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Single-Crystal Study of a Nickel(III)-Oxime Complex[1]

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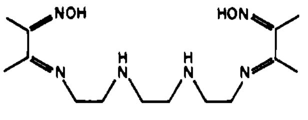
Upon exposure to air the pseudooctahedral complex of 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime with Ni(IV) becomes paramagnetic. Examination of a single crystal of the material at 90 K in an EPR spectrometer indicates the formation of Ni(III) centers from Ni(IV) ions of the unexposed lattice.

Introduction

The recent resurgence of interest[2-7] in the high oxidation states of nickel, Ni(III) and Ni(IV), is due in large measure to the stabilization of those states achieved by complexing with long-chain[3,8] (N_6) or macrocyclic (N_4, N_5) ligands.[4,6,7,9] Oxime ligands of the type **1** (**1** ≡ H_2L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime), for example, readily form pseudooctahedral complexes[8] (e.g., **2**) with both Ni(II) and Ni(IV). Interconversion of the complexed Ni^{2+} and Ni^{4+} ions may be achieved both chemically and electrochemically[8,10,11] in a two-electron redox process:



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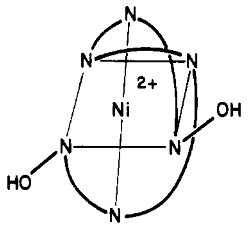

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$$Ni^{II}H_2L \rightarrow Ni^{IV}L^{2+} + 2H^+ + 2e^- \qquad E^\circ = 0.95\ V$$

Current research is being directed toward the detection and characterization of intermediates in such concerted electron-proton-transfer processes. Lappin[11] has recently shown that controlled electrochemical oxidation of $[Ni^{II}H_2L]^{2+}$ yields a relatively long-lived Ni(III) species characterized by a frozen-solution EPR spectrum having $g_\parallel = 2.033$ and $g_\perp = 2.155$. Similar parameters have been reported for species generated by chemical oxidation[12] of $[Ni^{II}H_2L]^{2+}$ and by ^{60}Co γ-irradiation[13] of certain Ni(II) macrocycles in the solid state. In the latter case, examination of single crystals[13] enabled the precise determination of the g-tensor components and their location within the undamaged host lattice.

The complex $[Ni^{IV}L](ClO_4)_2$, if kept scrupulously dry in an inert atmosphere, is stable for long periods in the solid form. Slow decomposition takes place in air, however, and the solid becomes paramagnetic. In this article, we describe the anisotropic EPR spectrum observed in a single crystal of the slightly decomposed nickel(IV) perchlorate complex.

Table I. g^2 Tensor, Principal Values, and Directions for the Ni(III) Center

	g^2 tensor			direction cosines for principal values		
				z 4.1879	x 4.5324	y 4.6313
	l	m	n			
l	4.4773	±0.1263	0	∓0.3998	0.9166	0
m	±0.1263	4.2430	0	0.9166	±0.3998	0
n	0	0	4.6313	0	0	1
			+50° rotation about m			
	a	b	c^*			
a	4.5677	±0.0812	−0.0758	∓0.2570	0.5892	−0.7660
b	±0.0812	4.2430	±0.0967	0.9166	±0.3998	0
c^*	−0.0758	±0.0967	4.5409	∓0.3063	0.7022	0.6428

Experimental Section

The nickel(II) oxime $(NiH_2L)^{2+}$ was oxidized to the nickel(IV) state with concentrated nitric acid.[8] After dilution with ice-cold water, dark violet crystals were filtered off and washed with ethanol and ether. The product was kept over dry $CaCl_2$. Anal. Calcd: C, 29.60; H, 4.62; N, 14.80. Found: C, 29.25; H, 4.67; N, 15.04. Solutions of the nickel(IV) ion were reacted with Fe(II), confirming the Ni(IV) oxidation state. A crystal was exposed to air for 3 days, and an increasingly strong EPR signal was detected. Single-crystal EPR studies using a two-circle goniometer[14] were carried out at 90 K with a Varian E12 spectrometer. On prolonged exposure to air, the crystals showed little change in morphology, but a preliminary X-ray analysis[15] was consistent with a cation formulation $NiHL^{2+}$, one oxime being protonated with a N–O bond length considerably longer (~1.40 Å) than that of the unprotonated bond (~1.31 Å).

