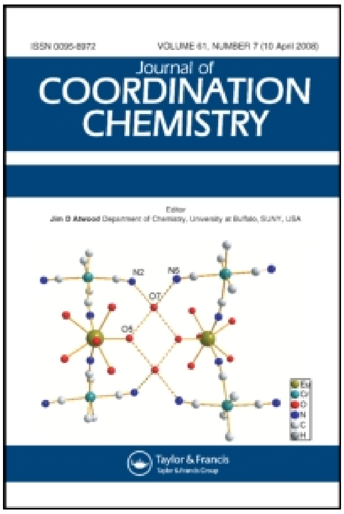

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ISOLATION, X-RAY STRUCTURE, AND IMMOBILIZATION ON SILICA SURFACES OF 5-AMINOMETHYL-5,12-DIMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-11-ENENICKEL(II) DIPERCHLORATE MONOHYDRATE

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ISOLATION, X-RAY STRUCTURE, AND IMMOBILIZATION ON SILICA SURFACES OF 5-AMINOMETHYL-5,12-DIMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-11-ENENICKEL(II) DIPERCHLORATE MONOHYDRATE

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The violet "arm on" title complex (1) has been isolated. It crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 10.184 (2), b = 12.719 (2), c = 17.096 (2) Å, V = 2214.4 Å^3, Z = 4 and was refined to $R(R_w)$ = 0.060 (0.066) for 1693 reflections. The complex was attached to γ-carboxypropylsilica. The "blue-to-yellow" conversion for bound complex is not completely reversible due to hydrogen bonding of complex species with the silica surface.

KEYWORDS: nickel(II), tetraazamacrocycle, X-ray structure, silica gel, immobilization

INTRODUCTION

Tetraazamacrocyclic complexes with pendant arms having additional ligating atoms have recently attracted considerable attention.[1,2] Donor arm availability in a flexible side chain can cause reactions of axial ligands to be reversible and makes it possible for covalent macrocyclic complex immobilization on the surface of a polymer or silica.[3]

In recent years a new C-functionalized macrocycle class has been prepared by Korybut-Daszkiewicz by nitromethane addition to the -C = N group of 14-member macrocyclic nickel complexes.[4] The molecular structure of *catena*-5,7,12,14-tetramethyl-5-aci-nitromethyl-1,4,8,11-tetraazacyclotetradec-11-enenickel(II) perchlorate dihydrate is described elsewhere.[5] Reduction of the nitro group gives aminomethyl derivatives. The relative configurations of substituents and macrocyclic ligand conformation of low-spin complexes with non-coordinate pendant groups have been elucidated through NMR data.[6]

This complex is of interest because the pendant aminomethyl chain is not long enough to secure axial coordination. In this case one can expect the coordination polyhedron to be an unusually distorted octahedron or the formation of polynuclear

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complexes. The present paper describes an alternative method of complex (1) isolation, its X-ray structure and immobilization on γ-carboxypropylsilica.

EXPERIMENTAL

Synthesis of Complex (I)

5-Nitromethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-11-enenickle (II) diperchlorate was prepared as described elsewhere.[4]. This complex (0.543 g, 0.001 mol) was dissolved in a mixture of water and concentrated HCl (15 cm^3 and 5 cm^3). Zinc dust (1.7g) was added to the solution, the mixture was stirred for 25 min, and the solution filtered. Saturated aqueous Na_2CO_3 (75 cm^3), NaOH (10 g) dissolved in water (20 cm^3) and $NaClO_4$ (1 g) were added into filtrate. Under these conditions basic zinc carbonate precipitate formed *in situ* was dissolved. The product was extracted with acetonitrile. High concentrations of salts prevented acetonitrile dissolving in the aqueous phase. The extract was dried over $MgSO_4$, then evaporated to small volume when violet crystals were precipitated upon ethanol addition. The compound was recrystallized from water; yield 35%. *Anal.*: Calcd. for (1): C, 29.40; H, 5.88; N, 14.18%. Found: C, 30.15; H, 5.80; N, 14.18%. I.R. (cm^{-1}): 3270 (NH); 3380 (NH_2); 1670 (C = N). Infrared spectra were recorded on a UR-20 spectrophotometer.

X-ray methods

The X-ray data for (1) were collected on a Syntex P1 automatic diffractometer (MoK_α radiation, Nb-filter). The intensity measurements were made by the $\theta/2\theta$ scan technique. Crystals of $NiC_{13}H_{31}N_5O_9Cl_2$ are orthorhombic. Crystal data and details of data collection and refinement are presented in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares. Some 1693 reflections with $I > 3\sigma(I)$ were used for solving and refining of the structure; final $R(R_w)$ factors: 0.060 (0.066). Calculations were carried out with SHELXTL package (Sheldrick, 1981) on a Nova-3 computer incorporated in the Nicolet R3 system.

