J. Am. Chem. Soc. **1982**, *104*, 7561-7563 7561

Single-Crystal EPR Spectra of Two Ni(III) Tetraazamacrocycle Complexes[1]

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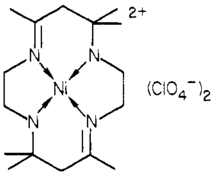
Abstract: γ irradiation of single crystals of two macrocyclic complexes of nickel(II), *rac*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate (A) and *rac*-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)nickel(II) perchlorate (B), yields the corresponding nickel(III) species. These ions adopt the symmetry of the host space group. g tensors measured for the centers in A (g_{xx} = 2.3614, g_{yy} = 2.4006, and g_{zz} = 2.0107) and in B (g_{xx} = 2.3445, g_{yy} = 2.3821, g_{zz} = 2.0149) are consistent with a low-spin d^7 system in which the unpaired electron occupies a d$_{z^2}$ orbital. On oxidation, a change in geometry occurs from a square-planar nickel(II) species to a tetragonally distorted octahedral nickel(III). There is evidence of movement within the crystal leading to weakly coordinated perchlorate ions. Values of Δ for A and B calculated from the g shifts are much smaller than those derived for nickel(III) macrocycles with axially coordinated chloride ions.

Although nickel(III) complexes have been known for some time,[2] their characterization as low-spin d^7 ions was only achieved recently by using EPR spectroscopy.[3] With the preparation of a variety of macrocyclic ligands, the stabilization of the tervalent state has been shown to be readily achieved, especially in solvents such as acetonitrile.[4-6] The chemistry of this oxidation state has been the subject of two recent reviews.[7,8] To date, however, almost all the data describing the EPR parameters of these systems have been obtained with frozen solutions of the nickel(III) species.[5,9-11] A similar situation obtains for analogous complexes having deprotonated amino acids as ligands.[12] In general, the spectra are consistent with a low-spin tetragonally distorted octahedral complex with approximately axial symmetry, having $g_\parallel \approx 2.02$ and $g_\perp \approx 2.2$. Attempts have been made to determine all three g values of the orthorhombic tensor by spectral simulation.

The only single-crystal data available at present are those for diphosphine[13] and diarsine[14] complexes, $(Ni(LL)_2X_2)^+$ (X = halide), doped in cobalt(III) host lattices. While preliminary single-crystal data are available for these systems, few crystallographic details are known.

We have found that on γ irradiation of nickel(II) tetraazamacrocycle complexes significant amounts of the corresponding nickel(III) species are formed. Use of single crystals of the complexed nickel(II) perchlorates enables the determination of the g tensors since the tervalent ion formed adopts the symmetry of the host space group. In this paper, we present the first single-crystal EPR data on studies of nickel(III) tetraazamacrocycles. The crystal and molecular structures of the related diimine complexes, *rac*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate[15] ([Ni(*rac-trans*-diene)]$^{2+}$, A), and the "cis" isomer, *rac*-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)nickel(II) perchlorate[16] ([Ni(*rac-cis*-diene)]$^{2+}$, B), have been reported. Both these compounds crystallize in the orthorhombic system but with different space groups.[15,16]



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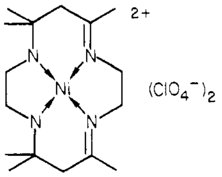

B

Table I. g^2 Tensors,[a] Eigenvalues, and Eigenvectors for the Centers Observed in A and B

	g^2			principal values and eigenvectors		
	a	*b*	*c*	4.0430	5.5763	5.7631
A	4.8801	0.52178	−0.59705	0.6866	0.6210	−0.3780
	0.52178	5.1859	0.46035	−0.5187	0.7828	0.3438
	−0.59705	0.46035	5.3164	0.5094	−0.0400	0.8596
	a	*b*	*c*	4.0600	5.3965	5.6744
B	4.2104	0	0.4399	0.9462	0.3236	0
	0	5.6744	0	0	0	1
	0.4399	0	5.3461	−0.3236	0.9462	0

[a] Tensors are given in the *abc* axis system of an orthorhombic crystal.

Experimental Section

Isomers A and B were prepared as the perchlorate salts according to the method of Curtis.[17] Crystals of suitable size were formed by slow evaporation of dilute perchloric acid solutions. After irradiation at 77 K for 6 h in a 2000 Ci ^{60}Co source, single crystals were mounted individually under liquid nitrogen on a two-circle goniometer[18] and were examined at −190 °C with a Varian E12 spectrometer and accessories.

