

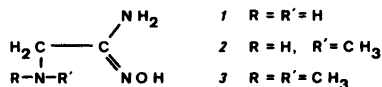
The Crystal and Molecular Structures of Three Nickel(II) Complexes Formed by 2-Aminoacetamidoxime and 2-(Dimethylamino)acetamidoxime

HEIKKI SAARINEN, JORMA KORVENRANTA, MARJATTA ORAMA and TUOVI RAIKAS

Division of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The crystal and molecular structures of the complexes $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (=I) and $[\text{Ni}(\text{HL})\text{L}]\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ (=II), where HL=2-aminoacetamidoxime ($\text{C}_2\text{H}_7\text{N}_3\text{O}$), and a complex $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2\cdot \text{H}_2\text{O}$ (=III), where HL=2-(dimethylamino)acetamidoxime ($\text{C}_4\text{H}_{11}\text{N}_3\text{O}$), have been determined from X-ray diffraction data and refined by least-squares methods. In all three structures the bidentate ligand is bonded to the nickel atom through its amino and oxime nitrogen atoms. In structure I the complex cation is centrosymmetric and displays a distorted *trans* octahedral coordination. The crystal data are: space group $P2_1/n$; $Z=2$; $a=7.556(3)$, $b=10.923(3)$, $c=8.005(3)$ Å, $\beta=100.49(3)^\circ$; $R=0.028$ for 1633 reflections with $I>2.5\sigma(I)$. In structure II nickel(II) is in a square-planar coordination environment in which there is a strong intramolecular hydrogen bridge between the *cis* oxime oxygen atoms. The crystal data are as follows: space group $C2/c$; $Z=8$; $a=10.214(4)$, $b=15.634(3)$, $c=14.007(3)$ Å, $\beta=100.45(3)^\circ$; $R=0.046$ for 2164 reflections with $I>2.5\sigma(I)$. In complex III the two bidentate ligands in *cis*-configuration and two of the water molecules are coordinated to nickel atom to form a distorted octahedron in which the amino nitrogens are *trans* to each other. The space group is $P2_1/c$; $Z=4$; $a=15.555(7)$, $b=8.041(4)$, $c=16.993(4)$ Å, $\beta=114.61(3)^\circ$; $R=0.036$ for 3496 reflections with $I>2.5\sigma(I)$.

In a previous report we have described the complex formation between nickel(II) ions and 2-aminoacetamidoxime 1, and its *N*-methylated derivatives 2 and 3 in aqueous solution.¹



The potentiometric data collected from acid and neutral solutions were shown to be consistent with the stepwise formation of complexes $\text{Ni}(\text{HL})_n^{2+}$ with $n=1,2,3$ ($\text{HL}=1$ and 2) and $n=1,2$ ($\text{HL}=3$), and the mononuclear deprotonated species NiHL_2^+ ($\text{HL}=1$ and 2). To support the proposed mode of coordination and to complete our studies on structural features of solid oxime complexes of nickel(II),^{2,3} we have isolated some of these compounds as chlorides in the crystalline state and determined their structures by X-ray diffraction methods. Results of the X-ray study on the complexes $\text{Ni}(\text{HL})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ ($\text{HL}=1$), $\text{Ni}(\text{HL})_2\text{Cl}_2\cdot 3\text{H}_2\text{O}$ ($\text{HL}=3$) and $\text{NiHL}_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ ($\text{HL}=1$) are given in this communication.

EXPERIMENTAL

Crystal preparations. Syntheses of 2-aminoacetamidoxime 1 and 2-(dimethylamino)acetamidoxime 3 have been described earlier.¹ The complexes $\text{Ni}(\text{HL})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and $\text{NiHL}_2\text{Cl}\cdot 1\frac{1}{2}\text{H}_2\text{O}$ with $\text{HL}=1$ were obtained in the crystalline state as a mixture of violet-blue and orange-red crystals by evaporation of an aqueous solution of 1 (2 mol equiv.) and NiCl_2 (1 mol equiv.) neutralized with NaOH to pH value of ca. 6. A similar procedure in which 3 was used instead of 1 yielded $\text{Ni}(\text{HL})_2\text{Cl}_2\cdot 3\text{H}_2\text{O}$ as green-blue crystals.

Table 1. Data for the X-ray diffraction studies.