Immobilization studies

γ-Carboxypropylsilica ($\rightarrow Si - (CH_2)_3 - COOH$) was prepared as described elsewhere.[7]

Procedure I

Dicyclohexylcarbodiimide (115 mg, 0.55 mmol) and triethylamine (0.2 cm^3) were added to a suspension of $\rightarrow Si - (CH_2)_3 - COOH$ in dimethylformamide. Complex (1) (100 mg, 0.2 mmol) was dissolved in a minimum amount of dimethylformamide and dropped into the suspension. The mixture was stirred for 48 h. Lilac solids were filtered off, washed with dimethylformamide and water. On drying, the lilac solid became yellow.

Table 1 Crystal data, data collection and refinement parameters for complex.

Mol. wt.	548.7
Dimen. mm	0.3 × 0.3 × 0.3
Space group	$P2_12_12_1$
Cell constants	
a, Å	10.184(2)
b, Å	12.719(2)
c, Å	17.096(2)
2θ limits of reflns (15) used to determine all constants	$20.0<2\theta<25.0$
Z	4
ρ_{calcd} g cm^{-3}	1.539
$\rho_{exptl.}$ g cm^{-3}	1.54
Diffractometer	Syntex P1
Monochromator (Bragg 2θ angle, deg.)	Nb filter
Radiation	MoK$_\alpha$, 0.71069
Take off angle, deg.	4.0
Scan method	$\theta/2\theta$
Scan speed, min/max, deg min^{-1}	3.4/12.0
Scan width, deg	1.0
Background/scan time ratio (TR)	1.0
No. of standards (monitoring freq./no. of reflcns)	3/100
2θ limits of data, deg	$3.5<2\theta<45$
h,k,l	0,0,0 to h,k,l
No. of data	1800
No. of data used in final refinement ($I > 3\sigma)(I)$	1693
No. of data/no. of variables	6.44
μ, cm^{-1}	11.68
$R = \{[\Sigma \| F_o - F_c \|]^2/[\Sigma \| F_o \|]^2\}^{1/2}$	0.060
$R_w = [\Sigma(\| F_o \|\| F_c \|)w^{1/2}]/[\Sigma(\| F_o \|)^{1/2}]$	0.066
$w = 1/6(F) + 0.0092F^2$	

Procedure II

Complex (1) (200 mg, 0.4 mmol) was dissolved in a minimum amount of water and a 10% aqueous solution of potassium hydroxide (0.05 cm^3) was added. In another vessel $\rightarrow Si - (CH_2)_3 - COOH$ (100 mg) with excess of $SOCl_2$ was heated for 1 h. The cooled modified silica gel was dropped into the macrocycle solution and mixture was stirred for 30 min. Solids were filtered off washed with water and dried. The surface complex concentration in both methods was of the same level: 0.17 and 0.13 mol/g (according to Ni and N analysis).

RESULTS AND DISCUSSION

The molecular structure of (1) is shown in Figure 1. Non-hydrogen atoms coordinates are listed in Table 2; interatomic distances and angles are given in Table 3. The nickel atom is in the N_4 plane and is bonded to a water molecule and the nitrogen atom of the pendant arm. The Ni-N distance in the macrocyclic plane is the common value for high spin 14-members tetraazanickel(II) complexes.[8] The shorter Ni-N2 distance (2.036 Å) with the imine nitrogen, probably, can be explained by additional π-bonding between these atoms. The most interesting feature of the structure is the angle between the NH_2-Ni-H_2O axis and the NiN_4 plane. The CH_2NH_2-bridge length gives no possibility for the nitrogen atom to be