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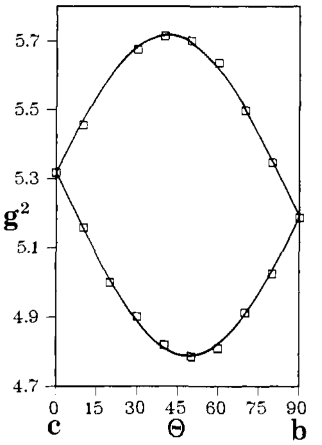

Figure 1. g^2 values for the two sites of isomer A in the *bc* crystallographic plane. Squares are the experimental values; the curves represent the least-squares best-fit sine curve to the experimental data.

Details of the technique of crystal alignment have been presented previously.[18] Crystal axes were identified from spectral coalescences observed during a preliminary exploration of the angular dependence of the EPR spectra. Magnetic field and microwave frequency measurements for these directions provided the diagonal elements of the g^2 tensor in the crystal-axis system. The off-diagonal elements were obtained from a computerized best fit to the angular variation of g^2 in all three crystal planes (see Figure 1).

Results

Isomer A. Spectra observed in γ-irradiated single crystals of A when the magnetic field coincided with the crystal axes consisted of a single line near $g = 2$ having a peak-to-peak width of approximately 10 G. Nuclear hyperfine structure was not detectable. This single line split into four lines of equal intensity for a general orientation of the magnetic field and into two lines for an off-axis direction within a crystal plane. This site-splitting behavior thus conformed to the space group symmetry (*Pbca*) of the undamaged orthorhombic crystal.[15]

g^2 values showed the expected sinusoidal dependence on angle in each crystal plane (e.g., Figure 1). The elements of the g^2 tensor in the crystal-axis system were derived (Table I) from measurements along the crystal axes and from least-squares fitted data, such as shown in Figure 1, for each crystal plane. The remaining ambiguity in the relative signs of the off-diagonal elements was removed by comparing computed and measured g^2 values for the skew orientation H_0 parallel to $3^{-1/2}$ (1, 1, 1). Table I gives the tensor for one site of the center detected in isomer A together with its principal values and direction cosines.

Isomer B. Crystal-axis spectra in γ-irradiated specimens of isomer B again consisted of a single line, $\sim$10 G wide, showing no resolvable hyperfine structure. In this case, however, only two sites were observed for a general orientation of the magnetic field, and site splitting was restricted to the *ac* crystallographic plane. This behavior is consistent with the lattice structure[16] of the orthorhombic crystal (*Pbcn*) in which Ni^{2+} cations lie on a diad axis (*b*).

The g^2 tensor for B was assembled and diagonalized as for A (Table I). Since the center was a two-site species, there was no sign ambiguity in the off-diagonal elements of the tensor.

Discussion

The similarity of the g tensors for the centers in A (2.0107, 2.3614, 2.4006) and in B (2.0149, 2.3445, 2.3821) to those obtained and attributed to Ni(III) in frozen solutions[5,9–12] leaves little doubt as to the identity of the carriers. The approximately axial tensors with large positive g shifts perpendicular to the z axis are indicative of a low-spin d^7 ion in a square-planar or tetragonally elongated octahedral environment.[19] In this situation, the unpaired electron in Ni^{3+} occupies the d_{z^2} orbital (z = 4-fold axis).

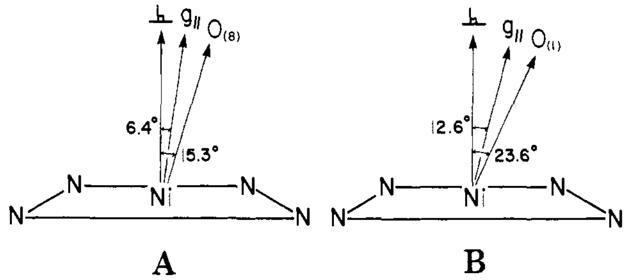

Figure 2. Directions of $g_{\parallel}$ compared with the shortest Ni–O bond directions in crystals of A and B. The plane of the paper is perpendicular to the NiN_4 plane and contains Ni–O.

Spin–orbit interaction between the $^2A_1$ ground state and the ^2E excited state, composed primarily of the degenerate d_{xz}, d_{yz} pair of orbitals, gives rise to a positive g shift when H_0 lies in the xy plane (i.e., positive $\Delta g_{\perp}$). In D_{4h} symmetry, there is no mechanism for spin–orbit interaction between the ground state and other excited states when H_0 is parallel to z, and hence no direct spin–orbital contribution to $\Delta g_{\parallel}$. However, in the lower symmetry environment for Ni^{3+} present in A (C_{2h}) and B (C_{2v}), the totally symmetric semioccupied orbital is a mixture of d_{z^2} and $d_{x^2-y^2}$. Coupling of $d_{x^2-y^2}$ to d_{xy} is then permitted for H_0 parallel to z and may account for the observed small positive $\Delta g_{\parallel}$.