	$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ HL=1	$[\text{Ni}(\text{HL})\text{L}]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ HL=1	$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ HL=3
Crystal parameters			
Cell refinement			
2 θ range, deg	24 refl. 7-30	20 refl. 10-25	22 refl. 9-25
<i>a</i> , Å	7.556(3)	10.214(4)	15.555(7)
<i>b</i> , Å	10.923(3)	15.634(3)	8.041(4)
<i>c</i> , Å	8.005(3)	14.007(3)	16.993(4)
β , deg	100.49(3)	100.45(3)	114.61(3)
<i>V</i> , Å ³	649.7(4)	2199.5(11)	1932.4(13)
<i>Z</i>	2	8	4
Space group	$P2_1/n$	$C2/c$	$P2_1/c$
<i>d_m</i> , g cm ⁻³	1.75	1.81	1.45
<i>d_x</i> , g cm ⁻³	1.758	1.802	1.436
Data collection			
Radiation	MoK α ($\lambda=0.71069$ Å)		
Method	ω -scan technique		
Stds	2 every 58 refl.; no significant decay		
μ , cm ⁻¹	38.3		
Scan rate	2.5-30.0	20.2	13.1
2 θ range	3.0-60.0	2.8-30.0	2.0-30.0
Dimens, mm	0.50×0.30×0.30	3.0-56.0	3.0-56.0
Unique refl.	1879	0.40×0.40×0.40 2670	0.40×0.30×0.30 4341
Structure refinement			
Total obs. refl.	1633	2164	3496
$I > 2.5\sigma(I)$	0.028	0.046	0.036
$R = \sum F_o - F_c / \sum F_o $			

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters^a ($\times 10^3$) for the non-hydrogen atoms.

Atom	x	y	z	$U_{eq}, \text{\AA}^2$	Atom	x	y	z	$U_{eq}, \text{\AA}^2$
[Ni(HL)₂(H₂O)₂]Cl₂ (HL=I)									
Ni	0000	0000	0000	20	N2	1535(3)	-1354(2)	1402(3)	25
Cl1	826.6(7)	3515.9(6)	7030.0(8)	36	N3	2179(3)	709(2)	5114(3)	39
O1	-48(2)	1961(2)	2896(2)	36	C1	1635(3)	277(2)	3527(3)	27
O _w 1	2370(2)	796(2)	-672(2)	32	C2	2426(4)	-915(2)	3078(3)	38
N1	532(2)	811(2)	2346(2)	25					
[Ni(HL)L]Cl · 1½H₂O (HL=I)									
Ni	1125.7(4)	6265.9(2)	409.1(2)	21	N3	2156(3)	3801(2)	328(2)	35
Cl1	2106.7(9)	2873.7(6)	-1782.9(5)	36	N4	1223(3)	6888(2)	-697(2)	24
O1	1796(2)	5058(1)	-988(1)	26	N5	646(3)	7348(2)	900(2)	28
O2	1684(3)	6581(2)	-1513(2)	32	N6	956(3)	8210(2)	-1474(2)	33
O _w 1	0000	9024(4)	2500	76	C1	1817(3)	4589(2)	557(2)	26
O _w 2	481(3)	159(2)	1024(2)	47	C2	1627(4)	4796(2)	1572(2)	33
N1	1636(3)	5227(2)	-41(2)	24	C3	875(3)	7683(2)	-743(2)	25
N2	927(3)	5626(2)	1542(2)	28	C4	379(4)	8004(2)	133(2)	32
[Ni(HL)₂(H₂O)₂]Cl₂ · H₂O (HL=3)									
Ni	2811.2(3)	1604.2(5)	862.0(2)	22	N4	1768(2)	2000(3)	-383(2)	27
Cl1	5611.2(6)	9628.4(2)	1736.8(6)	46	N5	3433(2)	3493(4)	322(2)	31
Cl2	9036.9(6)	1901.6(11)	1933.0(6)	35	N6	1063(2)	4118(4)	-1375(2)	43
O1	2433(2)	4901(3)	1712(2)	32	C1	1469(2)	2708(4)	1516(2)	29
O2	886(2)	1174(3)	-853(2)	34	C2	1155(2)	988(4)	1198(3)	32
O _w 1	4029(2)	1489(4)	2048(2)	39	C3	2510(3)	-543(6)	2186(3)	28
O _w 2	3429(2)	-449(3)	568(2)	38	C4	1606(3)	-1535(4)	732(3)	32
O _w 3	3178(2)	6768(4)	4032(2)	50	C5	1759(2)	3473(4)	-684(2)	46
N1	2222(2)	3215(3)	1446(2)	26	C6	2605(3)	4520(4)	-189(2)	40
N2	1975(2)	-35(3)	1270(2)	28	C7	3814(3)	2742(6)	-265(3)	44
N3	963(3)	3589(4)	1830(3)	47	C8	4172(3)	4584(6)	939(3)	47

$$^a U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 3. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3$) for the hydrogen atoms.

