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X-ray Structural Characterization of Nickel(II) and Nickel(IV) Complexes Formed by a Hexadentate Amine–Imine–Oxime Ligand

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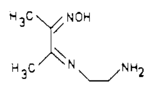
The crystal and molecular structures of two nickel complexes derived from 3,14-dimethyl-4,7,10,13-tetraaza-3,13-hexadecadiene-2,15-dione dioxime ($C_{14}H_{28}N_6O_2$, represented by H_2L in formulas) have been determined from X-ray diffraction data and refined by least-squares methods. The first compound, $[Ni(H_2L)](ClO_4)_2$, consists of Ni(II) complex cations and perchlorate anions and has crystal data as follows: space group $P\bar{1}$; $Z = 2$; $a = 8.492$ (2), $b = 12.217$ (4), $c = 12.959$ (4) Å; $\alpha = 66.96$ (2), $\beta = 72.80$ (2), $\gamma = 71.88$ (2)°; $R = 0.052$ for 4663 reflections with $I > 3\sigma(I)$. The second compound, $[NiL](ClO_4)_2$, obtained by oxidation of $[Ni(H_2L)](ClO_4)_2$ with concentrated nitric acid, consists of nickel(IV) complex cations and perchlorate anions. The crystal data is as follows: space group $P2_1/c$; $Z = 4$; $a = 7.611$ (2), $b = 15.125$ (4), $c = 19.529$ (5) Å; $\beta = 99.31$ (2)°; $R = 0.059$ for 2305 reflections with $I > 3\sigma(I)$. The nickel atoms in the two structures have a similar distorted-octahedral coordination environment in which the hexadentate ligand is bonded to nickel through its nitrogen donor atoms. Excepting the differences that result from the different oxime functions, the geometries of the ligand molecules in the compounds are very similar. The Ni–N bond lengths in the two nickel systems are distinctly unalike, however. In $[Ni(H_2L)](ClO_4)_2$ the average Ni–N(amine), Ni–N(imine), and Ni–N(oxime) bond lengths are 2.098 (4), 2.005 (5), and 2.119 (18) Å, respectively, and the corresponding distances in $[NiL](ClO_4)_2$ are 1.955 (6), 1.871 (4), and 1.953 (11) Å. The shorter Ni–N(amine) and Ni–N(imine) bonds in the latter complex are attributed to the increase in the formal oxidation state of nickel from +2 to +4, but most of the shortening in the Ni–N(oxime) distance is considered to be produced by the removal of the oxime protons on oxidation.

Introduction

Rapid advances have been made in the past few years in our understanding of the chemistry of nickel in its highest oxidation state, +4. This development, recently reviewed Nag and Chakravorty,[1] has mainly been associated with synthetic, electrochemical, magnetochemical, and spectroscopic studies, and the shortage of structural information from X-ray diffraction studies is striking by contrast. So far there seem to be only four nickel(IV) compounds that have been characterized by X-ray structural analysis. These include two tris complexes formed by bidentate *N,N*-di-*n*-butyldithiocarbamate[2] and the analogous selenium ligand[3] (though in view of the known ease of oxidation of these ligands, some doubt about the real state of nickel has been expressed[4]) and two bis complexes formed by tridentate 2,6-diacetylpyridine dioximate[5] and 2-((2-aminoethyl)imino)-3-butanone oximate[6] ligands.

The last of these structures, containing an octahedral NiN_6 coordination sphere made up of the nitrogen donor atoms derived from the anion of the amine–imine–oxime ligand **1** was determined in our laboratory. We showed that the Ni(IV)–N bond lengths in the complex are considerably shorter than the corresponding distances in an octahedral nickel(II) complex formed by **1**. In the work presently described, we have confirmed the extent of this contraction by determining the crystal structure of the nickel(IV) chelate system derived from a closely related hexadentate ligand, **2**. For comparison, the crystal structure of a nickel(II) complex formed by the same ligand has also been determined.



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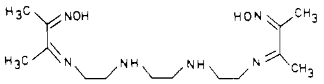

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Ligands **1** and **2** both belong to the series of oxime compounds used by Mohanty et al.[7] and Singh et al.[8] for the preparation of nickel(IV) complexes. The same authors have verified the diamagnetic nature of the compounds and thoroughly studied their redox behavior by cyclic voltammetric and coulometric techniques.

