite monochromated Cu K$\alpha$ radiation ($\lambda$ = 1.54178 Å). Lattice parameter was refined by a least-squares calculation of 54 $\theta$ values. Scans were in the $\omega$–$2\theta$ mode. A total of 1263 intensities measured in the range $3° < 2\theta < 120°$ by keeping $h$ greater or equal to $k$ and $l$ indices, 1033 unique, 49 with $F_o < 2\delta(F_o)$ were cut off. Three standard reflections were measured every hour, intensity variations 2%. Numerical absorption correction ($\mu$ = 37.72 cm$^{-1}$), transmission factors 0.23–0.49. Secondary extinction correction refined to 4.25(8) $\times 10^{-7}$ and $F_c$ multipled by $(1 - xF_c^2)\sin\theta$. X-ray measurements and calculations were performed on Micro VAX II in the Application Laboratory of Stoe & Cie (Darmstadt, F.R.G.).

### *Solution and Refinement*

The structure was solved and refined using the programs SHELX 76 and SHELX 86 [6, 7]. The parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions, constrained to 1.08 Å from their parent C and N atoms. $U_H$ fixed at 1.1 $U_{eq}$ of carrying atom. The residual electron density nowhere exceeded 0.8 e Å$^{-3}$. The final agreement indices $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \Sigma w^{1/2}F_o$ with weights $w = 2.143/\delta^2(F_o)$, were 0.069 and 0.065 respectively. The final atomic parameters and selected bond lengths and angles are listed in Tables 1 and 2 respectively.

TABLE 1. Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Non-hydrogen Atoms

| Atoms[a] | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ (Å$^2$)[b] |
|---|---|---|---|---|
| Ni(1) | 4008(1) | 4008(1) | 4008(1) | 69(1) |
| N(1) | 5329(6) | 5329(6) | 5329(6) | 98(4) |
| C(1) | 4774(7) | 4730(8) | 6111(7) | 106(7) |
| N(2) | 4085(6) | 3937(5) | 5663(5) | 90(4) |
| C(2) | 4403(6) | 2858(7) | 5921(7) | 92(6) |
| C(3) | 3797(6) | 2124(6) | 5270(7) | 92(6) |
| N(3) | 3991(5) | 2368(4) | 4156(5) | 77(4) |
| C(4)* | 4319(12) | 2412(12) | 6953(1) | 77(10) |
| C(5)* | 4108(12) | 1136(12) | 5637(13) | 91(12) |
| Cl(1) | 8563(1) | 8563(1) | 8563(1) | 67(1) |
| Cl(2) | 1998(2) | 1998(2) | 1998(2) | 104(1) |
| O(1) | 1378(7) | 1378(7) | 1378(7) | 168(6) |
| O(2) | 1659(5) | 3053(6) | 1970(6) | 132(3) |

[a] Starred atoms = 50% occupancy. [b] $U_{eq} = \frac{1}{2}(U_{11} + U_{22} + U_{33})$.

TABLE 2. Selected Bond Lengths and Angles

| Bond lengths (Å) | | | |
|---|---|---|---|
| Ni(1)–N(2) | 2.135(7) | C(3)–N(3) | 1.488(10) |
| Ni(1)–N(3) | 2.119(6) | C(2)–C(4) | 1.451(15) |
| N(1)–C(1) | 1.455(9) | C(3)–C(5) | 1.415(15) |
| C(1)–N(2) | 1.469(11) | Cl(2)–O(1) | 1.382(15) |
| N(2)–C(2) | 1.485(10) | Cl(2)–O(2) | 1.427(7) |
| C(2)–C(3) | 1.485(11) | | |
| Bond angles (°) | | | |
| N(2)–Ni(1)–N(3) | 82.4(3) | N(3)–C(3)–C(2) | 108.7(7) |
| Ni(1)–N(2)–C(2) | 106.0(6) | C(4)–C(2)–C(3) | 103.1(9) |
| Ni(1)–N(2)–C(1) | 112.9(5) | C(5)–C(3)–C(2) | 103.5(9) |
| Ni(1)–N(3)–C(3) | 107.4(5) | C(2)–N(2)–C(1) | 113.3(7) |
| N(2)–C(2)–C(4) | 123.6(9) | N(2)–C(1)–N(1) | 113.2(8) |
| N(3)–C(3)–C(5) | 117.6(10) | N(3)–Ni(1)–N(3) | 94.6(3) |
| N(2)–C(2)–C(3) | 108.9(7) | N(2)–Ni(1)–N(2) | 89.9(3) |

## Results and Discussion

The IR spectrum of the title complex exhibits a $\nu$(NH) vibration at 3230 and 3320 cm$^{-1}$ and the band at 1600 cm$^{-1}$ for $\rho_s(NH_2)$ vibration (shifted to ~1120 cm$^{-1}$ after deuteration), indicating the presence of primary amines. This band is absent in the corresponding sepulchrate structure.

