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Inorganica Chimica Acta 269 (1998) 337–341

**Inorganica
Chimica Acta**

Note

Synthesis and properties of nickel(III) complexes of hexaazamacrocyclic ligands

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Received 2 January 1997; revised 3 March 1997; accepted 19 June 1997

Abstract

The six-coordinate Ni(III) macrocyclic complexes $[\text{Ni}^{\text{III}}(\text{L})\text{X}_2]^+$ where L is 1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane (**1**), 1,8-bis(2-cyanoethyl)-1,3,6,8,10,13-hexaazacyclotetradecane (**2**) or 1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane (**3**) and X is Cl^- , Br^- or NO_3^- have been prepared by the oxidation of the square-planar Ni(II) complexes of the corresponding macrocyclic ligands with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HNO_3 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in H_2O or MeCN. Although the ligands **1** and **2** contain pendant-arms with potentially coordinating groups, the Ni(III) species are stabilized by the extra axial ligands. The six-coordinate Ni(III) complexes show anisotropic axial EPR powder spectra with g_{\perp} values being greater than g_{\parallel} values and the magnetic moments ranging from 1.88 to 2.29 BM, which indicate that the Ni(III) ions are in a low-spin d^7 state with the unpaired electron residing in the d_{z^2} orbital to adopt the tetragonally distorted octahedral geometry. © 1998 Elsevier Science S.A.

Keywords: Nickel(III) complexes; Azamacrocyclic complexes

1. Introduction

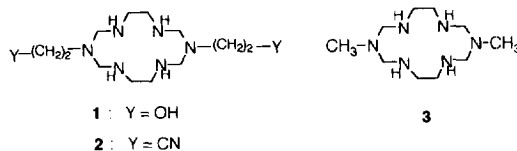
Ni(III) complexes are of interest because EPR spectroscopic evidence indicates that Ni(III) centers occur in several nickel-containing enzymes [1–4]. In addition, Ni(III) species have often been proposed to be involved in catalytic reactions [5]. Although many Ni(III) species have a relatively short life-time and may be regarded as transient species, certain tetraazamacrocycles (in particular cyclam) are capable of promoting the oxidation of the encircled metal ion and stabilizing high and otherwise unstable oxidation states [6,7]. Thus, some Ni(III) macrocyclic complexes have been prepared [8–18] and a few X-ray structures have been determined [9,15,16,19].

Stabilization of the Ni(III) state depends on the coordination number, stereochemistry, and type of ligand. In general, the high oxidation state of Ni(III) in a tetradentate macrocyclic ligand is stabilized by coordinating two extra ligands at the axial sites to form a tetragonally distorted octahedral complex. Ni(III) macrocyclic complexes with a square-planar geometry are extremely rare and their macrocyclic ligands are highly negatively charged [20]. In order to circumvent the need for an additional ligand for

stabilizing Ni(III) species, a few macrocyclic ligands bearing pendant-arms with potentially coordinating groups have been prepared [15,21–23].

We have recently prepared the Ni(II) complexes of tetradentate macrocyclic ligands **1** and **2** which contain pendant functional groups [24]. The hydroxyl pendant groups in **1** do not coordinate intra- or intermolecular Ni(II) ions at $\text{pH} = 7\text{--}13$ and $I = 1.0 \text{ M}$ (NaClO_4). However, the nitrile pendant groups in **2** coordinate intermolecular Ni(II) ions in the solid state, forming a coordination polymer.

In order to see whether the macrocyclic ligands **1** and **2** stabilize the Ni(III) oxidation state, we have attempted to synthesize their Ni(III) complexes. In the present paper, details of the synthesis and properties of the Ni(III) complexes of **1–3** are presented.



2. Experimental

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. For

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the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods [25]. $[\text{Ni}(\text{L})](\text{ClO}_4)_2$ ($\text{L} = \mathbf{1}\text{--}\mathbf{8}$) were prepared according to literature methods previously reported [24,26–29]. IR spectra were recorded with a JASCO IR-810 spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV–Vis spectrophotometer. Electron spin resonance spectra were recorded on a Bruker ER 200E spectrometer with powder samples at room temperature. Conductance measurements were performed using a TOA CM-30ET conductivity meter. Magnetic susceptibility was measured with a Faraday type magnetometer. Elemental analyses were performed by the Analytical Laboratory in Basic Science Center, Seoul.