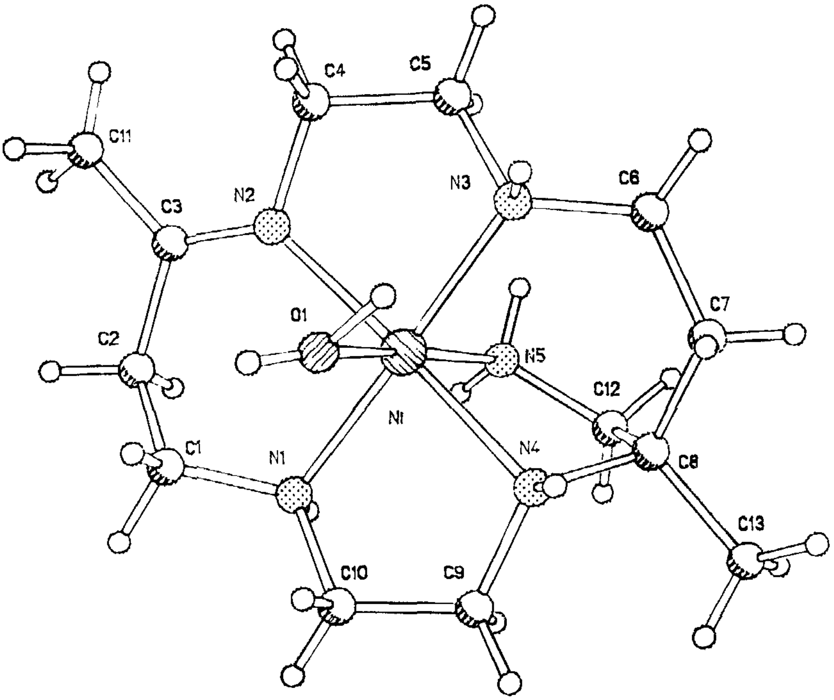

Figure 1 Structure of the complex cation.

placed exactly over the nickel ion and angle (N5-Ni-N_4 plane) is 81°. The coordinated water molecule deviates from perpendicular too, and is on the same axis as the pendant arm nitrogen and nickel atoms (Figure 2).

Unusual distorted axial ligand coordination leads to an increase of the bond distances between the nickel atom and nitrogen and oxygen atoms of axial ligands. The Ni-O and Ni-N distances are 2.24 and 2.15 Å, respectively; these are slightly longer than commonly observed values.[8] The ClO_4^- anion is not coordinated to Ni ion and is not hydrogen bonded to water molecules and protons of the amino group. The water oxygen and amine nitrogen atoms are not hydrogen bonded.

Each perchlorate anion has statistical disorder, occupying two equivalents positions. Formally, one can observe eight oxygen half-atoms around each chlorine.

The macrocyclic complex was prepared by a procedure similar to a literature method.[6] In contrast, the product was isolated by acetonitrile extraction from an aqueous salt solution. This procedure eliminates laborious complex clean-up from the zinc oxide precipitate.[6] The method can be used in other cases for macrocyclic complexes due to the hydrophobic nature of hydrocarbon fragments and their high solubility in acetonitrile.

Silica gel-bound complex has been prepared by two different methods. The complex can be attached to silica gel in weakly alkaline solution in each case. This appears to be a result of surface charge interaction with positively charged complex ions. In acidic media, positive surface charge prevents interaction with complex species.

Table 2 Final positional parameters for non-hydrogen atoms of the complex.

Atom	x/a	y/b	z/c
Ni	0.7448(1)	0.0410(1)	0.8686(1)
O1	0.8433(7)	0.1579(5)	0.9469(4)
N1	0.6854(8)	0.1587(7)	0.7952(4)
N2	0.9234(7)	0.0260(7)	0.8163(5)
N3	0.8101(8)	0.0728(7)	0.9443(5)
N4	0.5702(8)	0.0668(6)	0.9250(4)
N5	0.6268(8)	-0.0763(7)	0.8111(4)
C1	0.7945(11)	0.2125(10)	0.7595(6)
C2	0.8773(12)	0.1486(12)	0.7141(6)
C3	0.9691(8)	0.0713(11)	0.7560(6)
C4	1.0059(12)	-0.0447(11)	0.8626(8)
C5	0.9192(14)	-0.1247(10)	0.9032(9)
C6	0.7089(14)	-0.1501(10)	0.9722(7)
C7	0.5807(14)	-0.0985(12)	0.9943(8)
C8	0.5046(9)	-0.0366(9)	0.9357(5)
C9	0.4992(10)	0.1498(10)	0.8804(7)
C10	0.5915(13)	0.2226(8)	0.8431(6)
C11	1.0985(13)	0.0542(17)	0.7211(9)
C12	0.5019(12)	-0.0882(9)	0.8531(7)
C13	0.3603(13)	-0.0229(14)	0.9632(8)
C11	0.8560(2)	-0.1941(2)	0.6315(1)
O11	0.7513(12)	-0.1322(9)	0.6052(6)
O11A	0.8302(83)	-0.3058(72)	0.6173(42)
O12	0.8570(26)	-0.2956(22)	0.5955(16)
O12A	0.9694(30)	-0.1236(25)	0.6262(18)
O13	0.9780(16)	-0.1700(13)	0.5918(9)
O13A	0.7969(40)	-0.2342(33)	0.7063(23)
O14	0.8757(13)	-0.1901(10)	0.7183(8)
O14A	0.8837(50)	-0.2550(44)	0.5761(30)
C12	0.5440(2)	-0.4276(2)	0.8749(2)
O21	0.6526(19)	-0.3688(15)	0.8976(11)
O21A	0.5962(22)	-0.3380(18)	0.8205(12)
O22	0.5507(16)	-0.4906(12)	0.8064(10)
O22A	0.5999(23)	-0.4200(20)	0.9435(13)
O23	0.5345(22)	-0.5176(17)	0.9372(12)
O23A	0.5994(53)	-0.5172(40)	0.8470(28)
O24	0.4263(17)	-0.3628(16)	0.8806(9)
O24A	0.4035(22)	-0.4139(21)	0.8659(13)