The efficiency of the present ligand type in preparation of stable nickel(IV) species can evidently be attributed to the presence of two oximato donor groups in the complexes. It is assumed that each of the oxime functions is able to provide a facile pathway for the one-electron oxidation of nickel(II), and the stabilization of the high oxidation state is supported by the negative charge of the oxime oxygens through σ donation and inductive transmission.[1,7-9]

Experimental Section

Crystal Preparations. (a) The nickel(II) complex, $[Ni(H_2L)](ClO_4)_2$, was prepared by addition of a methanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (1 mol equiv) to a boiling methanolic solution containing 2,3-biacetyl monoxime (2 mol equiv) and triethylenetetramine (1 mol equiv). Slow evaporation of the cooled solution yielded reddish brown crystals, which were filtered off and recrystallized from aqueous methanol.

(b) The nickel(IV) complex, $[NiL](ClO_4)_2$, was prepared by oxidation of $[Ni(H_2L)](ClO_4)_2$ with concentrated nitric acid as described by Mohanty et al.[7] The deep violet needlelike crystals suitable for X-ray analysis were obtained by dissolving the crude product in water at room temperature, adding small amounts of solid $NaClO_4$, and cooling the solution to 2–3 °C. In open air the crystals remain externally unaltered at least for several days, but for retardation of possible decomposition the crystal selected for data collection was sealed in epoxy glue immediately after the preparation.

X-ray Crystallography. Unit cell parameters and the orientation matrices for both compounds were determined on a Nicole *P*3 four-circle diffractometer equipped with a graphite monochromator. Accurate cell dimensions and other crystallographic data are listed in Table I.

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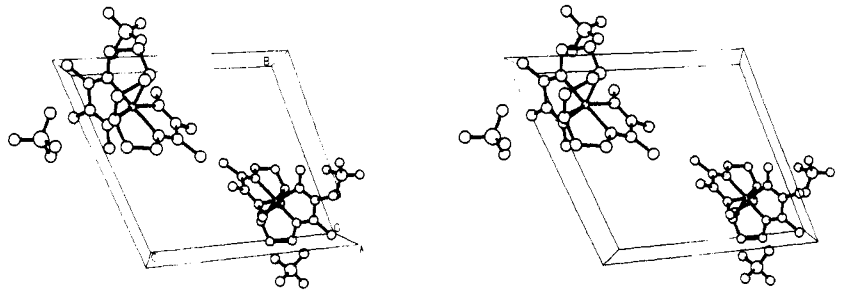

Figure 1. Stereoscopic view of the molecular packing of $[Ni(H_2L)](ClO_4)_2$ in the unit cell, with the hydrogens omitted for clarity.

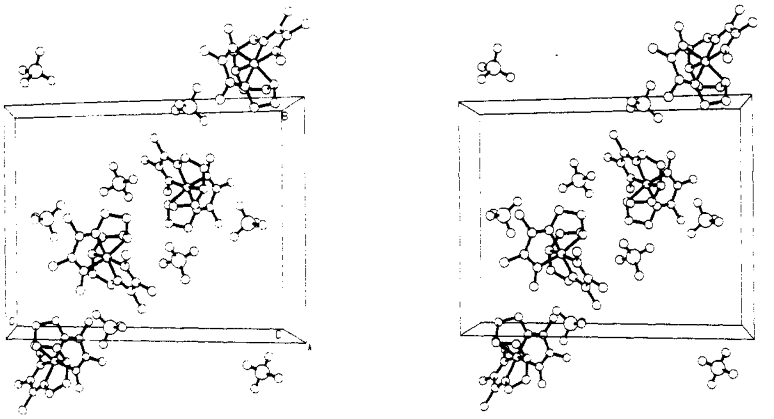

Figure 2. Stereoscopic view of the molecular packing of $[NiL](ClO_4)_2$ in the unit cell, with the hydrogens omitted for clarity.

X-ray intensities were measured by the ω-scan technique with variable scan speeds. The data were corrected for Lorentz and polarization factors, but no absorption corrections were deemed necessary.

The structures were solved by direct methods with the MULTAN[10] program. The nickel and six nitrogen atoms of both complexes were located in the initial E maps, and subsequent Fourier syntheses gave the positions of the other non-hydrogen atoms. The structures were refined by use of the block-diagonal least-squares methods of the X-RAY system.[11] All hydrogen atoms were located on difference Fourier maps. Isotropic temperature factors were used for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms.