2.1. Synthesis of the Ni(III) complexes

2.1.1. Dibromo[1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(III) perchlorate dihydrate, $[\text{Ni}(\mathbf{1})\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$

To a stirred aqueous solution (20 ml) of $[\text{Ni}(\mathbf{1})](\text{ClO}_4)_2$ (2.0 g) was slowly added excess $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.5 g), and the color of the solution turned green. The solution was filtered to remove insoluble material. HBr (3 ml) was slowly added dropwise to the green solution with stirring. The solution was allowed to stand in a refrigerator until red–brown crystals formed. The crystals were filtered, washed with MeOH, and dried in vacuo. Yield: ~45%.

2.1.2. Dichloro[1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(III) perchlorate hydrate, $[\text{Ni}(\mathbf{1})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$

This compound was prepared by the method used for $[\text{Ni}(\mathbf{1})\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ except that concentrated HCl (2.2 ml) was added instead of HBr for the axial ligand source. Red–brown crystals were filtered, washed with MeOH, and dried in vacuo. Yield: ~10%.

2.1.3. Dinitrato[1,8-bis(2-hydroxyethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(III) perchlorate, $[\text{Ni}(\mathbf{1})(\text{NO}_3)_2]\text{ClO}_4$

$[\text{Ni}(\mathbf{1})](\text{ClO}_4)_2$ (2.0 g) was dissolved in concentrated HNO_3 (5.0 ml). The solution immediately became dark green. To this was added H_2O or MeCN (8.0 ml) with stirring and the solution was allowed to stand in a refrigerator until a greenish-brown precipitate formed. The precipitate was filtered, washed with MeOH, and dried in vacuo. Yield: ~50%.

2.1.4. Dinitrato[1,8-bis(2-cyanoethyl)-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(III) perchlorate, $[\text{Ni}(\mathbf{2})(\text{NO}_3)_2]\text{ClO}_4$

$[\text{Ni}(\mathbf{2})](\text{ClO}_4)_2$ (2.0 g) was dissolved in concentrated HNO_3 (5.0 ml). The solution immediately became dark brown. To this was added H_2O or MeCN (8.0 ml) with stirring and the solution was allowed to stand in a refrigerator

until a dark red precipitate formed. The precipitate was filtered, washed with MeOH, and dried in vacuo. Yield: ~25%.

2.1.5. Dichloro[1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane]nickel(III) perchlorate hydrate, $[\text{Ni}(\mathbf{3})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$

$[\text{Ni}(\mathbf{3})](\text{ClO}_4)_2$ (0.65 g) was suspended in MeCN (30 ml) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.1 g) dissolved in MeCN (35 ml) was added. As the reaction progressed, the Ni(II) complexes dissolved, and the solution became deep red–brown. The solution was filtered and concentrated to half of the initial volume, and then allowed to stand at room temperature. Brown crystals formed, were filtered, washed with MeOH, and dried in vacuo. Yield: 55%.

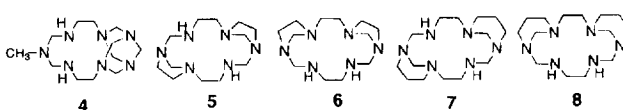
Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these compounds should be handled with great care.

3. Results and discussion

3.1. Synthesis of Ni(III) macrocyclic complexes

The Ni(III) complexes of saturated hexaazamacrocyclic ligands $\mathbf{1}\text{--}\mathbf{3}$ were prepared by oxidizing the corresponding Ni(II) complexes $[\text{Ni}(\text{L})](\text{ClO}_4)_2$ ($\text{L} = \mathbf{1}\text{--}\mathbf{3}$) with an excess amount of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, HNO_3 or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in H_2O or MeCN. The Ni(III) complexes were isolated as six-coordinate species $[\text{Ni}(\text{L})\text{X}_2]\text{ClO}_4$ where X is Br^- , Cl^- or NO_3^- . When $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or HNO_3 was employed as the oxidizing reagent, Cl^- or NO_3^- ions of the reagent were coordinated to the Ni(III) ion to form six-coordinate species. When persulfate was used as an oxidizing agent, an appropriate source of axial ligand such as HBr or HCl was added to stabilize the Ni(III) species. Without added axial ligands, $[\text{Ni}(\text{H}_2\text{O})_6]\text{SO}_4$ was obtained instead of Ni(III) complexes.