Results

A single crystal of the nickel–oxime complex exhibited an EPR spectrum consisting of two broad (70 G p–p) lines for an arbitrary orientation of the dc magnetic field, H_0. A coalesced spectrum consisting of a single line was observed for certain orientations and, in particular, was observed when H_0 lay in a certain plane of the crystal. g^2 values were determined at 10° intervals throughout that plane and plotted against angle. From the best-fit[16] sine curve to the data the maximum and minimum g^2 values and their directions were established. The latter (m, n) and their vector product (l) were defined as arbitrary axes within the crystal.

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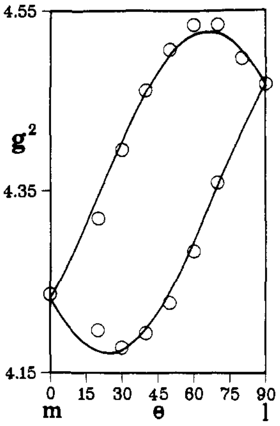

Figure 1. g^2 variation in the *lm* plane of a nickel oxime perchlorate crystal. Circles are experimental values; curves are the best-fit sinusoidal relationship to them.

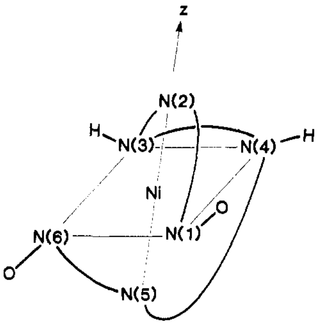

Figure 2. Structure of the nickel–oxime complex ion.

Preliminary measurements within the crystal planes defined by the (*l, m, n*) axis system showed that site splitting occurred in *lm* only. A sine curve (Figure 1) was fitted[16] to g^2 measurements in that plane and best-fit tensor components g^2_{ll}, g^2_{mm}, and g^2_{lm} derived therefrom. The full $\mathbf{g}^2$ tensor together with its principal values and directions is given in Table I.

Discussion

Comparison of the principal values of our **g** tensor (2.0464, 2.1289, 2.1521) with those attributed to Ni(III) centers in other hosts[11-13] clearly suggests an assignment to Ni(III) for the species in the nickel oxime perchlorate. The nearly axial **g** tensor and the large positive deviations of *g* from the free-spin value (2.0023) along directions perpendicular to the axis (*z*) are consistent with the presence of a low-spin d^7 ion in a tetragonally elongated octahedral environment.[17] Furthermore, consideration of preliminary crystallographic data[18] in conjunction with the principal directions of the **g** tensor (Table I) shows (see below) that the center is derived from a Ni^{4+} ion of the undamaged lattice and is, therefore, a pseudooctahedral complex of Ni^{3+} (Figure 2).

X-ray crystallographic examination of the nickel complex has shown[18] that it crystallizes in the monoclinic system with space group $P2_1/c$. Two magnetically distinguishable sites are, therefore, anticipated for a center that obeys the undamaged crystal symmetry, but site splitting should not occur in the *ac* crystal plane. Our observations are certainly consistent with this expected behavior. In particular, we note that the axis (*z*) of our Ni(III) species lies 24° from *m* in our (*l, m, n*) basis, an angle not too different from that (32°) between N(5)–N(2) and *b* in the crystal (Table II). Moreover, the N(4)–N(6) vector lies almost in the *ac* plane of the undamaged crystal. A simple explanation of our findings, therefore, is that, in our arbitrary axis system (*l, m, n*), *m* coincides with the twofold crystal axis *b* and *n*, a principal direction of g^2, lies along N(4)–N(6). In fact, a rotation of the (*l, m, n*) basis by 50° about *m* (Table I) places the eigenvectors of one site in near coincidence with the N–N directions of Table II.