Atom	x	y	z	$U, \text{\AA}^2$	Atom	x	y	z	$U, \text{\AA}^2$
[Ni(HL)₂(H₂O)₂]Cl₂ (HL=I)									
Ni(O1)	-155(4)	192(3)	251(4)	46	H1(N3)	295(5)	16(3)	597(5)	68
H1(O _w)	290(6)	26(4)	-107(6)	89	H2(N3)	161(4)	134(3)	544(4)	43
H ₂ (O _w)	309(5)	105(3)	11(5)	59	H1(C2)	237(5)	-150(4)	386(5)	73
H1(N2)	221(5)	-165(3)	90(4)	55	H2(C2)	385(5)	-82(3)	307(5)	73
H2(N2)	76(4)	-196(3)	156(4)	49					
[Ni(HL)L]Cl · 1½H₂O (HL=I)									
H(O2)	161(6)	596(4)	-157(4)	40	H1(N5)	120(4)	742(3)	124(3)	32
H1(O _w 1)	-91(15)	892(12)	247(10)	502	H2(N5)	-13(5)	726(3)	111(3)	47
H1(O _w 2)	46(11)	12(8)	151(9)	153	H1(N6)	125(4)	800(2)	-196(3)	25
H2(O _w 2)	132(9)	16(6)	97(7)	123	H2(N6)	70(5)	859(3)	-146(4)	42
H1(N2)	119(4)	594(3)	211(3)	46	H1(C2)	122(4)	436(3)	186(3)	35
H2(N2)	7(4)	560(2)	145(3)	30	H2(C2)	257(5)	484(3)	205(3)	38
H1(N3)	227(5)	336(3)	75(4)	56	H1(C4)	83(4)	849(3)	31(3)	38
H2(N3)	216(4)	367(3)	-21(3)	38	H2(C4)	-60(5)	808(3)	-11(3)	52
[Ni(HL)₂(H₂O)₂]Cl₂ · H₂O (HL=3)									
Ni(O1)	310(5)	493(8)	230(4)	117	H1(C3)	215(3)	-113(6)	238(3)	68
H(O2)	102(3)	42(5)	-104(3)	52	H2(C3)	317(4)	-118(7)	236(3)	84
H1(O _w 1)	418(3)	228(6)	237(3)	55	H3(C3)	279(4)	47(7)	265(3)	78
H2(O _w 1)	450(4)	90(7)	206(3)	82	H1(C4)	200(3)	-215(5)	75(3)	51
H1(O _w 2)	333(3)	-65(6)	18(3)	68	H2(C4)	113(3)	-214(5)	89(3)	55
H2(O _w 2)	423(5)	-45(9)	99(5)	148	H3(C4)	121(3)	-117(6)	9(3)	57
H1(O _w 3)	263(3)	672(6)	367(3)	70	H1(C6)	27(3)	532(6)	-62(3)	58
H2(O _w 3)	334(3)	611(6)	379(3)	70	H2(C6)	234(3)	525(5)	10(3)	54
H1(N3)	46(3)	298(6)	191(3)	72	H1(C7)	450(3)	202(6)	8(3)	70
H2(N3)	108(3)	458(6)	197(3)	58	H2(C7)	399(3)	359(6)	-51(3)	58
H1(N6)	102(4)	521(8)	-149(4)	115	H3(C7)	337(3)	207(5)	-64(2)	42
H2(N6)	47(4)	373(8)	-156(4)	117	H1(C8)	436(3)	556(6)	62(3)	62
H1(C2)	72(2)	108(4)	60(2)	29	H2(C8)	464(3)	400(6)	120(3)	58
H2(C2)	80(3)	45(6)	151(3)	57	H3(C8)	401(3)	508(6)	135(3)	62

Crystal and intensity data. Unit cell parameters and the orientation matrices for the complexes were determined on a Nicolet P3 four-circle diffractometer equipped with a graphite monochromator. Accurate cell dimensions and other crystallographic data are listed in Table 1.