The atomic scattering factors for the non-hydrogen atoms were those of Cromer and Mann[12] and for hydrogen atoms those of Stewart, Davidson, and Simpson.[13] Since no experimental information about the actual electron density at the nickel atom in the oxidation state +4 was available, we considered it more objective to use the atomic scattering factors for Ni^0 rather than those for Ni^{2+} or Ni^{3+} in the calculation of the structure of $[NiL](ClO_4)_2$. The choice made here has only a marginal effect on the final structure. Anomalous dispersion corrections ($\Delta f'$, $\Delta f''$)[14] were included for Ni and Cl. The final R values were 0.052 for $[Ni(H_2L)](ClO_4)_2$ and 0.059 for $[NiL](ClO_4)_2$.

Final parameters for all non-hydrogen and hydrogen atoms in both complexes are listed in Tables II and III, respectively. Observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material.

Results and Discussion

Description of the Structures. The molecular structures of the oxidized and nonoxidized complexes are much alike. Both of them consist of divalent complex cations and perchlorate anions interconnected by hydrogen bonding. The arrangements of the ions in the respective unit cells are illustrated in Figures 1 and 2. The nickel atom can be found to have a similar distorted-octahedral environment in the two structures:

Table I. Data for the X-ray Diffraction Studies of $[Ni(H_2L)](ClO_4)_2$ and $[NiL](ClO_4)_2$

	$[Ni(H_2L)](ClO_4)_2$	$[NiL](ClO_4)_2$
	Crystal Parameters	
cell refinement	20 reflctns	24 reflctns
2θ range, deg	29-31	8-19
a, Å	8.492 (2)	7.611 (2)
b, Å	12.217 (4)	15.125 (4)
c, Å	12.959 (4)	19.529 (5)
α, deg	66.96 (2)	90
β, deg	72.80 (2)	99.31 (2)
γ, deg	71.88 (2)	90
V, Å	1152.3 (5)	2218.5 (10)
Z	2	4
space group	$P\bar{1}$	$P2_1/c$
d_o, g cm^{-3}	1.64	1.69
d_c, g cm^{-3}	1.64	1.70
	Data Collection	
radiation	Mo Kα (λ = 0.710 69 Å)	
method	ω-scan technique	
bkgd	offset 1.0° and −1.0° in ω from K$\alpha_{1,2}$ max	
stds	2 every 58 reflctns; no significant decay	
μ, cm^{-1}	11.4	11.8
scan rate, deg min^{-1}	3.0-30.0	2.0-30.0
2θ range, deg	3.0-58.0	3.0-52.0
dimens, mm	0.70 × 0.60 × 0.25	0.40 × 0.25 × 0.25
unique reflctns	6119	4372
	Structure Refinement	
quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
wt, Cruickshank	$A = 15.0, B = 0.025$	$A = 60.0, B = 0.0085$
total obsd reflctns		
$I > 3.0\sigma(I)$	4663	2305
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma\lvert F_o\rvert$	0.052	0.059
goodness of fit[a]	0.87	0.26
largest shift/esd	0.87	0.85

[a] $GOF = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_{obsd} - N_v)]^{1/2}$.

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(13) Stewart, R. F.; Davidson, E.; Simpson, W. *J. Chem. Phys.* **1968**, *42*, 3175.

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Table II. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Thermal Parameters (× 10^3) for the Non-Hydrogen Atoms

