Synthesis and structure of the [Ni(H_2L)Cl]Cl complex with the chiral pentadentate nitrogen-containing ligand H_2L derived from the natural terpenoid (+)-3-carene*

S. V. Larionov,[a]★ L. I. Myachina,[a] L. A. Glinskaya,[a] R. F. Klevtsova,[a] S. N. Bizyaev,[b] and A. V. Tkachev[b]

[a]*A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrentieva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 330 9489. E-mail: lar@che.nsk.su*

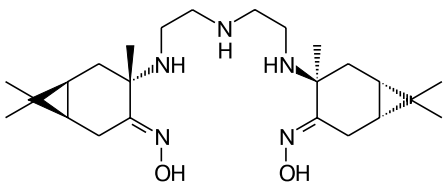
[b]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383) 330 9752. E-mail: benzol@nioch.nsc.ru*

The reaction of $NiCl_2$ with the chiral pentadentate nitrogen-containing ligand H_2L derived from the natural terpenoid (+)-3-carene produced the paramagnetic [Ni(H_2L)Cl]Cl complex. The crystal structure of this complex was established by X-ray diffraction.

Key words: nickel(II) complexes, synthesis, chirality, polydentate ligands, terpenoids, X-ray diffraction study.

Investigations of the complex formation of biologically active metals with organic ligands derived from natural compounds is a promising field of coordination and bioinorganic chemistry. Ligands derived from optically active natural compounds are of special interest. In particular, the development of procedures for the synthesis and studies of metal complexes with derivatives of chiral natural terpenoids are presently underway.[1—4] This class of chiral polydentate ligands containing both open-chain and macrocyclic heteroatomic fragments has attracted considerable attention. Earlier,[4—8] we have synthesized a series of 3*d* transition metal coordination compounds with chiral tetradentate ligands derived from terpenoids, as well as a seven-coordinate Co^{II} complex with a chiral pentadentate nitrogen-containing macrocyclic ligand derived from the monoterpene (−)-α-pinene.[9]

The aim of the present study was to synthesize a Ni^{II} complex with the chiral pentadentate nitrogen-containing ligand, *N,N*-di(2-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}ethylamino)amine (H_2L), having an open-chain topology of the heteroatomic fragments and to determine its structure.



H_2L

* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

Results and Discussion

The reaction of $NiCl_2$ with H_2L in EtOH followed by crystallization from CH_3CN afforded the crystalline [Ni(H_2L)Cl]Cl compound (**1**).

According to the X-ray diffraction study, complex **1** has a ionic structure consisting of the $[Ni(H_2L)Cl]^+$ cations and Cl^- anions. The fragment of the crystal structure of complex **1** (all atoms occupy general positions) is presented in Fig. 1. The Ni^{II} atom (coordination number 6) is coordinated by the N atoms of the pentadentate ring-forming ligand, *viz.*, the H_2L molecule, resulting in the closure of four five-membered chelate NiN_2C_2 rings. The Ni—N distances are in the range of 2.062(2)—2.181(2) Å, the shortest bonds being observed with the N atoms of the oxime groups and the N atom of the central NH group of the diethylenetriamine fragment. The coordination sphere of the Ni atom also involves the Cl atom. The resulting $NiClN_5$ coordination unit can be described as a distorted octahedron slightly elongated along the line between the apical N(1) and Cl(1) atoms (N(1)—Ni(1)—Cl(1) angle is 155.1(1)°). The additional five-membered NiNOHCl ring is formed by a strong O—H...Cl hydrogen bond (Cl(1)...O(1), 2.985(3) Å) involving the inner-sphere Cl(1) atom.

Four five-membered chelate NiN_2C_2 rings are nonplanar (see Fig. 1). The chelate rings involving the N atoms

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1708—1711, September, 2007.