X-ray intensities were measured by the ω -scan technique with variable scan speeds. The data were corrected for Lorentz and polarization effects, but not for adsorption.

The structure of $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ with $\text{HL}=1$ was solved by Patterson and Fourier techniques using the X-RAY system.⁴ The structures of the two other complexes were solved by direct methods with the MULTAN program.⁵ The nickel and 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 block-diagonal least-squares methods.⁴ All hydrogen atoms were located from difference Fourier maps. Isotropic temperature factors were applied for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms. The atomic scattering factors were those used by the programme. Anomalous dispersion corrections ($\Delta f'$, $\Delta f''$) were included for Ni and Cl.⁶

Final parameters for all non-hydrogen and hydrogen atoms in the complexes are listed in Tables 2 and 3, respectively. Observed and calculated structure factors and anisotropic thermal parameters can be obtained on request from the authors.

RESULTS AND DISCUSSION

Structures of $\text{Ni}(\text{HL})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{HL}=1$) and $\text{Ni}(\text{HL})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ($\text{HL}=3$). The structures of

the violet-blue ($\text{HL}=1$) and green-blue ($\text{HL}=3$) crystals contain both $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$ complex cations and uncoordinated chloride ions. With ligand 3 there are, in addition, uncoordinated water molecules joined in the structure through hydrogen bonding. Stereo views of the molecular packings in the respective unit cells are illustrated in Figs. 1 and 2.

The complex cation formed by 1 is centrosymmetric and displays a distorted *trans* octahedral coordination around nickel in which the bidentate organic ligand is bonded to the metal through its amino and oxime nitrogen atoms. An ORTEP drawing of the cation and the bond lengths are shown in Fig. 3; the bond angles are given in Table 4. In the complex with 3 the mode of chelation is the same as that with 1 but in this case the two bidentate ligands occupy *cis* positions in the coordination octahedron. The complex geometry with the numbering of the atoms and the bond lengths are shown in the schematic representation in Fig. 4; the selected bond angles are listed in Table 4.

In these two octahedral structures the chemically equivalent bond distances of the ligand molecules 1 and 3 are all equal within the experimental error and can be considered normal for a coordinated oxime compound. As could be expected, the Ni-N(amine) bond with 1 [2.078(2) Å] is considerably shorter than the corresponding bonds with 3 [2.158(3) and 2.196(4) Å], which contains two methyl groups on the amine nitrogen. Likewise, the Ni-N(oxime) bond with $\text{HL}=1$ is slightly but significantly shorter [2.049(2) Å] than the same bond with 3 [2.064(3) and 2.086(3) Å]. The lengthening of these Ni-N distances is

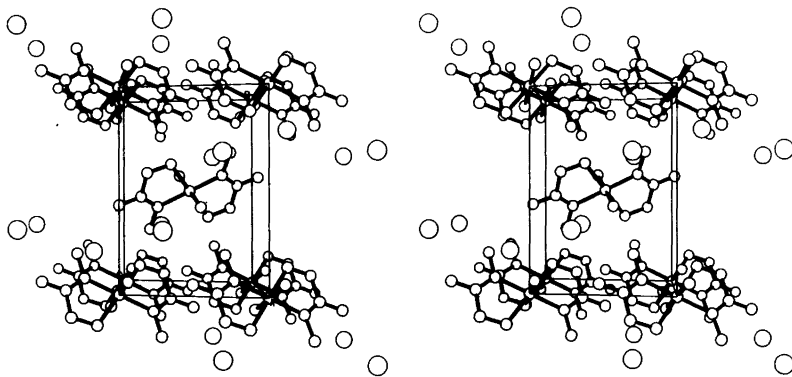


Fig. 1. Stereoscopic view of the molecular packing of $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$, $\text{HL}=1$, in the unit cell.

