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Stable Octahedral, Low-Spin Nickel(III) Complexes of a Tetradentate Macrocyclic Ligand Having Saturated Nitrogen Donors

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The new complexes $[Ni(Me_2[14]aneN_4)X_2]ClO_4$ have been prepared for X = Br, Cl, NCO, NO_3, and $^1/_2SO_4$. $Me_2[14]aneN_4$ is the tetradentate macrocycle 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane. The Ni(III) complexes are prepared by oxidation with $(NH_4)_2S_2O_8$ in aqueous solution or concentrated HNO_3. They have been characterized by the usual physical measurements, which show them to be uni-univalent electrolytes in polar solvents and low spin in electronic configuration with magnetic moments consistent with their formulation as tetragonally distorted octahedral Ni(III) derivatives. This is confirmed by the results of epr measurements. These Ni(III) complexes are exceptionally stable.

Introduction

Ni(III) is reported to form with a variety of ligands including amines,[1–4] arsines,[5–7] phosphines,[8–10] bidentate ligands containing two -NH$^-$ functions,[11,12] two -S$^-$ functions (1,2-dithiolates),[13,14] and one -NH$^-$ and one -S$^-$ function,[15] and monoacido ligands such as fluoride.[16] In only a few cases has the geometry of the Ni(III) complexes been supported by data other than gross physical and chemical properties. Two structures determined by X-ray diffraction have been reported. The geometries of these complexes are octahedral in the case of [Ni(*o*-phenylenebisdimethylarsine)$_2$Cl$_2$]Cl[17] and trigonal bipyramidal for the Ni[(CH$_3$)$_3$P]$_2$Br$_3$ complex.[18] A third structure, that for the bis(maleonitriledithiolato)nickel complex, has not been determined directly but the compound was found to be isomorphic[19] to the corresponding square-planar Co(II) complex.[20] In addition, the geometry of the hexafluoronickelate(III) anion was shown to be a tetragonally distorted octahedron[21] by a detailed analysis of its visible spectrum.

A much more important problem than the geometry of supposed Ni(III) complexes is the authenticity of the Ni(III) state. Most authors have based their claims for Ni(III) mainly on the results of magnetic moment measurements which have been consistent with the presence of one unpaired electron in the structure. However, magnetic moment measurements do not provide us with complete information on the electronic structure of the complexes. Moments corresponding to one unpaired electron could also be interpreted as Ni(II)-stabilized ligand cation radicals in which the unpaired electron was localized on the ligands. When the so-called Ni(III) complex [Ni(*o*-phenylenebisdimethylarsine)$_2$Cl$_2$]Cl was reexamined[17] by X-ray diffraction and epr, the authors concluded that indeed this complex would be more properly described as a Ni(II)-stabilized ligand cation radical. In the light of these results the authenticity of all the nickel(III)-arsine complexes[5–7] must be considered suspect. Other workers have also made use of epr to determine the electronic structure of the nickel(III)-bis(maleonitriledithiolato) complex,[13] and although there is some controversy over the results,[14] it appears that the unpaired electron in this complex cannot be considered to be a pure metal d electron but must be considered to be significantly delocalized over the dithiolate

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Table I. Physical Properties of the Complexes $[Ni(Me_2[14]aneN_4)X_2]ClO_4$[a]

X	Magnetic moment, μ_{eff}, BM	Molar conductance, $cm^2\ ohm^{-1}\ mol^{-1}$	N-H str freq,[b] cm^{-1}	Uv-vis spectral band max, cm^{-1} (molar extinction coeff)
Cl	1.90	151	3180, 3120	31,400 (1.17×10^4), 12,900 (26), 10,500 (19)
Br	1.74	160	3150 sh,[c] 3120	32,800 (5.12×10^3), 27,800 sh (3.54×10^3), 13,000 (39), 10,000 (17)
NCO	2.05	143	3180 sh, 3130, 2180,[d] 610[d]	32,900 (1.88×10^3), 14,850 (16), 10,370 (9)
NO_3	1.93	151	3200	32,000 (1.11×10^4), 14,000 (42)
$^1/_2SO_4$	1.56	168[e]	3180	32,600 (4.26×10^3), 27,000 sh (2.46×10^3), 15,900 (43)[e]

[a] Solution values in CH_3CN unless otherwise stated. [b] Nujol mull. [c] sh = shoulder. [d] C≡N stretch. [e] In H_2O.

ligands.