	$[Ni(H_2L)](ClO_4)_2$				$[NiL](ClO_4)_2$			
atom	x	y	z	U_{eq},[a] Å^2	x	y	z	U_{eq}, Å^2
C1	−19 (5)	3108 (3)	3901 (3)	33	222 (10)	7562 (5)	4483 (4)	37
C2	−1723 (5)	3882 (3)	3693 (3)	35	1864 (11)	7965 (5)	4341 (4)	42
C3	−3944 (5)	4287 (4)	2682 (4)	47	4296 (12)	7795 (6)	3661 (5)	52
C4	−3896 (6)	4118 (4)	1575 (4)	53	4325 (12)	7320 (6)	2999 (5)	54
C5	−4044 (6)	1948 (4)	2046 (4)	49	4716 (10)	5701 (6)	3339 (5)	46
C6	−4118 (5)	1349 (4)	3331 (4)	44	4638 (10)	5655 (6)	4098 (5)	46
C7	−1419 (5)	−216 (3)	3609 (3)	43	1739 (12)	4871 (6)	4195 (5)	49
C8	−463 (6)	−228 (4)	2414 (4)	44	916 (12)	4666 (5)	3455 (5)	46
C9	1422 (5)	1001 (3)	979 (3)	33	−864 (10)	5605 (5)	2591 (4)	38
C10	1926 (4)	2195 (3)	547 (3)	34	−1116 (11)	6497 (6)	2343 (4)	45
C11	1003 (7)	3394 (4)	4482 (4)	54	−853 (14)	7877 (7)	4998 (5)	64
C12	−2622 (7)	4762 (5)	4324 (5)	62	2594 (14)	8784 (7)	4710 (6)	63
C13	2278 (7)	79 (4)	391 (4)	56	−1924 (12)	4864 (7)	2216 (5)	62
C14	3458 (6)	2438 (5)	−360 (5)	60	−2356 (14)	6806 (8)	1716 (5)	73
N1	464 (3)	2223 (3)	3499 (2)	29	−223 (8)	6868 (5)	4109 (3)	38
N2	−2279 (4)	3685 (3)	2986 (3)	35	2597 (9)	7562 (4)	3884 (3)	37
N3	−2996 (4)	2873 (3)	1536 (3)	39	3530 (8)	6417 (4)	3003 (3)	40
N4	−2416 (4)	1018 (3)	3605 (3)	34	2761 (8)	5719 (4)	4230 (3)	38
N5	239 (4)	864 (3)	1861 (3)	32	305 (8)	5513 (4)	3128 (3)	38
N6	936 (4)	2957 (3)	1037 (2)	32	−57 (9)	7083 (5)	2723 (4)	46
O1	2071 (3)	1532 (3)	3633 (3)	43	−1562 (8)	6385 (4)	4150 (4)	60
O2	1469 (4)	4038 (3)	666 (3)	43	44 (10)	7887 (4)	2604 (4)	70
Cl1	4219 (1)	−1546 (1)	3389 (1)	44	2532 (3)	4864 (2)	1389 (1)	59
Cl2	−878 (1)	3468 (1)	−1730 (1)	46	3519 (4)	−1706 (2)	1008 (2)	77
Ni	−1003 (05)	2280 (04)	2414 (03)	26	1474 (12)	6532 (06)	3510 (05)	31
O3	2610 (6)	−956 (6)	3892 (5)	107	2822 (23)	4269 (11)	1905 (8)	220
O4	4068 (8)	−2427 (4)	3003 (5)	96	2511 (32)	5645 (10)	1657 (8)	258
O5	5225 (7)	−2017 (6)	4214 (5)	118	3728 (18)	4793 (8)	952 (7)	167
O6	4865 (11)	−623 (6)	2431 (5)	140	954 (17)	4892 (16)	1008 (8)	254
O7	127 (6)	4256 (4)	−1759 (4)	75	4645 (12)	−1867 (6)	508 (4)	95
O8	−747 (12)	3411 (6)	−2774 (4)	152	4456 (16)	−1341 (6)	1581 (4)	121
O9	−424 (10)	2319 (4)	−950 (6)	134	2777 (18)	−2508 (8)	1214 (6)	145
O10	−2542 (8)	3860 (8)	−1183 (8)	153	2203 (11)	−1121 (6)	668 (4)	91

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Table III. Fractional Atomic Coordinates (× 10^3), Isotropic Thermal Parameters, and Bond Distances (Å) for the Hydrogen Atoms

