

# The Crystal Structure of a Complex Containing Nickel in the Formal Oxidation State IV: Bis[2-(2-aminoethyl)imino-3-butanone oximato]nickel(IV) Diperchlorate

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The crystal structure of the title compound,  $\text{Ni}(\text{C}_6\text{H}_{12}\text{N}_3\text{O})_2(\text{ClO}_4)_2$  [ $=\text{NiL}_2(\text{ClO}_4)_2$ ], obtained by oxidation of the parent Ni(II) complex  $\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$  with concentrated nitric acid, has been determined from X-ray diffraction data and refined by least-squares methods. Crystal data are as follows: space group  $P2_1/c$ ,  $a=8.152(2)$ ,  $b=18.072(5)$ ,  $c=14.571(3)$  Å,  $\beta=99.49(2)^\circ$ ,  $Z=4$ ;  $R=0.069$  for 2008 observed reflections. The structure consists of discrete, strongly distorted octahedral nickel(IV) complex cations and perchlorate anions. The tridentate ligand is coordinated to the nickel through its nitrogen atoms, the average Ni–N(oxime), Ni–N(imine) and Ni–N(amine) bond lengths being 1.967(4), 1.873(4) and 2.006(4) Å, respectively. A comparison of these distances with those obtained previously for  $\text{Ni}(\text{HL})_2^{2+}$  and other octahedral Ni(II) complexes of similar ligands reveals a considerable shortening of the Ni–N(imine) and Ni–N(amine) bond lengths, while the Ni–N(oxime) bond is somewhat less affected. The ligand dimensions in the structure are in agreement with those found in other oximato complexes of this ligand.

Reports on the stabilization of the highest oxidation state of nickel, Ni(IV), by various ligands appear occasionally in the literature and at present there are several compounds proposed to contain tetravalent nickel.<sup>1,2</sup> However, the assignment of the oxidation state of the metal is not straightforward and detailed structural and spectral reexaminations have proved many of the complexes originally formulated as nickel(IV) species to be, for example, inclusion-like compounds of nickel(II) or nickel(II)-stabilized radical ligand complexes.<sup>1</sup> In any case

information on Ni(IV) systems is very limited and, owing to the instability of the compounds, X-ray structural determinations are almost non-existent.

The best characterized nickel(IV) compounds seem to be six-coordinate complexes in which the octahedron about nickel is made up of electro-negative elements such as fluorine, oxygen and nitrogen, or they are complexes of the sandwich-type, derived from cyclopentadienyl and related ligands.<sup>3–5</sup> In particular, the oxime ligands have been found to be effective for stabilization of higher oxidation states of nickel and the formal  $d6$  nickel complexes of 2,6-diacetylpyridine dioxime, studied by Drago and Baucom<sup>3,4</sup> and by Sproul and Stucky<sup>5</sup> at the beginning of the 1970's, are among the most thoroughly studied Ni(IV) compounds. Drago and Baucom have also discussed the factors involved in the stabilization of the uncommonly high oxidation states of nickel and proposed that strong  $\sigma$  donor properties and a strong spherical component in the ligand field are important characteristics of Ni(IV) complexes. More recently, Mohanty *et al.*<sup>6</sup> and Singh *et al.*<sup>7</sup> have prepared some diamagnetic, presumably six-coordinate nickel complexes of different tridentate and hexadentate amino-imino-oxime ligands which, from chemical and electrochemical evidence, contain nickel in its formal oxidation state IV.<sup>6,7</sup> Using cyclic voltammetric measurements they also determined the formal electrode potentials of the Ni(IV)–Ni(III) and Ni(III)–Ni(II) couples involved in the systems.

In the course of our studies on oxime compounds, we have previously determined the X-ray structures of some metal complexes containing similar amino-imino-oxime ligands including that

of an octahedral nickel(II) chelate,  $\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$ , formed with the tridentate 2-(2-aminoethyl)imino-3-butanone oxime (=HL) ligand.<sup>8</sup> We have now oxidized this complex with concentrated nitric acid and obtained a crystalline product formulated as  $\text{NiL}_2(\text{ClO}_4)_2$  which shows identical properties to those of the compound prepared by Singh *et al.*<sup>7</sup> The deep-violet oxidized complex proved to be sufficiently stable for X-ray measurements and the results of a crystal structure determination are given in this communication.

