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Diaxial Complexation in a Sterically Hindered Nickel(III) Tetraaza Macrocycle: An ESR Study

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In recent years, a number of studies have appeared regarding the tendency for simple anions to dramatically stabilize the +3 oxidation state of nickel in tetraaza macrocyclic complexes in aqueous media through axial coordination [1, 2]. The ability of the macrocyclic complex to accept *either* one or two axial ligands is, of course, determined by the structure of the ligand and the question of five- *vs.* six-coordination has been discussed by Busch for Co(II) complexes [3].

For the Ni(III) complex of the unsubstituted 14-membered ring of [14]aneN$_4$ ($\equiv L_1 \equiv$ cyclam), diaxial complexation is relatively unhindered and, indeed complexes of the type $Ni^{III}L_1X_2^{M+}$ have been characterized in both aqueous and nonaqueous media [2, 4, 5]. For the substituted macrocycles *meso*-Me$_6$[14]aneN$_4$ ($L_2 \equiv$ *teta*) and its diastereoisomer *β-rac*-Me$_6$[14]aneN$_4$ (β-L_3), steric effects favor pentacoordination and thus inhibit the second hydrolysis of the aquated Ni(III) complexes under conditions (pH 9–11) where $Ni_{L_1}(OH)_2^+$ is the principle form of the cyclam complex [6]. On the other hand, studies of complexation on the centrosymmetric $Ni^{III}L_2$, including a crystal structure determination for the phosphate complex, have shown that steric effects are not so great as to prevent coordination by two axial ligands [1].

The tendency for four methyl groups to interfere considerably with one of the axial sites in the Ni^{II} complex [7] led us to wonder whether or not sufficiently large structural changes in the macrocycle are possible so as to allow diaxial complexation in β-$Ni^{III}L_3$. Electrochemical results in sulfate media were surprising in that they suggested the presence of the β-$NiL_3(SO_4)_2^-$ ion while pulse radiolysis results indicate that indeed major conformational changes are necessary before complexation by sulfate can occur [1].

Because of the characteristic electron spin resonance spectra of low spin Ni(III) and the well resolved superhyperfine splitting patterns found in other axially coordinated Ni(III) complexes, ESR has been widely accepted as a definitive technique for the verification of the +3 oxidation state and for determining the extent of axial coordination [2, 4, 5, 8]. Thus, in the present study, we have looked at the effect of chloride ion (nuclear spin, $I = 3/2$) on the electron spin resonance spectrum of β-$Ni^{III}L_3$ in order to determine unequivocally its maximum degree of complexation.

Experimental

The β-L_3 complex of nickel(II) was prepared as the perchlorate salt [7]. The identity of this isomer was confirmed by comparison of its proton NMR spectrum in deuterated DMSO with the published spectrum of Warner and Busch [7]. Oxidation of β-Ni(II)L_3 by nitric acid in 1 molar HCl followed by addition of $HClO_4$ resulted in a red-brown solid whose spectrum in 0.3 *M* SO_4^{2-} confirmed the presence of Ni(III) in high yield. Elemental analysis gave results which were compatible with the formula $[Ni(III)L_3Cl](ClO_4)_2$ but which also indicated some contamination, probably from Ni(II) and/or ligand degradation products. Such decomposition products should not have any significant effect on the ESR results and, indeed, are to be expected due to the relative instability of the Ni(III) complex.

X-band ESR spectra were recorded on a Varian E-4 spectrometer at 77 K for samples of the solid which were dissolved in the appropriate medium and immediately frozen.

Results and Discussion

For all media employed, two principle ESR resonances were observed. The g values (Table I) are indicative of low spin nickel(III) in an axially symmetric tetragonal field with the unpaired electron in the d_{z^2} orbital.

The last two entries in Table I provide unambiguous evidence that, at high ligand concentration, the macrocyclic Ni(III) complex contains two axial chloride ligands. As demonstrated in Fig. 1, the $g_\parallel$ resonance is split into seven evenly spaced lines ($A = 28$ G) with relative intensities close to the expected ratio of 1:2:3:4:3:2:1. The g values and splittings are almost identical to those reported by Desideri *et al.* for $Ni^{III}L_1Cl_2$ [4]. There is no evidence for hyperfine coupling in the $g_\perp$ region for any of the solutions studied.

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TABLE I. ESR spectra of frozen $Ni^{III}L_3 \cdot Cl$ solutions at 77 K.[a]

Medium	$g_\parallel$	$g_\perp$	A (gauss)
CH_3CN	2.039	2.169	
3 *M* $HClO_4$	2.015[b]	2.199	~25
3 *M* HCl	2.024[c]	2.188	28
3 *M* Et_4NCl	2.025[c]	2.181	28

[a] ~5 × 10^{-4} *M* in $[NiL_3Cl](ClO_4)_2$. [b] Poorly resolved quartet. [c] Septet.