Table II. Certain N–N Distances and Directions in the Lattice of the Nickel Oxime Perchlorate

		direction cosines[a]		
	dist, Å	*a*	*b*	*c**
N(1)–N(3)	4.114	0.5517	0.4907	0.6744
N(4)–N(6)	4.057	−0.7918	−0.0821	0.6052
N(5)–N(2)	3.959	−0.3398	0.8491	−0.4047

[a] *a* and *b* are crystal axes of the monoclinic crystal; *c** is 90° from *a* in the *ac* crystal plane.

It would thus appear that the direction of minimum *g*, i.e. the *z* axis, lies very nearly along N(5)–N(2), the shortest of the N–N distances listed in Table II. At first glance, this situation approximately resembles that of a tetragonally *compressed* octahedron, and one would anticipate occupation of a Ni $d_{x^2-y^2}$ orbital by the unpaired electron with $g_\parallel > g_\perp$. Since this is contrary to the experimental observations, we conclude that, in spite of their proximity, the axial nitrogens (2 and 5) interact more weakly with the Ni ion than the equatorial nitrogens (1, 3, 4, and 6). The unpaired electron unquestionably occupies an orbital having considerable Ni $3d_{z^2}$ character. However, in the low-symmetry environment of the oxime ligand (Figure 2), admixture of $d_{x^2-y^2}$ into the predominantly d_{z^2} semioccupied orbital is permitted. Coupling of this $d_{x^2-y^2}$ component of the ground state to an excited state of d_{xy} character via the spin–orbit interaction then accounts[6,13] for the positive *g* shift ($\Delta g_\parallel$) along *z*. The large value of $\Delta g_\parallel$ for this system is an indication that the $d_{x^2-y^2}$ and d_{z^2} orbitals are close in energy.

The substantial *g* shifts ($\Delta g_\perp$) along *x* and *y* arise from spin–orbit coupling between the ground state (d_{z^2}) and excited states having d_{xz} or d_{yz} character. We may estimate Δ, the energy difference between these states, from the relationship

$$\Delta g_\perp = -6\lambda/\Delta$$

with[19] $\lambda = -272\ \text{cm}^{-1}$ for Ni^{3+}. From the average $\Delta g_\perp = 0.14$, we obtain $\Delta = 11\,800\ \text{cm}^{-1}$ for the Ni(III)–oxime complex, a value that falls in the middle of the range, 4000–16 000 cm^{-1}, observed for Ni(III) species.[6,13] Variations in Δ may be interpreted[13] in terms of differing extents of overlap of Ni $3d_{z^2}$ and axial ligand orbitals: weakly interacting ClO_4^- ligands in Ni(III) macrocycles, for example, give rise to small Δ and large $\Delta g_\perp$ values; strongly interacting halide ions[20,21] in dichlorobis(phosphine)nickel(III) lead to large Δ and small $\Delta g_\perp$. The intermediate value observed for the oxime complex provides confirmation of the retention of axial nitrogen coordination following reduction of the Ni(IV) species.

Somewhat disappointingly, nitrogen hyperfine structure was not detected in the EPR spectra. The greatly increased line width compared to that in Ni(III) macrocycles[13] could be an indication of the presence of unresolved ^{14}N hyperfine structure. In view of the low symmetry of the center and the admixture of $d_{x^2-y^2}$ to the semioccupied orbital, the failure to resolve such structure is, however, not too surprising. A large, temperature-dependent natural line width due to an efficient spin–lattice relaxation mechanism might be anticipated for this system. Cooling to 4 K reduced the spectral line width

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but unfortunately did not result in the resolution of hyperfine structure. It is conceivable that strain broadening[22,23] is significant for the nickel–oxime crystal, in which case operation at a lower microwave frequency[22] might improve the resolution.

Note Added in Proof. Shortly after acceptance of this paper for publication, a complete X-ray diffraction study of both Ni(II) and Ni(IV) complexes appeared in the literature.[24] N–N direction cosines computed from the data for the Ni(IV) complex agree reasonably well with those given in our Table II when allowance is made for the difference in numerical labeling of the ligand nitrogens.

Registry No. $[Ni^{IV}L](ClO_4)_2$, 55188-34-6; $[NiHL](ClO_4)_2$, 85894-12-8.