## EXPERIMENTAL

The complex was prepared by oxidation of bis[2-(2-aminoethyl)imino-3-butanone oxime]nickel(II) diperchlorate,  $\text{Ni}(\text{HL})_2(\text{ClO}_4)_2$ , with conc.  $\text{HNO}_3$  as described by Singh *et al.*<sup>7</sup> The deep-violet needle-like crystals were obtained by dissolving the crude product in an aqueous solution containing small amounts of  $\text{HNO}_3$  and  $\text{NaClO}_4$ , and cooling. In a desiccator over fused  $\text{CaCl}_2$  the crystals remained externally unaltered for several weeks, but to retard possible decomposition, the crystal used for data collection was sealed in epoxy glue immediately after the preparation. The crystal used had dimensions of ca.  $0.2 \times 0.2 \times 0.4$  mm.

Weissenberg photographs showed the crystals to be monoclinic. The space group, determined from systematic absences, is  $P2_1/c$ . The accurate cell parameters were obtained by least-squares analysis of 20 automatically centered reflections measured with a Syntex  $P2_1$  diffractometer. The crystal data

for  $[\text{NiL}_2](\text{ClO}_4)_2$  are:  $a=8.152(2)$ ,  $b=18.072(5)$ ,  $c=14.571(3)$  Å,  $\beta=99.49(2)^\circ$   $Z=4$ , space group  $P2_1/c$ ,  $D_x=1.700$  g cm<sup>-3</sup>,  $D_m=1.69$  g cm<sup>-3</sup> (by flotation),  $V=2117.4$  Å<sup>3</sup>,  $\mu(\text{MoK}\alpha)=21.0$  cm<sup>-1</sup>,  $\lambda(\text{MoK}\alpha)=0.7107$  Å.

X-Ray intensities were measured by the  $\omega$ -scan technique with graphite monochromated  $\text{MoK}\alpha$ -radiation. The scan rate varied from 1.5 to 29° min<sup>-1</sup>, depending on the intensity of the reflection. No significant fluctuations were observed in the data collection. A total of 3855 reflections in the range  $3^\circ < 2\theta < 50^\circ$  were measured; 2008 reflections with  $I > 2.5\sigma(I)$  were regarded as observed. The data were corrected for Lorentz and polarization effects, but not for absorption.

*Structure determination and refinement.* The structure was solved by direct methods with the MULTAN program.<sup>9</sup> The remaining computations were carried out with the X-RAY 76 program system.<sup>10</sup> The nickel atom and the nitrogen atoms were located in an  $E$  map. Subsequent Fourier maps revealed the remaining non-hydrogen atoms.

Atomic scattering factors were those included in the program. Since no experimental information about the electron density at the nickel atom in the oxidation state IV seems available, the atomic scattering factors for  $\text{Ni}^0$  were used in the calculations. The anomalous dispersion corrections ( $\Delta f'$ ,  $\Delta f''$ ) were included for Ni and Cl.<sup>11</sup>

Block-diagonal least-squares refinement with anisotropic parameters and weights  $w=4 F_o^2/\sigma_f^2$  led to an  $R$  value 0.069 for the 2008 observed reflections; the maximum shift/e.s.d. value of variable parameters was 0.46. The hydrogen atoms were not included in the calculations since they could not

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms in  $[\text{NiL}_2](\text{ClO}_4)_2$ .

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
C1	2607(10)	6396(4)	3463(5)	N4	2336(8)	7913(3)	4670(4)
C2	920(10)	6348(4)	3654(5)	N5	2668(7)	8616(3)	3236(4)
C3	-1671(9)	7072(4)	3642(6)	N6	630(8)	7851(4)	1980(4)
C4	-1732(10)	7847(5)	4094(6)	O2	1911(7)	7508(3)	5285(4)
C5	3805(10)	5774(4)	3415(6)	Ni	1287(1)	7805(1)	3367(1)
C6	192(12)	5619(5)	3931(6)	The perchlorate groups			
N1	3061(7)	7079(3)	3266(4)	O3	-1817(11)	5837(5)	1842(6)
N2	98(7)	6955(4)	3583(4)	O4	292(12)	5030(5)	1667(5)
N3	-717(7)	8366(3)	3616(4)	O5	-1467(11)	5492(7)	405(6)
O1	4399(6)	7269(3)	3047(4)	O6	384(15)	6189(6)	1283(11)
C7	3481(9)	8432(4)	4799(5)	Cl1	-622(3)	5630(1)	1256(2)
C8	3678(10)	8813(4)	3945(6)	O7	7153(12)	7871(5)	917(7)
C9	2669(11)	8857(5)	2267(5)	O8	7361(9)	9065(4)	418(5)
C10	1007(11)	8630(5)	1706(6)	O9	6750(8)	8818(5)	1889(5)
C11	4415(11)	8571(5)	5762(6)	O10	4780(8)	8639(6)	619(5)
C12	4990(10)	9389(5)	3908(6)	C12	6462(3)	8599(1)	934(2)