While the presence of well resolved superhyperfine splitting of $g_\parallel$ in Fig. 1 may be taken as clear evidence that $NiL_3Cl_2^+$ is the principle species in chloride media, the absence of nitrogen (I = 1) superhyperfine splitting does not provide any additional information about the coordination sphere of Ni(III) in acetonitrile. In other studies with Ni(III) macrocycles, splitting due to axial MeCN was observed only in the presence of added electrolyte [8]. The broadening and splitting of $g_\parallel$ in 3 *M* $HClO_4$ as compared to MeCN, is an indication that the single, axial chloride of the parent solid remains largely coordinated during sample preparation (≲1 min) in the former case but not in the latter. Partial exchange of Cl^- in the $HClO_4$ solution, however, could account for the observed weakening of the total signal and poorer resolution of $g_\parallel$ since i) loss of Cl^- would give a mixture of chloro- and aqua- (or uncoordinated) Ni(III) and ii) the relative instability of these species should lead to interfering decomposition products including possibly Ni(II)-ligand radical intermediates.

In the pulse radiolysis study of $\beta\text{-}NiL_3^{2+}$ oxidation, the very rapid reaction

$$\beta\text{-}NiL_3^{2+} + \cdot OH \rightarrow \beta\text{-}NiL_3^{3+} \qquad (1)$$

yielded a product for which the initial macrocycle conformation must be identical to that in the nickel(II) precursor [1]. The disappearance of a transient absorbance at 550 nm upon complexation with sulfate suggested a change from the hindered initial conformation to hexa-coordination. In the present investigation, however, we cannot definitively say at what point this conformational change occurs or, indeed, how great an adjustment is necessary. Among the possible configurations for NiL_3X_2 are i) retention of the basic geometry of the nickel(II) complex (Fig. 6a in ref. 7) with the two blocking methyl groups 'pushed aside' by an axial ligand; this would create ring strain which must then be overcome by the stability of the resulting complex; ii) inversion at one of the nitrogen atoms to produce a conformation of $\beta\text{-}NiL_3$ with less interference by methyl groups (Fig. 6b in ref. 7); iii) conversion to a diaxially coordinated complex of $\alpha\text{-}NiL_3$ (Fig. 5f in ref. 7); while there is a great deal of ring strain in this isomer [7], there is also less axial hindrance.

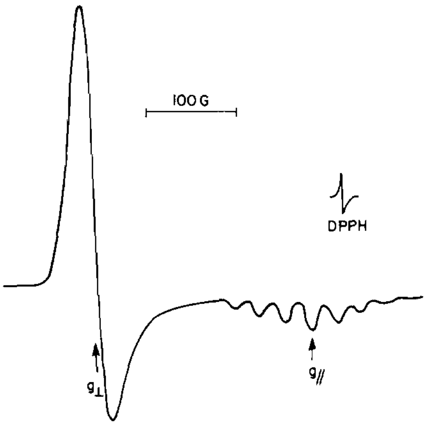

Fig. 1. ESR spectrum of NiL_3Cl_2 in 3 *M* HCl.

For nickel(II), the equilibrium

$$\alpha\text{-}NiL_3^{2+} \rightleftarrows \beta\text{-}NiL_3^{2+} \qquad (2)$$

lies far to the right. This process does not occur in acid and involves subsequent deprotonations and inversions at two nitrogens, the intermediate corresponding to the β-conformation of case (ii). With nickel(III), the higher charge of the metal may labilize the amine protons sufficiently to allow inversion to occur even in HCl so that the six-coordinate complex has one of the more open structures (ii) or (iii). That this is highly likely is seen by the fact that the ESR spectra are very similar in both HCl and in Et_4NCl and that the observed g values are almost identical to those of $NiL_1Cl_2^+$ and $Ni(Me_2cyclam)Cl_2^+$. A reversal of equilibrium (2) has indeed been observed for the nickel(II) system, the driving force being precipitation of $\alpha\text{-}NiL_3(NCS)_2$ [7].

Although differences in electrochemical behavior, UV–visible spectra and stability are not major when α and $\beta\text{-}NiL_3^{2+}$ are oxidized electrochemically, it does seem that two distinct disulfate complexes result [6]. It, thus, seems reasonable to assert that the conformation of case (ii) is most likely for the oxidation product of $\beta\text{-}NiL_3^{2+}$ in the presence of axial chloride or sulfate while oxidation of αNiL_3^{2+} in acidic sulfate results in retention of the α configuration.

The similarity of ESR spectra of the various chloro-complexes of Ni(III) does not extend the acetonitrile solution. The difference in our values (Table I) and those for other macrocycles (*e.g.* $g_\parallel$ = 2.020–2.029 and $g_\perp$ = 2.205–2.215 for L_1, L_2 and $Me_2cyclam$) seems significant and can be attributed to the same uncoordinated conformation of $\beta\text{-}NiL_3$ which is stable for nickel(II) in a variety of solvents [7] and which is initially produced by pulse radiolytic oxidation of $\beta\text{-}NiL_3^{2+}$ to Ni(III).

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