The behaviour of bound complex with pH change is worthy of attention. The samples prepared in under mild conditions (carbodiimide procedure) keep their lilac colour in moist, weakly alkaline media. On acidifying with acetic acid the expected "blue-to-yellow" conversion occurred and was partially reversible, the lilac colour being restored on ammonia addition. However, it is impossible to regenerate the lilac colour of the dried sample. On drying the "anchored" complex moiety, presumably, binds to the surface with hydrogen bonds due to interaction of N-atoms with Si-OH groups. It is known that additional hydrogen bonding leads to irreversible sorption of metal complexes.[9] Hydrogen bonded complexes do not react with additional ligands and high-spin complex formation is impossible. The "anchored" complex cannot be washed-out of the silica by dilute sulfuric acid, but can be removed by combined treatment with oxidant ($Na_2S_2O_8$, $NaBrO_3$) and acid.

Table 3 Interatomic distances (Å) and angles (deg) for the complex.

Distances			
Ni-N1	2.044 (8)	Ni-N2	2.036 (7)
Ni-N3	2.052 (9)	Ni-N4	2.049 (8)
Ni-N5	2.152 (4)	Ni-O1	2.239 (1)
N1-C1	1.441 (14)	N1-C10	1.499 (14)
N2-C3	1.269 (1)	N2-C4	1.464 (16)
N3-C5	1.470 (16)	N3-N6	1.502 (16)
N4-C8	1.486 (14)	N4-C9	1.489 (14)
N5-C12	1.469 (14)	C2-C1	1.405 (17)
C3-C2	1.534 (17)	C3-C11	1.463 (17)
C4-C5	1.515 (19)	C6-C7	1.510 (20)
C7-C8	1.492 (17)	C8-C12	1.557 (15)
C8-C13	1.553 (16)	C9-C10	1.466 (16)
Angles			
Ni-N1-N2	93.6 (3)	Ni-N1-N3	177.5 (3)
N2-Ni-N3	85.5 (3)	N1-Ni-N4	85.1 (3)
N2-Ni-N4	175.5 (3)	N3-Ni-N4	95.6 (3)
Ni-N1-C1	112.4 (7)	Ni-N1-C10	104.5 (6)
C1-N1-C10	117.8 (9)	Ni-N2-C3	129.9 (7)
Ni-N2-C4	109.4 (7)	C3-N2-C4	120.5 (9)
Ni-N3-C5	105.1 (7)	Ni-N3-C6	116.0 (7)
C5-N3-C6	112.1 (9)	Ni-N4-C8	107.8 (6)
Ni-N4-C9	107.1 (6)	C8-N4-C9	118.1 (8)
N1-C1-C2	114.9 (11)	C1-C2-C3	118.6 (9)
N2-C3-C2	116.5 (8)	N2-C3-C11	126.4 (12)
C2-C3-C11	117.0 (11)	N2-C4-C5	109.0 (10)
N3-C5-C4	111 0(10)	N3-C6-C7	112.9 (10)
C6-C7-C8	120.7 (11)	N4-C8-C7	108.4 (9)
N4-C8-C12	105.6 (8)	C7-C8-C12	113.3 (10)
N4-C8-C13	111.3 (10)	C7-C8-C13	110.3(10)
C12-C8-C13	107.8 (9)	N4-C9-C10	111.0 (9)
N2-C10-C9	107.7 (9)	N5-C12-C8	112.7 (9)

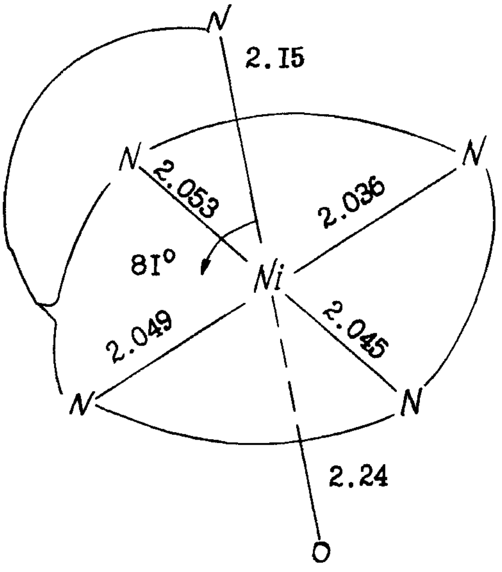

Figure 2 Schematic diagram for the coordination polyhedron.

Supplementary material

Lists of thermal parameters, bond lengths and angles, and observed and calculated structure factors are available from S.S.S. upon request.

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