1066-5285/07/5609-1771

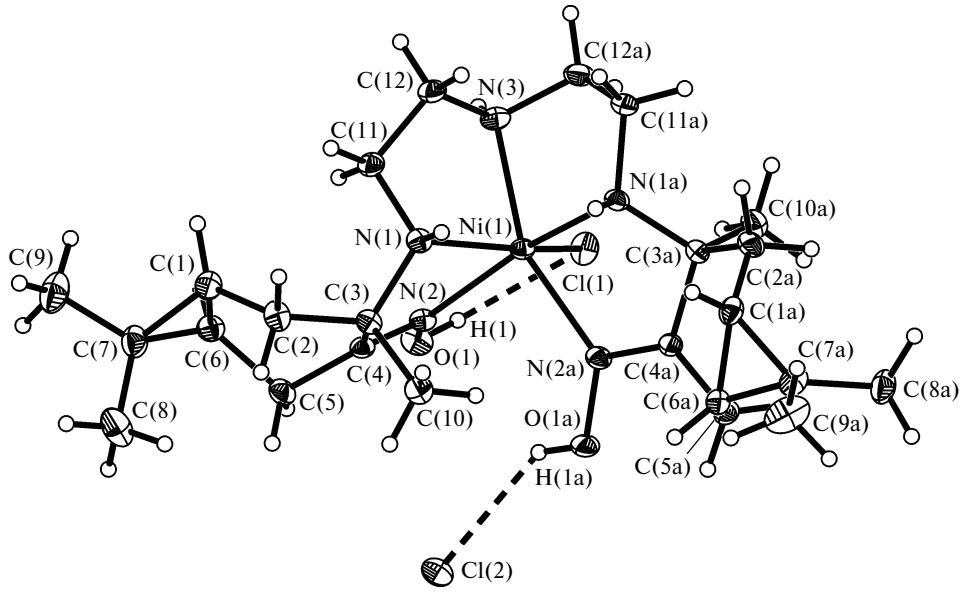


Fig. 1. Fragment of the crystal structure of complex **1**. The atoms are represented by displacement ellipsoids at the 50% probability level.

of the oxime and amino groups adopt an envelope conformation with the N(1) and N(1a) atoms deviating from the planes through the other four atoms of the rings by 0.659(3) and −0.521(3) Å, respectively. The rings involving the N atoms of only the amino groups also have an envelope conformation with the C(11) and C(12a) atoms deviating from the planes through the other four atoms of the rings by 0.629(3) and 0.627(4) Å, respectively. Both six-membered carbocycles adopt a distorted boat conformation with the C(2) and C(5) atoms and the C(2a) and C(5a) atoms locating on one side of the C(1)C(3)C(4)C(6) and C(1a)C(3a)C(4a)C(6a) planes, respectively; the corresponding deviations are 0.485(4), 0.673(3), 0.429(4), and 0.690(3) Å. The angles between the dimethylcyclopropane fragments, which share the C(1)—C(6) and C(1a)—C(6a) bonds with the six-membered carbocycles, and the planes through the C(1)C(3)C(4)C(6) and C(1a)C(3a)C(4a)C(6a) atoms are 141.1 and 138.3°, respectively. The hydrogen-bonded five-membered Ni(1)N(2)O(1)H(1)Cl(1) ring is virtually planar; the average deviation from the mean plane is 0.024(1) Å.

The mutual arrangement of the complex $[Ni(H_2L)Cl]^+$ cations and the outer-sphere Cl^- anions in the crystal structure is shown in Fig. 2. The outer-sphere $Cl(2)^-$ anion forms a hydrogen bond with the OH group of the adjacent complex cation; d(Cl(2)...O(1a)) = 3.138(3) Å. In addition to the hydrogen bonds, there are also short contacts at the van der Waals level; d(Cl(2)...N(3)) = 3.424(2) Å. As a result, the cations are linked to each other by a network of hydrogen bonds and van der Waals contacts to form chains running along the *b* axis.