The form of the observed g tensor leaves little doubt that the unpaired electron occupies d_{z^2}. An alternative ordering of the d orbitals in which d_{xy} lies above d_{z^2}, d_{xz} and d_{yz} but below $d_{x^2-y^2}$ may be envisaged for a square-planar complex or an octahedral complex having two very weakly bound trans ligands. However, a low-spin d^7 species for such an orbital scheme would show a substantial *negative* $\Delta g_{\parallel}$; a d^9 ($d_{x^2-y^2}$) species would have all positive g shifts, but with $\Delta g_{\parallel} > \Delta g_{\perp}$. These predictions are contrary to the experimental observations. Furthermore, the detection of substantial unpaired spin density[8] on the trans ligands in $[Ni(cyclam)(NCS)_2]^+$ is a clear indication that the semioccupied orbital in Ni(III) species is totally symmetric, i.e., d_{z^2} rather than d_{xy}.

By use of the average value of $\Delta g_{\perp}$, estimates of Δ, the energy difference between the ground and excited states, may be made for both species. From the relationship $\langle g_{\perp} \rangle = 2.0023 - 6\,\lambda/\Delta$ ($\lambda = -272$ cm^{-1} for Ni(III)[20]), values of $\Delta = 4310$ cm^{-1} (trans, A) and 4520 cm^{-1} (cis, B) are found. These are the smallest values of Δ so far observed for complexes of this ion and reflect the weakly coordinating properties of the perchlorate ion. Typically,[8] $\Delta g_{\perp}$ for Ni(III) octahedral complexes is $\simeq 0.2$, corresponding to a Δ value $\simeq 8000$ cm^{-1}. For the dibromo- and dichlorocyclam complexes, for example,[10] Δ values of 9730 cm^{-1} and 9180 cm^{-1} may be calculated from the polycrystalline spectra. At the other extreme, the dichlorobis(diphosphine) complex ion[13] $[Ni(DP)_2Cl_2]^+$ exhibits a small $g_{\perp}$ shift corresponding to a Δ of 15 600 cm^{-1}.

These differences in Δ may be rationalized in terms of varying extent of overlap between Ni ($3d_{z^2}$) and axial ligand orbitals. The disposition of the antibonding d_{z^2} orbital with respect to the filled, nonbonding d_{xz}, d_{yz} pair determines $\Delta g_{\perp}$. Strong σ bonding between d_{z^2} and axial ligand orbitals, such as halide ion p_z, destabilizes the semioccupied orbital, resulting in a large Δ and small $\Delta g_{\perp}$. On the other hand, weak axial bonding (or, indeed, the absence of bonding) will result in a very large $g_{\perp}$ shift. Spectra of Ni(III) in frozen, aqueous solutions of high ClO_4^- concentration show,[8] in fact, that tervalent nickel coordinates weakly, if at all, with perchlorate ion. It is, therefore, not too surprising perhaps that Ni(III) should exhibit a large $\Delta g_{\perp}$ in A and B, where the only available anionic ligand is ClO_4^-.

Unlike the situation in fluid media, Ni^{3+} cannot readily achieve the preferred[21] octahedral coordination when formed in a rigid crystal lattice. In the undamaged host Ni(II) lattices of A and

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Table II. Comparison of Principal Directions of the g Tensors and Certain Directions in the Undamaged Crystals[a]

	vector	direction cosines *a*	*b*	*c*	angle between vectors, deg
A	g_1	0.6866	−0.5187	0.5094	6.4
	$\perp^b$	0.6054	−0.5906	0.5335	
	g_2	0.6210	0.7828	−0.0400	12.2
	$N_{(1)}$–Ni	0.5977	0.7832	0.1711	
	g_3	−0.3780	0.3438	0.8596	9.0
	$N_{(2)}$–Ni	−0.4588	0.2093	0.8635	
	$O_{(8)}$–Ni	0.6512	−0.3637	0.6660	
B	g_1	0.9462	0	−0.3236	12.6
	$\perp^b$	0.9958	0	−0.1042	
	g_2	0.3236	0	0.9462	12.6
	bisector$_1$	0.1042	0	0.9958	
	g_3	0	1	0	0.0
	bisector$_2$	0	1	0	
	$O_{(1)}$–Ni	0.8699	−0.1051	−0.4820	

[a] Crystallographic data and atom labels taken from ref 15 and 16. [b] Unit vector perpendicular to the Ni–N plane.