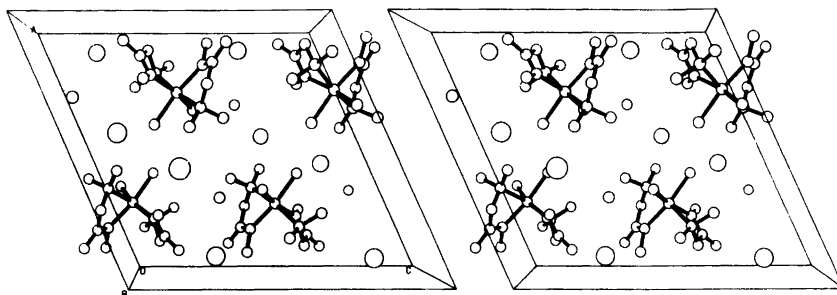


Fig. 2. Stereoscopic view of the molecular packing of $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{HL}=3$, in the unit cell.

probably indicative of weaker metal-ligand interactions in the complex containing **3** than in the complex containing **1**. This is also suggested by the values of the stability constants of the aqueous complexes which are considerably lower with ligand **3** than with **1**.¹

The characteristic Ni–N(oxime), C=N(oxime), N–O and C–N(amide) bond lengths, and the C–N–O bond angles of the complexes are shown in Table 5 together with the corresponding values of other known octahedral nickel(II) complexes containing undissociated oxime groups. Although the chemically equivalent bond lengths and angles are relatively constant in all these structures, some minor systematic differences can be found: in the first four amidoxime compounds the Ni–N(oxime) bonds are all slightly shorter (average 2.076 Å) and the N–O bonds all slightly longer (average 1.423 Å) than the corresponding distances (average 2.120 and 1.383 Å) in the rest of the compounds, which contain a hydrogen or methyl group in place of the amide group. The differences cannot be

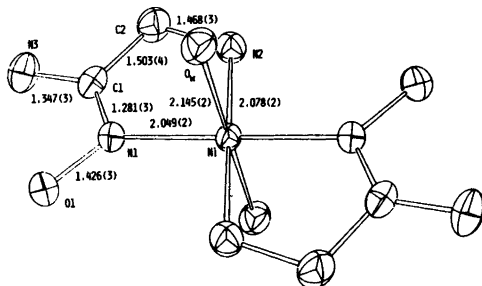


Fig. 3. ORTEP drawing of the complex ion $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$, $\text{HL}=1$, showing bond lengths (Å).

explained *e.g.* by steric or packing effects, but possibly the shorter Ni–N(oxime) and longer N–O distances in the amidoxime compounds are consistent with the delocalization of the lone electron pair formally on the amide nitrogen by resonance with the adjacent oxime group. This latter effect increases the electron density on the oxime nitrogen atom and is clearly seen in the values of the C–N(amide) distances (average 1.34 Å), which are considerably shorter than the typical C–N single bond (=1.47 Å).

Structure of $\text{NiHL}_2\text{Cl} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ($\text{HL}=1$). Dissociation of the oxime proton from $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$ when $\text{HL}=1$ allows rearrangements in the ligand positions as well as in the coordination number of nickel(II), and the

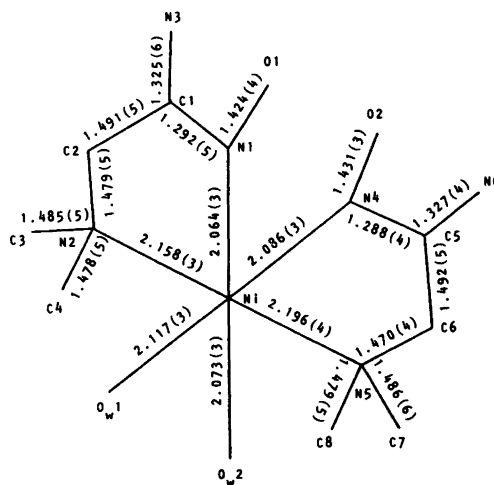


Fig. 4. Schematic representation of the complex ion $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]^{2+}$, $\text{HL}=3$, showing bond lengths (Å).