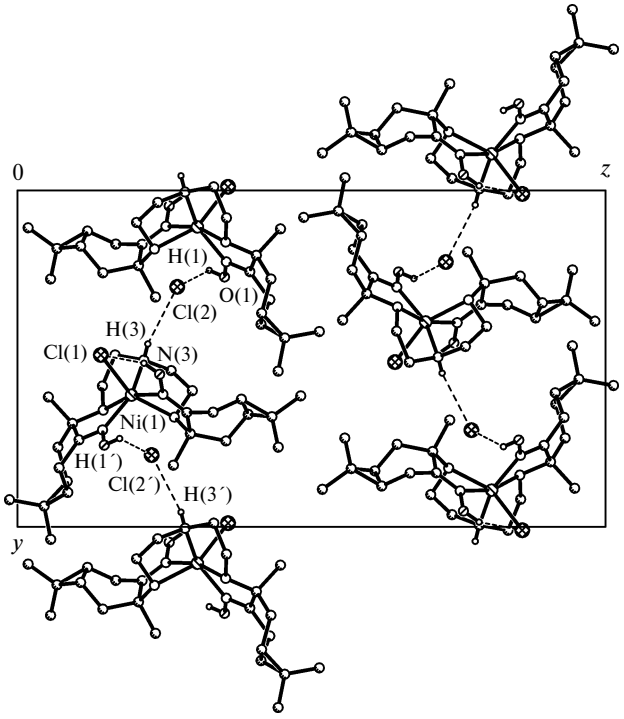


Fig. 2. Crystal structure projected onto the (100) plane. The hydrogen bonds and intermolecular contacts resulting in the formation of chains are indicated by dashed lines (hydrogen atoms are omitted).

For paramagnetic compound **1**, μ_{eff} = 3.14 μ_B corresponds to the high-spin state of the d^8-electron configuration (octahedral ligand field).

Table 1. Crystallographic characteristics and the X-ray data collection and refinement statistics for compound **1**

Parameter	Characteristics
Molecular formula	$C_{24}H_{43}Cl_2N_5NiO_2$
Molecular weight	563.24
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	7.9925(2)
b/Å	14.2761(3)
c/Å	24.9516(7)
V/Å^3	2847.02(12)
Z	4
ρ_{calc}/g cm^{-3}	1.314
μ/mm^{-1}	0.898
Crystal dimensions/mm	0.3×0.21×0.20
F(000)	1200
θ-Scan range/deg	1.63—27.49
Number of measured reflections	22035
Number of independent reflections	6547
R_{int}	0.0281
Number of reflections with $I > 2\sigma(I)$	5950
Number of variables	356
GOOF on F^2	1.018
R factor based on reflections with $I > 2\sigma(I)$	
R_1	0.0286
wR_2	0.0726
R factor based on all I_{hkl}	
R_1	0.0355
wR_2	0.0810
Absolute structure parameter	0.007(9)

Compound **1** is the first complex with a chiral pentadentate ligand derived from terpene having an open-chain topology of heteroatomic fragments.

Experimental

Rectified EtOH and $NiCl_2 \cdot 6H_2O$ of analytical grade were used. The ligand H_2L was prepared according to a known procedure,[10] m.p. 144—146 °C (from CH_2Cl_2—MeOH), $[\alpha]_{578}^{22}$ +170 (*c* 1.78, Py).