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Structural and Magnetic Investigations on the CT Ion-Radical Salt (*p*-(Dimethylamino)phenyl)dimethylammonium Bis(maleonitriledithiolato)nickelate(III)

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A detailed study of (TMPD)Ni(mnt)$_2$ by a variety of physical methods—X-ray crystallography, electronic absorption spectroscopy, magnetic susceptibility, electrical conductivity, and EPR—has been carried out. Though Ni(mnt)$_2^-$ and TMPD$^+$ form segregated stacks along the "*a*" axis in the triclinic modification $P\bar{1}$, a number of short contacts between the units facilitate charge transfer from TMPD$^+$ to Ni(mnt)$_2^-$. Both susceptibility and EPR studies indicate two temperature regions, $T < 100$ K and $T > 100$ K. In the $T < 100$ K region, where the behavior is Curie–Weiss type, the decomposition of total susceptibility shows that at 4.2 K about 90% of the contribution comes from the Ni(mnt)$_2^-$ stack. A value of exchange (~ 120 cm^{-1}) has been found from the dependence of χ on temperature in the $T > 100$ K region. Powder EPR studies yielded a ratio of D_e/J to be 1.94×10^{-2}. Single-crystal EPR studies at 77 K clearly indicate a change in the principal axis cosines and from line width analysis in the plane perpendicular to "*a*" give the best fit for $J = -6.5$ cm^{-1}, $D_e = -0.13$ cm^{-1}, and $\rho = 5$. The line shape analysis shows low-dimensional behavior for $B \| a$ and nearly Lorentzian behavior for $B \perp a$.

1. Introduction

Recently, considerable interest has been focused on crystalline solids with the gross anisotropy of at least one intensive variable such as conductivity, magnetic susceptibility, etc.[1-3] These variations are associated with a columnar crystallographic packing, and perhaps the best examples of these are based on TCNQ$^-$ ion-radical salts.[4,5]

Platelike transition-metal complexes which stack as columnar structures provide a chemically flexible class of such materials.[6] Maleonitriledithiolene metal complexes[7] $[M(mnt)_2]^{n-}$ are a well-studied class of coordination compounds which possess an overall planar geometry irrespective of the metal or its oxidation state. These undergo facile reversible electron-transfer reactions, have highly delocalized electronic structures, and are known for their ability to form donor–acceptor compounds with organic donor molecules[8-16] to give a D$^+$A$^-$ salt where D$^+$ and/or A$^-$ are paramagnetic.

In our effort to characterize new examples of quasi-1-D systems, we have synthesized and studied a new crystalline ion-radical salt, (*p*-(dimethylamino)phenyl)dimethylammonium (maleonitriledithiolato)nickelate(III) (TMPD$^+$Ni(mnt)$_2^-$), shown in Figure 1.

We report here a detailed study of TMPD$^+$Ni(mnt)$_2^-$ by a variety of physical methods—crystallography, electronic absorption spectroscopy, magnetic susceptibility, electrical conductivity, and electron paramagnetic resonance. Both the TMPD$^+$ and the Ni(mnt)$_2^-$ moieties are $S = {}^1/_2$ systems, are planar, and have highly delocalized electronic structures. Thus, TMPD$^+$Ni(mnt)$_2^-$ combines the advantages of the infinite variety of organic compounds with the electronic structural flexibility of the transition-metal complexes.

Our X-ray structure (section 3A) shows that the TMPD$^+$ ions and the Ni(mnt)$_2^-$ ions stack among themselves, forming segregated regular stacks. Though static susceptibility (section 3D) measurements yield interesting information, single-crystal EPR results (section 3E) yield a surprisingly detailed picture of the magnetic phenomena.

This compound has advantages over other similar compounds studied earlier on two counts, detailed crystal and molecular structural data and single-crystal EPR information. Though magnetic data[10,12-13] are available on compounds such as (phenothiazine)$^+$Ni(thiete)$_2^-$, TTF$^+$Ni(mnt)$_2^-$, and (perylene)$_2^+$Pd(mnt)$_2^-$, crystal and molecular structural information is lacking. Despite a knowledge of the detailed molecular structures[16,17] of ion-radical salts such as TTF$^+$Pt(thiete)$_2^-$ and TTF$^+$Ni(thiete)$_2^-$ large EPR line widths of the

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