The syntheses of Ni(III) complexes with macropolycyclic ligands $\mathbf{4}\text{--}\mathbf{8}$ have been attempted using similar preparative methods to those for the Ni(III) complexes of $\mathbf{1}\text{--}\mathbf{3}$, but the Ni(III) complexes of $\mathbf{4}\text{--}\mathbf{8}$ were not obtained. The electrochemical data [24,26–30] of the Ni(II) complexes of $\mathbf{1}\text{--}\mathbf{8}$ indicate that the complexes of monocyclic ligand $\mathbf{1}\text{--}\mathbf{3}$ and cyclam are oxidized to Ni(III) complexes at +0.91 to +0.94 V versus SCE [24] while those of polycyclic ligands $\mathbf{4}\text{--}\mathbf{8}$ are oxidized at +1.25 to +1.50 V versus SCE [26–30]. Apparently, easy formation of Ni(III) complexes of $\mathbf{1}\text{--}\mathbf{3}$ compared to those of $\mathbf{4}\text{--}\mathbf{8}$ is related with the low oxidation potential of the monocyclic Ni(II) complexes. It is noteworthy that the Ni(I) complexes of $\mathbf{4}\text{--}\mathbf{8}$ have been prepared by the reduction of the Ni(II) complexes with Na(Hg) in MeCN and their X-ray structures have been determined [30–32].



3.2. Properties of Ni(III) macrocyclic complexes

The IR spectra, conductance and analytical data are summarized in Table 1, and UV–Vis and EPR spectra as well as magnetic moments in Table 2. The Ni(III) complexes, $[\text{Ni}(\text{L})\text{X}_2]\text{ClO}_4$, are soluble in MeCN and Me_2SO , but insoluble in alcohols. The Ni(III) species are stable in the solid state under dry air. However, they turn into Ni(II) species in water at ~98% without extra oxidizing agent added, concomitantly increasing the acidity of the solution. This was verified by UV–Vis spectra.

The IR spectra (Nujol mull) of $[\text{Ni}(\mathbf{1})\text{X}_2]\text{ClO}_4$ ($\text{X} = \text{Br}^-$, Cl^- or NO_3^-) showed the ν_{OH} value of hydroxyl pendant groups at $3375\text{--}3310\text{ cm}^{-1}$ and the ν_{NH} value of secondary amines at $3195\text{--}3150\text{ cm}^{-1}$, respectively, which are comparable with the ν_{OH} value of 3520 cm^{-1} and the ν_{NH} value of 3270 and 3210 cm^{-1} for $[\text{Ni}(\mathbf{1})\text{Cl}_2]$ [24]. The decrease of the ν_{NH} values in the Ni(III) complexes indicates that the interaction of the secondary nitrogens of **1** with Ni(III) must be stronger than that with Ni(II). Complex $[\text{Ni}(\mathbf{2})(\text{NO}_3)_2]\text{ClO}_4$ shows the ν_{CN} value of pendant nitriles of the macrocycle **2** at 2253 cm^{-1} , indicating that they do not coordinate inter- or intramolecular Ni(III) ions. This is in contrast to the previous report for the Ni(II) complexes that the pendant nitriles coordinate intermolecular metal ions to form coordination polymers [24]. The contrasting results between Ni(III) and Ni(II) complexes must be attributed to