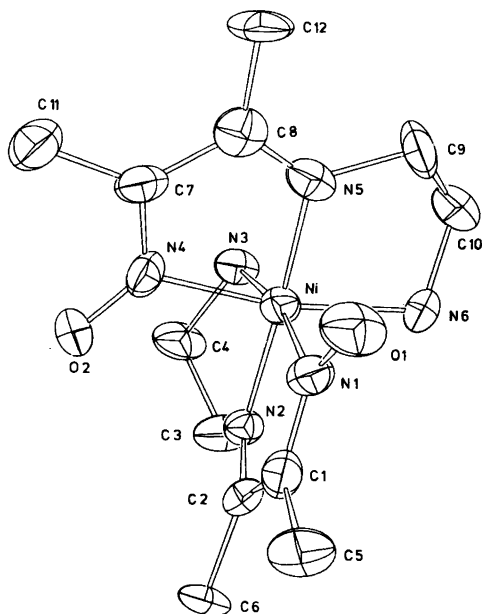


Fig. 1. A perspective view of the complex ion with 50% probability ellipsoids.

all be located in the difference Fourier map.

The atomic coordinates together with their standard deviations are given in Table 1. A list of the observed and calculated structure factors is obtainable on request from the authors.

## RESULTS AND DISCUSSION

The ORTEP drawing of the divalent complex cation and the numbering of the atoms are shown in Fig. 1, the bond lengths are given in the schematic representation in Fig. 2, and the bond angles are collected in Table 2. A comparison of the coordination geometry of nickel in this Ni(IV) complex with that previously found in Ni(HL)<sub>2</sub><sup>2+</sup> shows that no fundamental stereochemical changes have occurred during the HNO<sub>3</sub> oxidation.<sup>8</sup> As in the parent Ni(HL)<sub>2</sub><sup>2+</sup> complex the coordination environment of nickel is distorted octahedral, the two tridentate ligands are in a meridional arrangement and bonding to the metal is through the oxime, imine and amine nitrogen atoms.

There is no symmetry due to a crystallographic twofold axis as in Ni(HL)<sub>2</sub><sup>2+</sup>. Nevertheless, the two halves of the chelate show a close structural similarity. In general the coordination octahedron

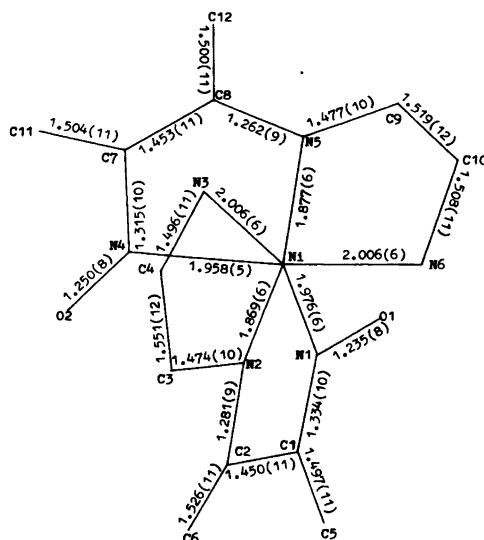


Fig. 2. Schematic representation of the complex ion showing bond lengths (Å).

in NiL<sub>2</sub><sup>2+</sup> is somewhat less distorted than that in Ni(HL)<sub>2</sub><sup>2+</sup>, the bond angles about nickel vary between 81.2(3)° and 98.3(3)° and between 166.8(3)° and 174.0(2)°, whereas the respective ranges in Ni(HL)<sub>2</sub><sup>2+</sup> are 75.8(1)–107.7(1)° and 156.4(1)–175.2(8)°.<sup>8</sup>

The Ni–N bond lengths in the two structures are distinctly different, however. The mean Ni–N(oxime), Ni–N(imine) and Ni–N(amine) distances of the present compound are 1.967(4), 1.873(4) and 2.006(4) Å, respectively. These distances are all significantly shorter than the corresponding distances of 2.135(4), 2.008(3) and 2.128(3) Å found in Ni(HL)<sub>2</sub><sup>2+</sup>. Since the Ni(II)–N(imine) and Ni(II)–N(amine) bond lengths in octahedral Ni(HL)<sub>2</sub><sup>2+</sup> can be considered normal, the pronounced shortening of these distances in the present complex argues for the presence of nickel(IV).