	$[Ni(H_2L)](ClO_4)_2$					$[NiL](ClO_4)_2$				
atom	x	y	z	U, Å^2	bond length	x	y	z	U, Å^2	bond length
C3(H1)	−417 (6)	521 (4)	258 (4)	0.045	1.05 (5)	462 (15)	853 (7)	364 (6)	0.094	1.14 (11)
C3(H2)	−485 (7)	394 (5)	341 (5)	0.055	1.06 (5)	506 (9)	768 (5)	394 (3)	0.025	0.76 (6)
C4(H1)	−340 (7)	461 (5)	94 (5)	0.059	0.88 (5)	349 (11)	766 (5)	258 (4)	0.053	1.08 (8)
C4(H2)	−490 (7)	439 (6)	125 (5)	0.065	0.97 (7)	505 (11)	735 (6)	288 (4)	0.055	0.64 (9)
C5(H1)	−338 (6)	132 (4)	152 (4)	0.048	1.13 (6)	412 (11)	515 (5)	318 (4)	0.051	0.97 (8)
C5(H2)	−512 (5)	232 (4)	185 (4)	0.037	0.95 (5)	577 (10)	571 (5)	330 (4)	0.042	0.81 (8)
C6(H1)	−449 (5)	59 (4)	354 (4)	0.038	0.99 (5)	520 (9)	509 (5)	430 (4)	0.036	1.00 (7)
C6(H2)	−490 (6)	187 (4)	377 (4)	0.048	0.98 (5)	526 (10)	606 (5)	436 (4)	0.044	0.88 (7)
C7(H1)	−223 (7)	−71 (5)	393 (5)	0.060	0.95 (6)	230 (10)	442 (5)	438 (4)	0.041	0.85 (7)
C7(H2)	−55 (5)	−51 (4)	413 (3)	0.029	1.03 (5)	94 (12)	498 (6)	448 (5)	0.061	0.90 (10)
C8(H1)	32 (7)	−104 (5)	246 (5)	0.072	1.00 (5)	−8 (9)	427 (5)	347 (4)	0.033	0.97 (7)
C8(H2)	−111 (6)	−24 (4)	190 (4)	0.048	0.99 (6)	182 (9)	442 (5)	317 (4)	0.032	1.02 (8)
C11(H1)	112 (7)	414 (5)	420 (5)	0.062	0.86 (6)	−145 (16)	839 (8)	486 (6)	0.121	0.91 (11)
C11(H2)	51 (9)	324 (6)	537 (6)	0.103	1.07 (7)	−128 (17)	753 (8)	507 (6)	0.110	0.65 (13)
C11(H3)	206 (8)	280 (6)	447 (6)	0.092	0.97 (6)	−23 (14)	821 (7)	535 (6)	0.088	0.92 (10)
C12(H1)	−218 (10)	539 (8)	407 (7)	0.148	0.86 (10)	240 (13)	864 (7)	507 (5)	0.079	0.78 (11)
C12(H2)	−287 (10)	449 (7)	514 (7)	0.115	0.95 (8)	351 (13)	900 (7)	456 (5)	0.088	0.86 (11)
C12(H3)	−368 (7)	512 (5)	416 (5)	0.070	0.92 (6)	166 (6)	919 (7)	475 (6)	0.111	0.95 (12)
C13(H1)	145 (9)	−21 (7)	29 (6)	0.099	0.93 (10)	−223 (11)	442 (10)	256 (8)	0.157	1.00 (15)
C13(H2)	294 (9)	36 (6)	−44 (6)	0.096	1.03 (6)	−103 (17)	456 (8)	202 (7)	0.143	0.95 (13)
C13(H3)	283 (9)	−48 (7)	65 (6)	0.108	0.72 (6)	−250 (21)	512 (11)	173 (9)	0.155	1.06 (14)
C14(H1)	408 (11)	279 (8)	−24 (7)	0.128	0.86 (12)	−259 (15)	646 (7)	139 (6)	0.116	0.82 (11)
C14(H2)	292 (11)	313 (8)	−104 (8)	0.153	1.06 (8)	−245 (16)	732 (8)	183 (6)	0.099	0.82 (13)
C14(H3)	399 (9)	189 (7)	−61 (6)	0.106	0.81 (8)	−175 (18)	695 (9)	137 (7)	0.108	0.91 (15)
N3(H)	−250 (7)	286 (5)	84 (5)	0.064	0.88 (6)	309 (10)	624 (5)	255 (4)	0.048	0.94 (8)
N4(H)	−252 (6)	117 (5)	440 (4)	0.053	1.09 (7)	274 (9)	588 (5)	466 (3)	0.030	0.87 (7)
O1(H)	231 (6)	100 (4)	337 (4)	0.043	0.80 (6)					
O2(H)	93 (7)	436 (5)	99 (5)	0.065	0.67 (6)					

the six nitrogen donor atoms of the hexadentate ligand are located in such a way that the two planes defined by the three successive nitrogens on both halves of the ligand are nearly perpendicular to each other. This coordination geometry is expected and resembles the meridional arrangement of the two tridentate ligands in the nickel complexes formed by **1**.[6]

In the case of the nonoxidized compound it is clear that the complex moiety can be formulated as $[Ni(H_2L)]^{2+}$, which