Chloro[*N*,*N*-di-(2-{(1*S*,3*S*,6*R*)-4[(*E*)-hydroxyimino]-3,7,7-trimethylbicyclo[4.1.0]hept-3-yl}ethylamino)amine]nickel(II) chloride [Ni(H_2L)Cl]Cl (1). Solutions of $NiCl_2 \cdot 6H_2O$ (0.048 g, 0.2 mmol) and H_2L (0.087 g, 0.2 mmol) in minimum amounts of EtOH heated to 50 °C were mixed. The beaker with the solution was closed with a lid and kept in air for 7 days. The blue viscous oil that formed after evaporation of the solvent was dissolved in CH_3CN, and the solution was kept in air for 2 days. The blue crystals that precipitated were filtered off by suction, washed with CH_3CN and hexane, and dried in air. The yield was 0.063 g (56% based on consumed [Ni(H_2L)Cl]Cl). Found (%): C, 52.0; H, 7.8; N, 12.4. $C_{24}H_{43}N_5NiCl_2O_2$. Calculated (%): C, 51.2; H, 7.6; N, 12.4. IR, ν/cm^{-1}: 3334, 3225, 3148, 3088, 3011, 2925, 2874, 1647, 1336, 1301, 1240, 1229, 1171, 1144, 1101, 1056, 1019, 1004, 980, 930, 841, 810, 762, 721, 687, 629, 602, 553, 531, 506, 440. The IR spectrum of the H_2L ligand is consistent with that described earlier.[10] Microanalyses were carried out on Hewlett Packard 185 and Carlo Erba 1106 analyzers. The magnetic susceptibility of polycrystalline complex **1** was measured by the Faraday method at 20 °C. The IR spectra were recorded on a Scimitar FTS 2000 spectrometer in the 4000—400 cm^{-1} region. Samples were prepared as Nujol mulls and in fluorinated oil.

For the X-ray diffraction study, a prismatic crystal was selected from the crystalline product of the synthesis. The unit cell parameters and the intensities of reflections were measured on an automated Bruker X8Apex CCD diffractometer according to a standard procedure at room temperature (Mo-Kα radiation, graphite monochromator). The crystallographic characteristics and the selected X-ray data collection and refinement statistics

Table 2. Selected interatomic distances (d) and bond angles (ω) in the structure of complex **1**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Ni(1)—N(2)	2.062(2)	N(2)—Ni(1)—N(3)	109.1(1)	N(1a)—Ni(1)—N(1)	94.7(1)
Ni(1)—N(1)	2.181(2)	N(2)—Ni(1)—N(1a)	162.7(1)	N(2)—Ni(1)—N(2a)	94.0(1)
Ni(1)—N(3)	2.088(2)	N(3)—Ni(1)—N(1a)	81.87(8)	N(3)—Ni(1)—N(2a)	156.4(1)
N(1)—C(11)	1.466(3)	N(1a)—Ni(1)—N(2a)	76.83(7)	N(3)—Ni(1)—N(1)	82.5(1)
N(1)—C(3)	1.489(3)	N(2)—Ni(1)—N(1)	74.3(1)	N(2a)—Ni(1)—N(1)	109.0(1)
N(2)—C(4)	1.269(3)	N(2)—Ni(1)—Cl(1)	87.1(1)	N(2a)—Ni(1)—Cl(1)	88.3(1)
N(2)—O(1)	1.393(2)	N(3)—Ni(1)—Cl(1)	88.40(6)	N(1a)—Ni(1)—Cl(1)	107.0(1)
N(3)—C(12)	1.476(3)	N(1)—Ni(1)—Cl(1)	155.1(1)	C(12)—N(3)—Ni(1)	109.7(1)
C(3)—C(4)	1.525(3)	C(11)—N(1)—C(3)	114.3(2)	C(12a)—N(3)—Ni(1)	105.0(1)
C(11)—C(12)	1.509(3)	C(11)—N(1)—Ni(1)	103.5(1)	C(11a)—N(1a)—Ni(1)	111.1(1)
Ni(1)—N(2a)	2.111(2)	C(3)—N(1)—Ni(1)	108.8(1)	C(3a)—N(1a)—Ni(1)	112.1(1)
Ni(1)—N(1a)	2.102(2)	C(3a)—N(1a)—C(11a)	117.6(2)	C(12)—N(3)—C(12a)	113.3(2)
Ni(1)—Cl(1)	2.475(1)	C(4)—N(2)—O(1)	116.0(2)	C(4a)—N(2a)—O(1a)	111.5(2)
N(1a)—C(11a)	1.498(3)	C(4)—N(2)—Ni(1)	121.3(1)	C(4a)—N(2a)—Ni(1)	117.3(1)
N(1a)—C(3a)	1.491(3)	O(1)—N(2)—Ni(1)	122.7(1)	O(1a)—N(2a)—Ni(1)	131.3(1)
N(2a)—C(4a)	1.284(3)				
N(2a)—O(1a)	1.409(2)				
N(3)—C(12a)	1.479(3)				
C(3a)—C(4a)	1.528(3)				
C(11a)—C(12a)	1.512(4)				

