Enantiomeric Conformations of the Ni(II) Perchlorate Complex with Tris(((aminoethyl)-amino)methyl)amine

ANNA ARKOWSKA, EWA GRAŻYŃSKA*

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University, 50370 Wrocław, Poland

RYSZARD KUBIAK† and HELMUT PAULUS

Technical University Darmstadt, Petersenstrasse 15, 61 Darmstadt, F.R.G.

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One of the most important classes of metal template reactions is the formation of compounds which are classified as cryptates [1]. Condensation of $NiCl_2$ with formaldehyde, ethylenediamide and ammonia provides two types of Ni(II) complexes: sepulchrates [2] and semisepulchrates. The synthesis and spectroscopic properties of the Ni(II) perchlorate complex tris(((aminoethyl)amino)methyl)amine (trivial name, semisepulchrate) has been recently published [3]. However, structural data have not been reported yet. As a part of our systematic studies on encapsulated metal ions we have undertaken the X-ray determination of the crystal structure.

Experimental

The complex was synthesized by a procedure described in ref. 3. *Anal.* Calc. for $NiC_9H_{27}N_7Cl_2O_8$: C, 22.02; H, 5.55; N, 19.97; Cl, 14.44; Ni, 11.96. Found: C, 22.27; H, 5.56; N, 19.59; Cl, 15.31; Ni, 11.93%. The spectroscopic properties were: an IR band at 1590 cm^{-1} for $\rho_s(NH)$, indicating the presence of primary amines; absorption maxima at 338 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) and 530 nm ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$), typical of a pseudooctahedral $Ni-N_6$ chromophore. These and a magnetic moment of 3.11 B.M. at 298 K suggested the Ni(II)–semisepulchrate type of complex.

Crystal Data

$C_9H_{27}N_7Ni \cdot ClO_4$: $a = b = c = 12.385(2)$ Å; $V = 1899.7$ Å; regular space group $P2_13$; $Z = 4$, $D_{calc} = 1.72$ g cm^{-3}, $D_{measd} = 1.70$ g cm^{-3}; $F(000) = 1024$, μ(Cu Kα) = 44.18 cm^{-1}, λ(Cu Kα) = 1.54178 Å.

The intensities of 1079 reflections ($3 < 2\theta < 120°$) were recorded on a Stoe-Simens AED diffractometer using Cu Kα radiation and $\omega/2\theta$ scan. The structure was solved and anisotropically refined, using the programs SHELX86 [4] and SHELX76 [5], to an R value of 0.044 for 920 significant $F_o > 2\delta(F_o)$ reflections. The structure consists of discrete ions $C_9H_{27}N_7Ni^{2+}$ and perchlorate ions. Moreover, the structure analysis revealed that, in the crystal, two enantiomeric conformations of Ni(II)–tris(((aminoethyl)amino)methyl)amine exist, which hindered

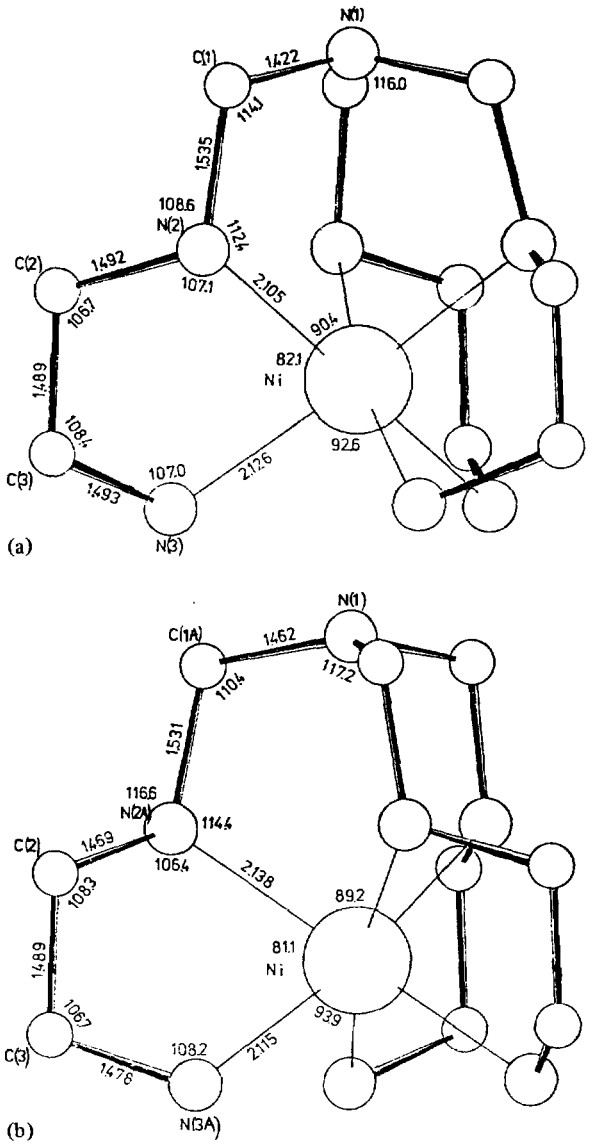

Fig. 1. Perspective view of Ni(II)–tris(((aminoethyl)amino)-methyl)amine with the labelling scheme used: (a) and (b) are enantiomeric conformations. The N(1) and Ni(1) atoms lie on a three-fold axis. Bond distances and angles have e.s.d. values of 0.006–0.023 Å and 0.2–1.2°.

*Author to whom correspondence should be addressed.

†Permanent address: Institute for Low Temperature and Structure Research PAN, pl. Katedralny 1, 50950 Wrocław, Poland.

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TABLE 1. Positional Parameters ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^3$). $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$

Atom[a]	*x/a*	*y/b*	*z/c*	U_{eq} ($Å^2$)
Ni(1)	5207(1)	5207(1)	5207(1)	31(1)
N(1)	3811(3)	3811(3)	3811(3)	55(2)
C(1)	4620(8)	4149(8)	3069(6)	79(3)
C(1A)	3839(16)	4789(18)	3151(16)	57(4)
N(2)	5515(5)	4841(5)	3576(4)	55(3)
N(2A)	4622(11)	5613(12)	3635(12)	39(4)
C(2)	5574(5)	5887(5)	2983(5)	67(3)
C(3)	6279(5)	6614(6)	3631(5)	68(3)
N(3)	5785(6)	6749(5)	4723(6)	66(3)
N(3A)	6593(12)	6005(13)	4609(15)	51(4)
Cl(1)	7416(1)	7416(1)	7416(1)	50(1)
O(1)	8070(4)	8070(4)	8070(4)	103(2)
O(2)	7710(5)	7492(5)	6331(4)	116(3)
Cl(2)	341(1)	341(1)	341(1)	48(1)
O(3)	975(5)	975(5)	975(5)	166(3)
O(3A)	−321(34)	−321(34)	−321(34)	134(4)
O(4)	919(8)	−473(6)	−193(8)	139(4)
O(4A)	1229(18)	−288(19)	478(22)	120(4)

[a]Atoms denoted simultaneously with lables (*n*) and (*n*A) are statistically distributed. Population parameter was refined to 74.83% and 25.23% for (*n*) and (*n*A) atoms respectively.

refinement. Therefore no attempts were made to localize the hydrogen atoms. The atomic parameters are given in Table 1. Bond distances and angles for both enantiomeric conformations are shown in Fig. 1.

We are continuing physicochemical investigations of related complexes with other diamines as well as their crystallographic structural measurements.

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