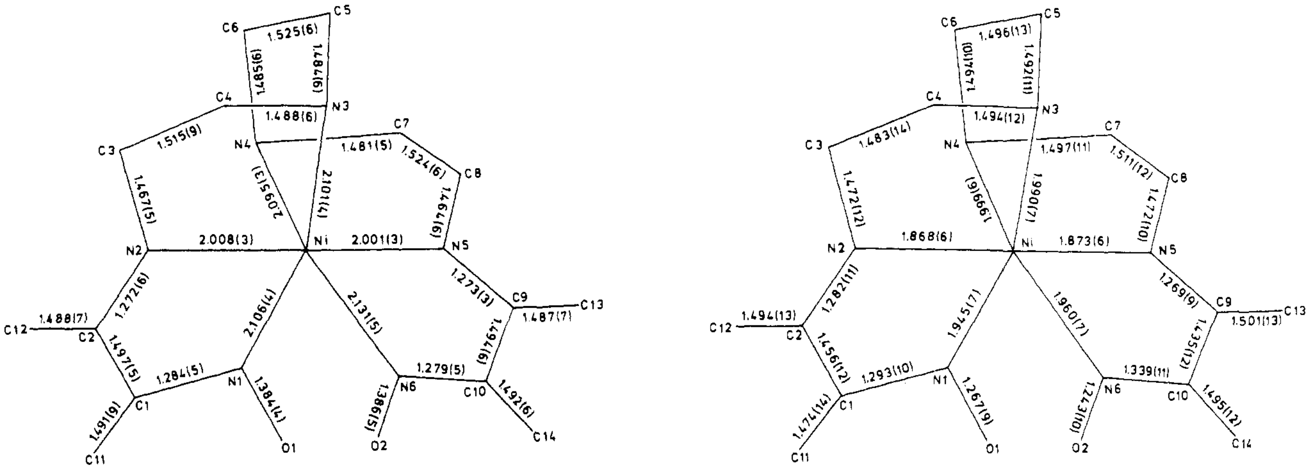

Figure 3. Schematic representations of the complex ions $[Ni(H_2L)]^{2+}$ (left) and $[NiL]^{2+}$ (right) showing bond lengths (Å).

Table IV. Selected Interatomic Bond Angles (Deg)

	$[Ni(H_2L)](ClO_4)_2$	$[NiL](ClO_4)_2$
N1-Ni-N2	76.2 (1)	81.6 (3)
N6-Ni-N5	75.9 (1)	81.6 (3)
N1-Ni-N3	159.1 (1)	166.9 (3)
N6-Ni-N4	158.2 (1)	167.1 (3)
N1-Ni-N4	98.0 (1)	92.1 (3)
N6-Ni-N3	99.8 (1)	93.5 (3)
N1-Ni-N5	104.1 (1)	97.8 (3)
N6-Ni-N2	105.1 (1)	97.3 (3)
N1-Ni-N6	86.1 (1)	89.6 (3)
N2-Ni-N3	82.8 (1)	85.4 (3)
N5-Ni-N4	82.3 (1)	85.5 (3)
N2-Ni-N4	96.7 (1)	95.6 (3)
N5-Ni-N3	96.9 (1)	95.2 (3)
N2-Ni-N5	179.0 (1)	178.8 (3)
N3-Ni-N4	84.1 (1)	87.8 (3)
O1-N1-C1	114.0 (4)	124.9 (7)
O2-N6-C10	112.9 (3)	126.5 (7)

indicates that the oxime ligand is coordinated to nickel(II) as a neutral group. The preliminary information about the stoichiometry and physical and chemical properties of the oxidized complex correspond to the composition $[NiL](ClO_4)_2$. With this formula the necessary qualifications for the description of the complex as nickel(IV) species are as follows: (i) the oxime protons have been removed on coordination, and (ii) no distinct oxidation on the divalent ligand anion has occurred.

Ligand Geometries. For comparison, the bond lengths for both complexes are presented in schematic illustrations in Figure 3. The angles of interest are shown in Table IV.

In Figure 3 and Table IV there is unequivocal structural evidence for the absence of the oxime protons in $[NiL]^{2+}$. As can be seen the average N–O and C–N(oxime) bond lengths and the average C–N–O bond angle for $[NiL]^{2+}$ are 1.255 (17) Å,[15] 1.316 (33) Å, and 125.7 (11)°, respectively, whereas the same values for $[Ni(H_2L)]^{2+}$ are 1.385 (1) Å, 1.282 (4) Å, and 113.5 (8)°. All the latter values fall well inside the corresponding ranges 1.38 ± 0.03 Å, 1.29 ± 0.02 Å, and 112 ± 2° reported to be characteristic for the uncoordinated oxime group as well as for octahedral nickel(II) complexes containing undissociated oxime groups,[16] and the values for the first compound are in satisfactory agreement with the ranges 1.26 ± 0.01 Å, 1.36 ± 0.02 Å, and 121 ± 2° found valid for several octahedral oximato complexes.[6] From this view the shortness of the N–O bond lengths and the large values for the C–N–O angles definitively rule out the possibility of oxime protons being present in $[NiL]^{2+}$.