We wish to report the preparation and characterization of a series of low-spin, octahedral Ni(III) complexes of the form $[Ni^{III}(Me_2[14]aneN_4)X_2]ClO_4$, where $Me_2[14]aneN_4$ is the macrocyclic ligand 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane and X = Br, Cl, NCO, NO_3, and $^1/_2SO_4$. The Ni(III) state has been established for these new compounds by epr studies.

Experimental Section

$Ni(Me_2[14]aneN_4)(ClO_4)_2$ was prepared by the method given by Barefield.[3a]

Preparation of $[Ni^{III}(Me_2[14]aneN_4)(SO_4)](ClO_4)$. A solution of $Ni(Me_2[14]aneN_4)(ClO_4)_2$ was prepared by dissolving 4.86 g (0.01 mol) of the compound in 40 ml of water. To this was added a solution of 1.15 g of $(NH_4)_2S_2O_8$ (0.005 mol), dissolved in a minimum amount of water. The solution turned green instantly and a green precipitate formed rapidly. This was isolated by filtering, washed several times with water, and dried at 60° in a vacuum oven. *Anal.* Calcd for $C_{12}H_{28}N_4NiSO_4ClO_4$: C, 29.86; H, 5.85; N, 11.60; S, 6.64; Cl, 7.35. Found: C, 29.81; H, 6.10; N, 11.61; S, 6.52; Cl, 7.72.

Preparation of $[Ni(Me_2[14]aneN_4)Br_2]ClO_4$. A solution of 1.15 g of $(NH_4)_2S_2O_8$ was added to a solution of 4.86 g of $Ni(Me_2[14]aneN_4)(ClO_4)_2$ in 40 ml of water. The green precipitate was filtered and an excess of concentrated HBr was added to the filtrate. The color changed to brown and a dark red-brown precipitate formed. This was isolated by filtering, washed several times with water, and dried in a vacuum oven at 60°. *Anal.* Calcd for $C_{12}H_{28}N_4NiBr_2ClO_4$: C, 26.38; H, 5.17; N, 10.25; Ni, 10.75. Found: C, 26.48; H, 5.41; N, 10.30; Ni, 10.25.

Preparation of $[Ni(Me_2[14]aneN_4)Cl_2]ClO_4$. This compound was prepared in the same way as $[Ni(Me_2[14]aneN_4)Br_2]ClO_4$ but with HCl substituted for HBr. The compound was ochre. *Anal.* Calcd for $C_{12}H_{28}N_4NiCl_3O_4$: C, 31.51; H, 6.17; N, 12.24; Ni, 12.84; Cl, 23.25. Found: C, 31.78; H, 6.22; N, 12.21; Ni, 12.52; Cl, 22.95.

Preparation of $[Ni(Me_2[14]aneN_4)(NCO)_2]ClO_4$. This compound was prepared in the same manner as $[Ni(Me_2[14]aneN_4)Br_2]ClO_4$ but with NaNCO substituted for HBr. The compound is yellow-green. *Anal.* Calcd for $C_{14}H_{28}N_6NiClO_6$: C, 35.74; H, 6.00; N, 17.85; Cl, 7.53. Found: C, 35.59; H, 6.05; N, 17.59; Cl, 7.72.

Preparation of $[Ni(Me_2[14]aneN_4)(NO_3)_2]ClO_4$. $Ni(Me_2[14]aneN_4)(ClO_4)_2$ (1 g) was dissolved in 2 ml of concentrated HNO_3. The solution immediately turned dark green. To this solution, 6 ml of H_2O was added slowly and with stirring. A lime green precipitate was obtained and collected by filtration, washed with methanol, and dried *in vacuo*. *Anal.* Calcd for $C_{12}H_{28}N_6NiClO_{10}$: C, 28.23; H, 5.53; N, 16.46; Cl, 6.94. Found: C, 28.33; H, 5.67; N, 16.40; Cl, 6.87.