As to the Ni–N(oxime) distance the situation is more complicated. Formulation of the present complex cation as NiL<sub>2</sub><sup>2+</sup> necessarily requires that in oxidation of Ni(HL)<sub>2</sub><sup>2+</sup> the electron transfer process is coupled with dissociation of the oxime protons. In our previous paper we have pointed out that the length of the Ni–N(oxime) bond is considerably dependent on whether or not the oxime proton is preserved on coordination.<sup>8</sup> For instance, the Ni–N(oxime) bonds in octahedral tetraqua(1,2-naphthoquinone-1-oximato-sulfo-

Table 2. Bond angles (°) for  $[\text{NiL}_2]^{2+}$  ion.

C2—C1—C5	127.7(7)	C8—C7—C11	127.6(7)	N1—Ni—N2	82.7(2)
C2—C1—N1	113.7(7)	C8—C7—N4	113.0(6)	N1—Ni—N3	167.7(3)
C5—C1—N1	118.5(7)	C11—C7—N4	119.4(7)	N1—Ni—N4	86.0(2)
C1—C2—C6	121.7(7)	C7—C8—C12	122.7(7)	N1—Ni—N5	93.0(3)
C1—C2—N2	115.7(7)	C7—C8—N5	114.7(7)	N1—Ni—N6	91.7(2)
C6—C2—N2	122.7(7)	C12—C8—N5	122.6(7)	N2—Ni—N3	85.7(2)
C4—C3—N2	104.8(6)	C10—C9—N5	107.1(7)	N2—Ni—N4	94.3(2)
C3—C4—N3	108.0(7)	C9—C10—N6	108.2(6)	N2—Ni—N5	174.0(2)
C1—N1—O1	127.0(6)	C7—N4—O2	126.2(6)	N2—Ni—N6	98.3(3)
C1—N1—Ni	111.5(5)	C7—N4—Ni	113.4(5)	N3—Ni—N4	90.8(3)
O1—N1—Ni	121.5(5)	O2—N4—Ni	120.5(4)	N3—Ni—N5	98.2(3)
C2—N2—C3	128.5(6)	C8—N5—C9	126.6(7)	N3—Ni—N6	94.0(3)
C2—N2—Ni	116.0(5)	C8—N5—Ni	117.3(5)	N4—Ni—N5	81.2(3)
C3—N2—Ni	115.5(4)	C9—N5—Ni	115.0(5)	N4—Ni—N6	166.8(3)
C4—N3—Ni	107.3(5)	C10—N6—Ni	105.9(4)	N5—Ni—N6	85.9(3)

nate)nickel(II) [2.007(5) Å]<sup>12</sup> and tris(4-chloro-1-quinone-2-oximate)nickel(II) anion [2.009 Å, av.]<sup>13</sup> in which the oxime protons are displaced, are markedly shorter than this bond in  $\text{Ni}(\text{HL})_2^{2+}$  [2.135(4) Å],<sup>8</sup> bis(2,2'-iminobis(acetamidoxime))nickel(II) [2.075 Å, av.]<sup>14</sup> and dichlorotetrakis(acetaldoxime)nickel(II) [2.114 Å, av.]<sup>15</sup> which are octahedral chelates containing undissociated oxime groups. As can be seen, the bond lengths in the first-mentioned compounds are not markedly longer than the distance found here [1.967 Å, av.]. Thus the Ni—N(oxime) bond length in the present compound cannot be considered exceptionally short. There is, moreover, an excellent agreement with the Ni—N(oxime) bond distance reported for bis(2,6-diacetylpyridine dioximate)nickel(IV) [1.973(3) Å]<sup>4</sup> which is the only comparable structure assumed to contain Ni(IV).

In the refinement of the structure the hydrogen atoms could not be located. This being the case, we do not have any direct proof of the absence of the oxime protons in  $\text{NiL}_2^{2+}$ . The indirect evidence is convincing, however. The geometry of the uncoordinated oxime group has been shown to be remarkably constant, with the N—O(H) and C=N bond lengths and the C—N—O bond angle of  $1.38 \pm 0.03$  and  $1.29 \pm 0.02$  Å, and  $112 \pm 2^\circ$ , respectively.<sup>16</sup> In mononuclear six-coordinate metal complexes ( $M = \text{Ni}^{2+}$ ) these dimensions are found to be practically unaltered when the oxime protons are preserved on chelation, but the corresponding values are  $1.26 \pm 0.01$  and  $1.36 \pm 0.02$  Å, and  $121 \pm 2^\circ$  if coordination to the metal ( $M = \text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{3+}$ ) is accompanied by removal of the oxime protons.<sup>8</sup>

Although the C—N distances obtained here are possibly somewhat shorter and the C—N—O angle somewhat larger than the expected values, the presence of the oxime protons of  $\text{NiL}_2^{2+}$  is definitely ruled out by the shortness of the N—O bonds.