Another result that follows from the different acid–base nature of the oxime groups in the two structures is the difference between the $C(sp^2)$–$C(sp^2)$ single-bond lengths. In $[NiL]^{2+}$ the average value of this bond is 1.446 (15) Å, while in $[Ni(H_2L)]^{2+}$ the bond is significantly longer, 1.496 (2) Å. The difference is expected and reflects the enhanced degree of cyclic delocalization in the five-membered chelate rings including oximate and imine nitrogen atoms. It may be noted that the influence of the oxime proton no longer appears in the C–N(imine) bond lengths, which are very similar in the two structures.

The remaining bond lengths and angles of the ligand molecule in the structures do not differ significantly and can be considered to be within their normally expected values. The conformations of the respective five-membered chelate rings are nearly identical. The rings including the (aminoethyl)amino and (aminoethyl)imino fragments adopt the usual gauche configuration. In $[Ni(H_2L)]^{2+}$ the chelate rings including oxime and imine nitrogen donors show slight but significant deviations from planarity, as indicated by the "gauche" angles of 9.0 (5) and 12.1 (4)°. For $[NiL]^{2+}$ the same torsional angles do not deviate markedly from 0° and the respective rings are distinctly more planar in nature.

When they are taken together, the bond distances and angles as well as the ligand conformations in the two complexes are in good agreement with the geometry one could assume for a neutral oxime and divalent oximato anion. There are no indications of destructive alterations such as might be expected to result from the nitric acid oxidation of $[Ni(H_2L)]^{2+}$.

Coordination Environments. The coordination octahedron in the oxidized complex is somewhat less distorted than that in the nonoxidized complex. In $[NiL]^{2+}$ the N(oxime)–Ni–N(amine) trans angles are 166.9 (3) and 167.1 (3)°, whereas the same angles in $[Ni(H_2L)]^{2+}$ are 159.1 (1) and 158.2 (1)° (Table IV). The N(imine)–Ni–N(amine) trans angles are almost equal, 178.3 (3) and 179.0 (1)°, in the two structures.

The N–Ni–N cis angles range from 76.2 (1) to 105.1 (1)°. As expected the largest values are found for those angles that are not included in the chelate rings and the smallest values for angles inside the rings. In general, the values of each angle type are slightly different in the two complexes but within each complex almost identifical. It is clear that most of these points involve differences in the bond lengths between nickel and the different nitrogen functional groups.

The Ni–N bond lengths in the two complexes are distinctly different (cf. Figure 3). For $[Ni(H_2L)]^{2+}$ the average Ni–N(amine), Ni–N(imine), and Ni–N(oxime) bond lengths are

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(15) The standard deviation given in parentheses following an average bond distance or angle, $\bar{x}$, is defined as $\sigma = [\sum_i (x_i - \bar{x})^2/(N-1)]^{1/2}$, where N is the number of observations, x_i.

(16) Korvenranta, J.; Saarinen, H.; Näsäkkälä, E. *Finn. Chem. Lett.* **1979**, 81.

2.098 (4), 2.005 (5), and 2.119 (18) Å, respectively, which are all significantly longer than the corresponding average distances of 1.995 (6), 1.871 (4), and 1.953 (11) Å found for $[NiL]^{2+}$.

In the case of $[Ni(H_2L)]^{2+}$ the Ni–N bond lengths compare well with the analogous distances reported for other octahedral nickel(II) compounds. The Ni–N(oxime) is present in at least four other known structures. The values in bis[2,2′-iminobis(acetamidoxime)]nickel(II) (2.075 Å, average),[17] dichlorotetrakis(acetaldoxime)nickel(II) (2.114 Å, average),[18] tris(oxamidoxime)nickel(II) dichloride (2.087 Å, average),[19] and bis[2-((2-aminoethyl)imino)-3-butanone oxime]nickel(II) diperchlorate (2.135 (4) Å)[16] are all consistent with the present average value of 2.119 (18) Å. The last of these complexes also contains two Ni–N(imine) distances of 2.008 (3) Å and two Ni–N(amine) distances of 2.128 (6) Å, both of which values are in good agreement with those found here. In the several known structures with Ni–N(amine) bonds and octahedral coordination, the bond distance is generally just greater than 2.1 Å, which further supports the normality of the distance found in $[Ni(H_2L)]^{2+}$.