Epr Spectra. The epr spectra were recorded on a Varian V-4500 Model EPR spectrometer operating in the X band and equipped with a dual cavity. A sample of DPPH was placed in the reference cavity and its *g* value taken to be 2.0037. The *g* values of the powder spectra were calculated by the approximate method of Kneubuhl[22] and are accurate to ±0.005.

Results and Discussion

Preparation of the Nickel(III) Complexes. Ni(III) complexes have been prepared using a variety of oxidizing agents including halogens,[1,8-10] concentrated HNO_3,[2] $NOBF_4$,[3] and ClNO.[8] Some complexes have also been prepared electrochemically.[4,11,12,15,17] In this work we have used ammonium persulfate, $(NH_4)_2S_2O_8$, and concentrated HNO_3 as oxidizing agents. Dissolution of equivalent amounts of $[Ni(Me_2[14]aneN_4)](ClO_4)_2$ and $(NH_4)_2S_2O_8$ in water results in the immediate formation of a dark green solution with a green precipitate being deposited when the solution is concentrated. The precipitate is the sulfate complex $[Ni^{III}(Me_2[14]aneN_4)(SO_4)]ClO_4$. After the precipitate is filtered, the filtrate is saved and the chloride, bromide, or cyanato complexes are prepared by adding concentrated HCl, concentrated HBr, or a solution of NaNCO, respectively, to the solution, whereupon an immediate precipitate of the corresponding complex forms. The nitrato complex is prepared by dissolving the parent Ni(II) complex in concentrated HNO_3. Upon diluting in solution with H_2O, the nickel(III)-nitrato complex precipitates. The Ni(III) complexes are stable indefinitely in the solid state but decompose in solution after several hours.

Table II. Room-Temperature Epr Data for the Complexes $[Ni(Me_2[14]aneN_4)X_2]ClO_4$

X	$g_\perp$[a]	$g_\parallel$[a]	g_{soln}[b]
Br	2.171	2.022	2.121, $\langle A \rangle = 57$ G
Cl	2.181	2.025	2.124
NCO	2.169	2.055	2.129, $\langle A \rangle = 22$ G
NO_3	2.221, 2.182[c]	2.103	2.159
$^1/_2SO_4$	2.16[d]		2.165[e]

[a] Powder. [b] In CH_3CN unless otherwise stated. [c] Nonaxially symmetric. [d] Very broad (~1000 G) symmetric resonance. [e] In H_2O.

Characterization of the Nickel(III) Complexes. The data relevant to the characterization of the new complexes are given in Tables I and II. The magnetic moments for the Cl^-, NCO^-, and NO_3^- complexes are within this range; that for the Br^- is slightly low and the moment of the SO_4^{2-} complex is anomalously low. A similar result was noted[2] in the preparation of the SO_4^{2-} complex of Ni(III) with 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. An antiferromagnetic mechanism *via* superexchange through bridged SO_4^{2-} was invoked to explain the anomalous magnetic moment (1.54 BM at room temperature), but no experimental verification was offered.

The data for the molar conductances are consistent with the existence of the complexes as 1:1 electrolytes. Typical values for 1:1 and 2:1 electrolytes in CH_3CN are in the ranges 135-155 and 250-310 $cm^2\ ohm^{-1}\ mol^{-1}$, respectively.[23] For H_2O the ranges are 100-150 and 210-260.[24] Again the value for the SO_4^{2-} complex is somewhat anom-

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alous but it is well below the range for di-univalent electrolytes. Since the SO_4^{2-} complex is a 1:1 electrolyte in H_2O, it is most probable that the macrocycle adopts a cis configuration in this complex. While pertinent data are lacking, the general behavior of ligands of this class leads us to anticipate a trans configuration for the other three complexes.