B, the metal cation lies at the center of a square-planar arrangement of nitrogen atoms but is not bound to the perchlorate anions.[15,16] These are disposed at angles of 15.3° (A) and 23.6° (B) from the direction perpendicular to the NiN_4 plane (Figure 2) and in one case (A) make weak hydrogen bonds with ring nitrogens of the complex cation. There is some suggestion in our results, however, that Ni(III) formation is accompanied by a lattice rearrangement in which incipient bonding is established between the metal cation and the perchlorate anions.

The directions adopted by the unique $g_{\parallel}$ principal values, i.e., the directions of the d_{z^2} orbitals, provide evidence for a change in coordination (Table II). Dealing firstly with the trans ion (A), we note that $g_{\parallel}$ lies only 6° from the perpendicular to the nickel–nitrogen plane. Furthermore, the other two principal values lie approximately 10° from Ni–N directions. In the case of the cis ion (B), $g_{\parallel}$ lies 13° from the perpendicular to the nickel–nitrogen plane, and the larger of the remaining principal values lies along *b*, a bisector of a N–Ni–N angle. Thus, for both Ni(III) species the unpaired electron occupies a d_{z^2} orbital which lies only a few degrees off the anticipated direction, i.e., perpendicular to the Ni–N_4 plane of the undamaged crystal. Crystalline forces determine the directions of the large g values in B, whereas intramolecular forces are determinant in the case of isomer A.

Futher examination of the crystal structures[15,16] reveals a most interesting fact (Figure 2). In both A and B, $g_{\parallel}$ lies in a plane perpendicular to the NiN_4 plane which contains the shortest Ni–O distances. In each instance, $g_{\parallel}$ falls approximately midway between the perpendicular to the plane and the Ni–O vector (Figure 2). One is tempted to conclude that the d_{z^2} orbitals of the Ni(III) species are directed toward the ClO_4^- anions in order to achieve the preferred[21] octahedral coordination of the tervalent cation. This could conceivably be achieved by a concerted rotational motion (in opposite directions) of the perchlorate anions and the cation, leading to a new z axis for the ion, midway between Ni(II)–$OClO_3$ and the original z axis of the square-planar complex ion.

Conclusion

Spectroscopically detectable amounts of Ni(III) tetraazamacrocycle complexes are generated in the solid state by ^{60}Co γ irradiation of the corresponding Ni(II) species. The single unpaired electron in these d^7 ions is principally located in a Ni($3d_{z^2}$) atomic orbital which is directed a few degrees away from the perpendicular to the NiN_4 plane of the undamaged lattice. The proximity of the new z axis to Ni–$OClO_3$ directions suggests that Ni(III) formation is accompanied by a lattice rearrangment which results in incipient octahedral coordination of the nickel cation.

Registry No. A (Ni^{II}), 15392-95-7; A (Ni^{III}), 83602-86-2; B (Ni^{II}), 15308-64-2; B (Ni^{III}), 83572-90-1.

Mechanism of Ozonolysis of Acetylenes: Evidence for a Free-Radical Pathway for the Decomposition of Intermediates

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Abstract: Dimethylacetylene was ozonized at −78 °C and then warmed in the presence of spin traps. Acetoxyl and acetyl spin adducts are observed, indicating that radical reactions are, at least in part, involved in product formation. The temperature profile for spin adduct appearance suggests that the two spin adducts come from different precursors; on the basis of analogies with literature data, we suggest that the acetoxyl adduct comes from compound **5** and the acetyl adduct from compound **3**. We suggest that the acetoxyl radical in our system is too unstable to be scavengable by spin traps before it decarboxylates; therefore, we propose that **5** reacts with spin traps in a molecule-assisted decomposition process to give the acetoxyl adduct without involving free acetoxyl radicals. Spin adducts are observed even at −70 °C, and it is suggested that these adducts also result from an assisted decomposition of some type. Two possible mechanisms are suggested for this interaction, an electron transfer and a 1,3 dipolar addition. Some preliminary experiments on diphenylacetylene also are reported.

Mechanistic studies of the ozonolysis of acetylenes,[1] unlike the ozonolysis of olefins,[2] have been very limited. The reaction, as in the case of olefins, is believed to proceed via the intermediacy of the carbonyl oxide **2** as shown in Scheme I. All of the products (α-dicarbonyls, acid anhydrides, and polyperoxides) are believed to arise by the rearrangement or reactions of **2**.[1-10] On the basis

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