the π -backbonding nature of the nitrile groups. The values of molar conductance for $[\text{Ni}(\text{L})\text{X}_2]\text{ClO}_4$ ($\text{L} = \mathbf{1}\text{--}\mathbf{3}$, $\text{X} = \text{Br}^-$, Cl^- or NO_3^-) measured in MeCN or Me_2SO correspond to a 1:1 electrolyte [33], indicating that the axial ligands in the Ni(III) complexes are not dissociated from the complex in these polar solvents. The axial halide ligands of the corresponding Ni(II) complexes are very labile in such donating solvents [24]. The UV–Vis spectra of the Ni(III) complexes (Table 2) depend on the type of macrocyclic ligand as well as the axial ligand. The spectra of the Ni(III) complexes measured in MeCN or Me_2SO are dominated by the low-energy charge transfer bands around $320\text{--}380\text{ nm}$. The d–d transition band arising at $710\text{--}780\text{ nm}$ is attributed to the presence of an electron in the d_{z^2} orbital. EPR spectra of the Ni(III) complexes show rhombic or anisotropic axial spectra with g_{\perp} values greater than the g_{\parallel} values at room temperature (Table 2), which indicates that the Ni(III) ions are in a low-spin d^7 state with the unpaired electron residing in the d_{z^2} orbital to adopt the tetragonally distorted octahedral geometry [13,34–37]. The frozen Me_2SO solution of $[\text{Ni}(\mathbf{1})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ shows superhyperfine splitting with a septet ($A = 0.0026\text{ cm}^{-1}$) around the g_{\parallel} region due to the two axially bound Cl^- ions (Fig. 1). The values of magnetic moment of the Ni(III) complexes ranging from 1.89 to 2.29 BM also indicate that the Ni(III) ions have a low-spin d^7 electronic configuration.

Table 1
Physical and analytical data for nickel(III) macrocyclic complexes

Compound	IR ^a (cm^{-1})			A_M ($\Omega^{-1}\text{ cm}^{-1}\text{ M}^{-1}$)	Anal. found (calc.) (%)		
	ν_{NH}	ν_{OH}	ν_{CN}		C	H	N
$[\text{Ni}(\mathbf{1})\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$	3150	3375		48.7 ^b , 171 ^c	22.11 (22.37)	5.04 (5.32)	13.06 (13.04)
$[\text{Ni}(\mathbf{1})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$	3150	3310		31 ^b	26.30 (26.82)	5.76 (6.00)	15.38 (15.64)
$[\text{Ni}(\mathbf{1})(\text{NO}_3)_2]\text{ClO}_4$	3195	3350		185 ^c	25.22 (25.17)	4.93 (5.28)	19.87 (19.57)
$[\text{Ni}(\mathbf{2})(\text{NO}_3)_2]\text{ClO}_4$	3185		2253	145 ^c	28.32 (28.47)	4.48 (4.78)	23.32 (23.72)
$[\text{Ni}(\mathbf{3})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$	3175, 3130, 3210			153 ^c	25.79 (25.16)	6.16 (5.91)	17.86 (17.60)

^a Stretching frequencies for the macrocycles (Nujol mull).

^b Measured in Me_2SO .

^c Measured in MeCN.

Table 2
UV–Vis spectra, magnetic moments and EPR spectra of nickel(III) macrocyclic complexes

Compound	UV–Vis ^{a,b} λ_{max} (nm) (ϵ)	μ_{eff} ^c (BM)	EPR ^d
$[\text{Ni}(\mathbf{1})\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$	757 (94), 382 (7580), 290 (10600) ^a	1.90	$g_{\perp} = 2.176, g_2 = 2.131, g_3 = 2.083$
$[\text{Ni}(\mathbf{1})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$	777 (36), 318 (12200), 287 (11800) ^b	1.89	$g_{\perp} = 2.183, g_2 = 2.132, g_3 = 2.084$
$[\text{Ni}(\mathbf{1})(\text{NO}_3)_2]\text{ClO}_4$	298 (7650) ^a	2.29	$g_{\perp} = 2.109, g_{\parallel} = 2.022$
$[\text{Ni}(\mathbf{2})(\text{NO}_3)_2]\text{ClO}_4$	710 (sh), 297 (13000), 215 (14700) ^a	1.93	$g_{\perp} = 2.211, g_{\parallel} = 2.061$
$[\text{Ni}(\mathbf{3})\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$	280 (14000) ^a	1.88	$g_{\perp} = 2.182, g_{\parallel} = 2.023$

^a Measured in MeCN.