for the structure of the complex are given in Table 1. The acentric space group was chosen based on the analysis of systematic absences supported by calculations. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms with the use of the SHELX97 program package.[11] Two hydrogen atoms were located in difference Fourier maps and refined isotropically. Other hydrogen atoms were positioned geometrically and refined using a riding model. Selected interatomic distances and bond angles are given in Table 2. The complete tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structural Database (CCDC 652454) and can be obtained from the authors.

We thank L. A. Sheludyakova for recording the IR spectra and V. A. Daletskii for measuring the static magnetic susceptibility.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32147).

References

1. A. von Zelewsky and O. Mamula, *J. Chem. Soc., Dalton Trans.*, 2000, 219.
2. O. Mamula and A. von Zelewsky, *Coord. Chem. Revs*, 2003, **242**, 87.
3. A. V. Tkachev, *Ross. Khim. Zh.*, 1998, **42**, 42 [*Mendeleev Chem. J.*,1998, **42** (Engl. Transl)].
4. S. V. Larionov and A. V. Tkachev, *Ross. Khim. Zh.*, 2004, **48**, 154 [*Mendeleev Chem. J.*, 2004, **48** (Engl. Transl.)].
5. S. V. Larionov, L. I. Myachina, R. F. Klevtsova, L. A. Glinskaya, L. A. Sheludyakova, S. N. Bizyaev, and A. V. Tkachev, *Dokl. Akad. Nauk*, 2004, **397**, 214 [*Dokl. Chem.*, 2004, **397**, 156 (Engl. Transl.)].
6. S. V. Larionov, L. I. Myachina, R. F. Klevtsova, L. A. Glinskaya, L. A. Sheludyakova, S. N. Bizyaev, and A. V. Tkachev, *Zh. Neorg. Khim.,* 2005, **50**, 582 [*Russ. J. Inorg. Chem.*, 2005, **50**, 521 (Engl. Transl.)].
7. R. F. Klevtsova, L. A. Glinskaya, L. I. Myachina, and S. V. Larionov, *Zh. Strukt. Khim.,* 2005, **46**, 1141 [*Russ. J. Struct. Chem.*, 2005, **46**, 1104 (Engl. Transl.)].
8. S. V. Larionov, L. I. Myachina, L. A. Sheludyakova, E. G. Boguslavskii, S. N. Bizyaev, and A. V. Tkachev, *Zh. Neorg. Khim.,* 2007, **52**, 112 [*Russ. J. Inorg. Chem.*, 2007, **52**, 42 (Engl. Transl.)].
9. S. V. Larionov, A. V. Tkachev, L. I. Myachina, S. N. Bizyaev, L. A. Glinskaya, and R. F. Klevtsova, *Dokl. Akad. Nauk*, 2006, **411**, 198 [*Dokl. Chem.*, 2006, **411**, 206 (Engl. Transl.)].
10. A. P. Petukhov, S. N. Bizyaev, and A. V. Tkachev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2013 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2106].
11. G. M. Sheldrick, *SHELXS97 and SHELXL97. Programs for the Refinement of Crystal Structures.* Göttingen University, Göttingen, Germany, 1997.

Received July 12, 2007;
in revised form August 20, 2007