The electronic absorption spectrum of the complex shows maxima at 340 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) and 535 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$), typical for a octahedral Ni-N$_6$ chromophore. The magnetic susceptibility gave a magnetic moment of 3.01 BM at 298 K. This also supports the existence of a d$^8$ electronic system in pseudooctahedral geometry. The X-ray structure reveals that the title compounds contain discrete ions $(C_{12}H_{33}N_7Ni)^{2+}$ and chloride and perchlorate ions. The whole cation can be generated by threefold rotational symmetry, with the threefold axis passing through the central Ni ion and N(1) (Fig. 1). The Ni(II) ion is coordinated to the six nitrogen atoms in a pseudooctahedral arrangement with the average Ni–N bond distance 2.13 Å. All the bond distances and angles around the Ni(II) ion, presented in Table 2, are very similar to those of Ni sepulchrate [3]. This indicates that the differences in the next coordination sphere of the discussed Ni(II) semisepulchrate and Ni(II) sepulchrate do not exert a significant influence on the coordination geometry around the Ni(II) ion. The statistical distribution of methyl groups on positions C(4) and C(5) with a population parameter of 0.5 (Table 1) may also cause the chelate rings (built up by ethylenediamine [8] and isopropylenediamine) to be very similar in both compounds. The perchlorate groups in the title compound are probably also disordered which is manifested by rather large thermal parameters of appropriate Cl and O atoms.

We found that the metal ion can be removed in a few minutes from the title semisepulchrate. The following process has been carried out:

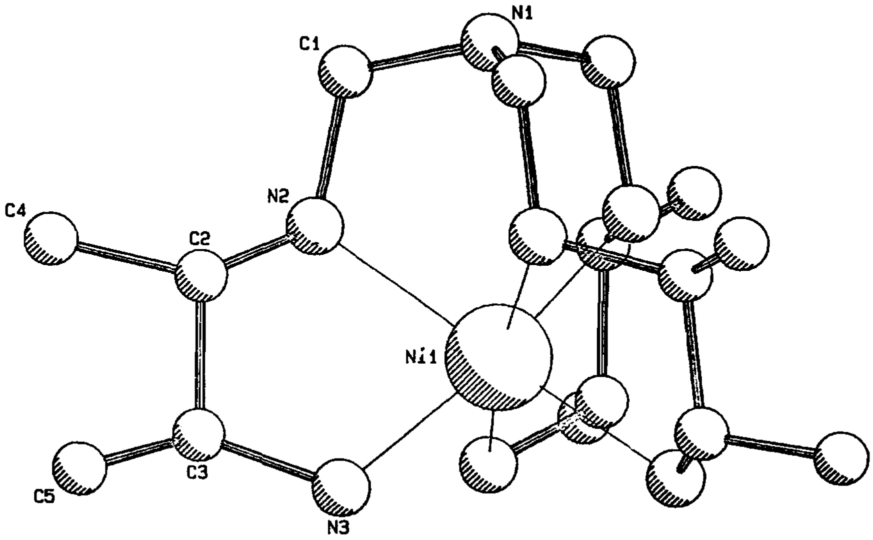

Fig. 1. Perspective view of Ni(II)–tris(((aminoisopropyl)amino)methyl)amine with the labelling scheme used. H atoms have been omitted.

$$\mathrm{Ni(II)\text{–}L + 4CN^- \longrightarrow Ni(CN)_4{}^{2-} + L} \qquad (1)$$

$$\mathrm{Ni(II)\text{–}L + L' \longrightarrow \underset{\text{pink precipitate}}{Ni(L')_2\downarrow} + L} \qquad (2)$$

L = tris(((aminoisopropyl)amino)methyl)amine
L′ = dimethylglyoxime

The $Ni(CN)_4{}^{2-}$ in reaction (1) has been identified by electronic spectra [8]. The free ligand, released during the above described reactions, probably decomposes in the following step due to the presence of the very unstable $R_2N–CH_2–CHR$ group [9].

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