^b Measured in Me_2SO .

^c At room temperature.

^d Measured with powder sample at room temperature.

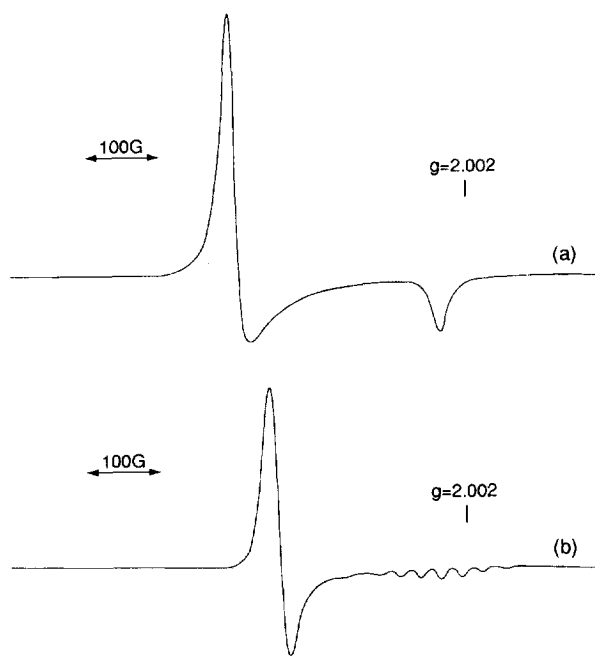
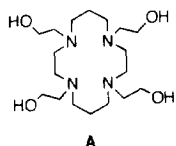


Fig. 1. EPR spectra of (a) the powder sample of $[\text{Ni}(2)(\text{NO}_3)_2]\text{ClO}_4$ and (b) the frozen Me_2SO solution of $[\text{Ni}(1)\text{Cl}_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$.

Although the macrocyclic ligands **1** and **2** contain potentially coordinating pendant groups as well as the tertiary nitrogens at the bridgehead position, none of them coordinates the Ni(III) ion. It was previously shown for the Ni(II) complexes that the tertiary nitrogens at the bridgehead position did not have coordinating ability due to their partial sp^2 character. It was also shown that the hydroxyl groups in $[\text{Ni}(1)](\text{ClO}_4)_2$ were inert at $\text{pH} = 7\text{--}13$ and 1.0 M NaClO_4 [24]. This stands in contrast to the report for $[\text{Ni}(\text{A})](\text{ClO}_4)_2$ whose hydroxyl pendants are deprotonated and coordinate the intramolecular Ni(II) ion in water to give the octahedral Ni(II) species, $[\text{Ni}(\text{AH}_{-2})]$ [38].



In order to see whether the hydroxyl pendants are able to coordinate the Ni(III) center upon deprotonation, triethylamine (dried) is added to the Me_2SO solution of $[\text{Ni}(1)\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. The UV–Vis spectrum of the Ni(III) complex is changed to that of the square planar Ni(II) complex, showing λ_{max} at 446 nm ($\epsilon = 70$). Furthermore, the EPR spectrum of the frozen Me_2SO solution of $[\text{Ni}(1)\text{Br}_2]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ which was anisotropic with superhyperfine splittings around g_{\parallel} disappears completely upon the addition of excess TEA. It is apparent that the N–H of the coordinated secondary amines of the Ni(III) complex is deprotonated instead of the hydroxyl groups and the deprotonated Ni(III) species turns into the Ni(II) complex by the intramolecular electron transfer [39]. It has been reported that the Ni(III) complexes of a saturated macrocyclic ligand

reacted with water at $\text{pH} = 9\text{--}11$ to result in the Ni(II) complexes with the oxidized macrocyclic ligand containing imine bonds [39,40]. The present complexes do not show such dehydrogenation phenomena in basic solutions, which was verified by the ^1H NMR spectra measured for the isolated product.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Center for Molecular Catalysis at Seoul National University (S.N.U.) and by the S.N.U. Daewoo Research Fund (95-05-2060).

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