The N–H stretching frequencies in the complexes are not unusual. They are the same as for Co(III) complexes of $Me_2[14]aneN_4$.[25] The bands at 2180 and 610 cm^{-1} for the NCO^- complex are typical of N-bonded NCO^- complexes.[26]

In order to establish the authenticity of these new Ni complexes as low-spin d^7 Ni(III) rather than Ni(II) complexes of ligands that are stabilized cation radicals, extensive use has been made of epr. If it is assumed that the four nitrogen atoms are coplanar with the Ni ion, then the symmetry of the ligand field can be approximated as D_{4h}. (This assumption has proved valid in interpreting the visible spectra of Co(III) and Ni(II) macrocyclic complexes.[27]) The most probable electronic structure for a low-spin d^7 Ni(III) complex with D_{4h} symmetry is that in which the unpaired electron is in the d_{z^2} orbital. For this situation the g factors can be predicted using the method outlined by Maki, *et al.*,[13] with the result that $g_\parallel = 2$ and $g_\perp = 2 - 6\lambda/\Delta$. λ is the spin-orbit coupling constant (negative in sign for Ni(III)) and Δ is the energy difference between the ground state with the unpaired electron in the d_{z^2} orbital and the excited state with the unpaired electron in the d_{xz} or d_{yz} orbital. We can estimate $g_\perp$ by choosing appropriate values for λ and Δ. The free ion value for λ is −730 cm^{-1} and in the complex this will be reduced in order to allow for covalency to a value on the order of −500 cm^{-1}. The parameter Δ will be of the same order of magnitude as the crystal field splitting which we can assume to be approximately 15,000 cm^{-1}. Thus an estimate for $g_\perp$ would be 2.20.

Theoretical calculations show that the effect of reducing the symmetry to D_{2h} is to split $g_\perp$ into two g factors, g_{xx} and g_{yy}, both of which will be approximately equal to 2.20.

If the complexes are Ni(II)-stabilized cation radicals, the g factors would be essentially the same as those found for organic free radicals. The g tensor would show very little anisotropy and all g factors would be close to the free electron value of 2.0023. Clearly our epr results (Table IV) are more consistent with the low-spin d^7 Ni(III) formulation. Strictly speaking the unpaired electron will not be in a pure d orbital, but since the macrocyclic ligand is completely saturated, no appreciable amount of delocalization of the unpaired electron is to be expected onto the macrocyclic ligand.

Two of the complexes exhibit superhyperfine coupling in solution. The bromo complex shows seven lines, $\langle A \rangle = 57$ G, and the cyanato complex five lines, $\langle A \rangle = 22$ G. These patterns are consistent respectively with two equivalent bromines and two equivalent nitrogens (from the cyanato groups). This equivalence is expected if the symmetry of the molecule is pseudo-D_{4h}. It is especially significant that this unequivocally establishes the coordination number for Ni(III) in these complexes as 6 and strongly supports the proposed pseudooctahedral, tetragonal structure.

The $g_\parallel$ values are significantly different from the predicted value of 2.00. This implies that the ground state is not pure d_{z^2} but contains a small admixture of $d_{x^2-y^2}$. This could be the result of two effects: vibronic interactions[28] or descent of the symmetry of the effective ligand field from D_{4h} to at least C_{2h}.[29,30]

The expression $g_\perp = 2 - 6\lambda/\Delta$ can be used to determine λ provided the energy difference, Δ, can be obtained from visible spectra. If, from among the two low-intensity bands, we arbitrarily assign the higher energy band to Δ, then we find the following values for λ: −370, −390, −420, and −530 cm^{-1} for the Br^-, Cl^-, NCO^-, and NO_3^- complexes, respectively. These values represent a reduction from 50 to 70% of the free ion value of λ. Since greater reduction is anticipated as the covalency of the ground state increases, one would expect the observed λ's to follow the nephelauxetic series and this is indeed the case.[31]

The Ni(III) complexes of $Me_2[14]aneN_4$ form with great ease and are indefinitely stable in the solid state in dry air. This unusual stability has been corroborated by electrochemical data obtained in this laboratory.[32] The oxidation potential for the process Ni(II) → Ni(III) is 0.67 V (solvent CH_3CN, reference electrode Ag–0.1 *M* $AgNO_3$) and is reversible.

Unequivocal evidence for the Ni(III) oxidation state and its stereochemistry has been rare to date. In this paper we have presented strong evidence for the existence of the Ni(III) oxidation state in a tetragonally distorted octahedral ligand field. The unusual stability of the Ni^{III}–$Me_2[14]aneN_4$ complexes recommends them for study when interest is directed toward Ni(III).

Registry No. Table I X = Cl, 36534-04-0; X = Br, 36534-05-1; X = NCO, 36534-06-2; X = NO, 36534-07-3; X = $^1/_2SO_4$, 36534-08-4.

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