The aminoethylimino parts of the structure adopt the usual *gauche* configuration, the torsional angles N2—C3—C4—N3 [46.2(7)°] and N5—C9—C10—N6 [−44.1(9)°] being very similar to the comparable angles in many ethylenediamine complexes as well as in  $\text{Ni}(\text{HL})_2^{2+}$ . The expected configuration, together with the C—C and C—N bond lengths which are in good agreement with the corresponding distances in  $\text{Ni}(\text{HL})_2^{2+}$ , indicate that no marked changes have occurred in this part of L on oxidation.

In their 2-imino-3-butanone oxime fragments the structures of  $\text{NiL}_2^{2+}$  and  $\text{Ni}(\text{HL})_2^{2+}$  are considerably different. The most prominent variances are connected with the geometry of the oxime group: on oxidation the N—O bond lengths is shortened from 1.385(5) to 1.243 (av.) Å, the C—N distance is lengthened from 1.285(5) to 1.325 (av.) Å, and the C—N—O angle is opened up from 113.4(4) to 126.6° (av.). As pointed out above, all these changes may well be due to the displacement of the oxime protons. Another result is, that on oxidation, the  $C(sp^2)$ — $C(sp^2)$  single bond distance is shortened from 1.498(6) to 1.452(av.) Å. In fact, this contraction is not very large but it is also found in other comparable structures.<sup>17</sup> Since the presence of the oxime protons in  $\text{Ni}(\text{HL})_2^{2+}$  will lower the degree of cyclic delocalization in the chelate rings,

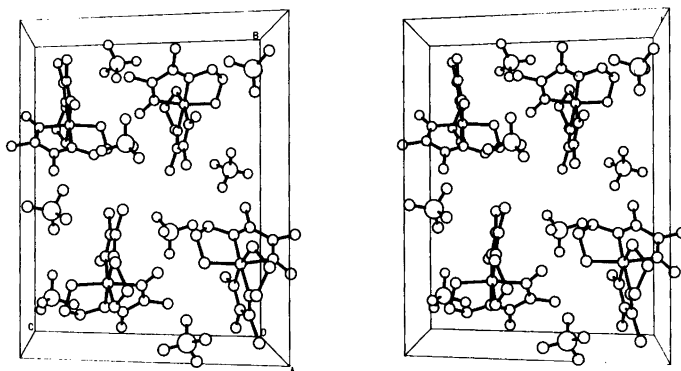


Fig. 3. A stereoscopic view of the unit cell contents.

the contraction can be understood in terms of absence of the oxime protons.

The geometry of the perchlorate groups in the structure shows some of the usual disorder. Thus the calculated Cl—O bond lengths for Cl1 range from 1.30(1) to 1.45(1) Å, while those for Cl2 are more reasonable varying between 1.37(1) and 1.43(1) Å. The O—Cl—O bond angles in each perchlorate anion [105(1)–114(1)° for Cl1 and 106(1)–115(1)° for Cl2] are still fairly close to those in a tetrahedral ion.

The packing of the complex cations and perchlorate anions in the unit cell is illustrated in Fig. 3. It is obvious that there are weak hydrogen bond contacts *via* the amino groups. Since the positions of the hydrogen atoms are not known, the details of the hydrogen bonding are uncertain but the most probable scheme is such that one of the amino groups is associated with two perchlorate oxygens [ $N3 \cdots O4(-x, \frac{1}{2} + y, \frac{1}{2} - z) = 3.064(10)$  Å and  $N3 \cdots O9(-1 + x, y, z) = 3.090(8)$  Å], while the other one is connected to a perchlorate oxygen [ $N6 \cdots O7(-1 + x, y, z) = 2.998(11)$  Å] and an oxime oxygen [ $N6 \cdots O2(x, \frac{3}{2} - y, -\frac{1}{2} + z) = 2.909(8)$  Å] atom.

**Conclusions.** The present compound was originally classified as a nickel(IV) complex on the basis of its stoichiometry, conductivity, diamagnetism, and spectral and oxidation properties.<sup>7</sup> In this crystal structure determination we have found that the Ni—N(amine) and Ni—N(imine) distances in the complex are markedly shorter and the Ni—N(oxime) distances at least somewhat shorter than expected for an octahedral nickel(II) complex. Furthermore, the geometry of the ligand molecule in the structure can be considered normal for the amino-imino-

oximate anion. These results support the chosen designation of the complex. It should be added that, in structures like the present one, it is quite possible that the increased positive charge associated with the electron removal from the parent nickel(II) complex is partly delocalized over the whole complex cation through the negative oxime groups.

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