In view of these observations the Ni–N(amine) and Ni–N(imine) bond lengths in $[NiL]^{2+}$ must be considered unusually short. At the same time, however, they are almost equal to the average values of 2.006 and 1.873 (6) Å found earlier for the respective bond in bis[2-((2-aminoethyl)imino)-3-butanone oximato]nickel(IV) diperchlorate.[6] From this one may estimate a shortening of ca. 0.10–0.13 Å for a Ni–N(amine) distance and a shortening of ca. 0.13–0.14 Å for a Ni–N(imine) distance when going from nickel(II) to nickel(IV).

Direct comparison of the Ni–N(oxime) bond lengths in $[Ni(H_2L)]^{2+}$ and $[NiL]^{2+}$ is not possible since the length of the bond can be found to depend considerably on whether or not the oxime proton is present. This is revealed in the values of the Ni–N(oximato) bonds reported for octahedral tetraaqua(1,2-naphthoquinone-4-sulfonate 1-oximato)nickel(II) (2.007 (5) Å)[20] and tris(4-chloro-1-quinone 2-oximato)nickel(II) anion (2.009 Å, average),[21] which are ca. 0.1 Å shorter than the Ni–N(oxime) distances referred to above. Accordingly, a value of ca. 2.01 Å rather than 2.10 Å can be regarded as a realistic reference when the lengths of the Ni–N(oximato) bonds in $[NiL]^{2+}$ are discussed.

The Ni–N(oximato) bond distances are now known for three different complexes presented as containing nickel(IV). Comparison of the average value of this bond obtained here (1.953 (11) Å) with the values reported for bis[2-((2-aminoethyl)imino)-3-butanone oximato]nickel(IV) ion (1.967 (13) Å)[6] and bis(2,6-diacetylpyridine dioximato)nickel(IV) (1.973 Å)[5] reveals no significant variations. Even though all these distances are somewhat shorter than the same bonds in the nickel(II) complexes discussed above, the difference of ca. 0.04–0.05 Å is markedly less than the differences in the Ni–N(amine) and Ni–N(imine) bonds. This may indicate some partial neutralization of the high positive charge on the nickel atom through the negative oximato groups. Nevertheless, we consider that the short Ni–N(amine) and Ni–N(imine) bond distances, together with the earlier chemical and electrochemical results, justify the classification of $[NiL](ClO_4)_2$ as a nickel(IV) complex and this description is not contradicted by the possible ambiguity in the Ni–N(oximato) bond lengths.

The Perchlorate Ions and Crystal Packings. In both structures the geometry of the perchlorate groups shows some of the usual disorder. Thus for $[Ni(H_2L)](ClO_4)_2$ the Cl–O bond lengths vary between 1.352 (7) and 1.456 (6) Å and for $[NiL](ClO_4)_2$ between 1.29 (2) and 1.42 (1) Å. Correspondingly, the O–Cl–O bond angles ranging from 100.9 (4) to 114.4 (6)° for $[Ni(H_2L)](ClO_4)_2$ and from 98 (1) to 118 (1)° for $[NiL](ClO_4)_2$ deviate considerably from the ideal tetrahedral value.

In $[Ni(H_2L)](ClO_4)_2$ the crystal packing is largely determined by the hydrogen bonding between the oxime oxygens and perchlorate oxygens: O1···O3 = 2.827 (8) Å, ∠O1–H···O3 = 141 (4)° and O2···O7($-x$, $1-y$, $-z$) = 2.757 (6) Å, ∠O2–H···O7 = 160 (7)°. The amine nitrogens may also be involved in weak hydrogen bonds. There are possible contacts of 3.172 (8) and 3.190 (10) Å to nearby perchlorate oxygens.

In the case of $[NiL](ClO_4)_2$ there are no oxime protons to participate in hydrogen bonding. This results in noticeable strengthening of the hydrogen bonds via the amine nitrogen: N3···O4 = 2.87 (2) Å, ∠N3–H···O4 = 168 (7)° and N4···O10(x, $^1/_2 - y$, $^1/_2 - z$) = 2.97 (1) Å, ∠N4–H···O10 = 168 (6)°.

Registry No. $[Ni(H_2L)](ClO_4)_2$, 55188-32-4; $[NiL](ClO_4)_2$, 55188-34-6.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors for $[Ni(H_2L)](ClO_4)_2$ and $[NiL](ClO_4)_2$ (31 pages). Ordering information is given on any current masthead page.

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