Table 4. Selected interatomic bond angles (°).^a

$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (HL = I)	N1-Ni-N2 ¹	100.6(1)	N1-Ni-O _{w1}	91.2(1)
N1-Ni-N2	N2-Ni-O _w	90.8(1)	N2-Ni-O _w	89.2(1)
N1-Ni-O _{w1}				
C1-N1-O1				
$[\text{Ni}(\text{HL})\text{L}]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ (HL = I)	N1-Ni-N4	96.6(1)	N1-Ni-N5	178.3(1)
N1-Ni-N2	N2-Ni-N5	95.2(1)	N4-Ni-N5	83.8(1)
N2-Ni-N4	N1-Ni-N3 ^{II}	114.8(2)	N1-Ni-N3 ^{II}	101.4(1)
C1-Ni-O1	N4-Ni-N3 ^{II}	87.8(1)	N5-Ni-N3 ^{II}	80.3(1)
N2-Ni-N3 ^{II}	N2-Ni-N6 ^{III}	88.7(1)	N4-Ni-N6 ^{III}	93.9(1)
N1-Ni-N6 ^{III}				
N5-Ni-N6 ^{III}				
$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (HL = β)	N1-Ni-N4	94.5(1)	N1-Ni-N5	97.3(1)
N1-Ni-N2	N1-Ni-O _{w2}	163.5(1)	N2-Ni-N4	95.8(1)
N1-Ni-N5	N2-Ni-O _{w1}	95.1(1)	N2-Ni-O _{w2}	89.6(1)
N2-Ni-N5	N4-Ni-O _{w1}	169.2(1)	N4-Ni-O _{w2}	96.9(1)
N4-Ni-N5	N5-Ni-O _{w2}	97.0(1)	O _{w1} -Ni-O _{w2}	82.8(1)
N5-Ni-O _{w1}				
C1-N1-O1	C5-N4-O2	110.8(1)		

^a Symmetry relations for atoms: I, -x, -y, -z; II, -x, 1-y, -z; III, $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

Table 5. Comparison of Ni-N(oxime), C=N, N-O and C-N(amide) bond lengths (Å) and C-N-O bond angle (°) in octahedral nickel(II) complexes.

Complex	Ni-N(oxime)	C=N	N-O	C-N(amide)	C-N-O	Ref.
$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2^a$	2.049(2)	1.281(3)	1.426(3)	1.347(3)	111.6(2)	This work
$[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}^b$	2.064(3)	1.292(5)	1.424(4)	1.325(6)	111.7(3)	This work
	2.086(3)	1.288(4)	1.431(3)	1.327(4)	110.8(2)	
$[\text{Ni}(\text{H}_2\text{L})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}^c$	2.068(2)	1.280(3)	1.425(2)	1.339(3)	111.6(2)	7
	2.081(2)	1.277(3)	1.414(2)	1.340(3)	111.0(2)	
$[\text{Ni}(\text{H}_2\text{L})_3]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}^d$	2.074(7)	1.27(2)	1.417(11)	1.369(17)	110.6(9)	8
	2.082(12)	1.296(15)	1.427(11)	1.33(3)	111(1)	
	2.104(12)	1.293(16)	1.42(2)	1.348(19)	111(1)	
$[\text{Ni}(\text{H}_2\text{L})](\text{ClO}_4)_2^e$	2.106(4)	1.279(5)	1.386(5)		112.9(3)	3
	2.131(5)	1.284(5)	1.384(4)		114.0(4)	
$[\text{Ni}(\text{HL})_2](\text{ClO}_4)_2^f$	2.135(4)	1.285(5)	1.385(5)		113.4(4)	9
$[\text{Ni}(\text{HL})_4]\text{Cl}_2^g$	2.112(2)	1.249(5)	1.378(5)		111.8(2)	10
	2.115(2)	1.253(3)	1.382(5)		111.5(2)	

^a HL = 2-aminoacetamidoxime, ^b HL = 2-(dimethylamino)acetamidoxime, ^c H₂L = iminobis(acetamidoxime), ^d H₂L = oxamide oxime, ^e H₂L = 3,14-dimethyl-4,7,10,13-tetraaza-3,13-hexadecadiene-2,15-dione dioxime, ^f HL = 2-(2-aminoethyl)imino-3-butanone oxime, ^g HL = acetaldoxime.

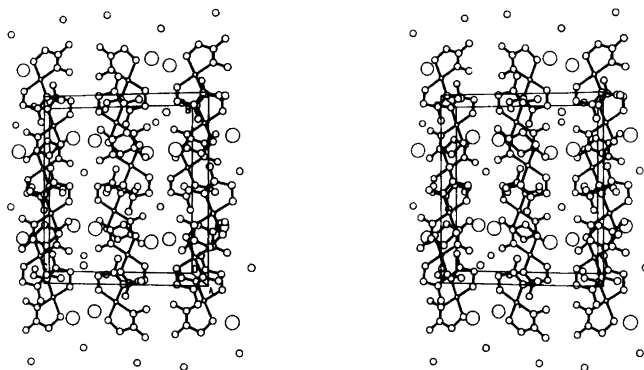


Fig. 5. Stereoscopic view of the molecular packing of $[\text{Ni}(\text{HL})\text{L}]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{HL}=\text{I}$, in the unit cell.

structure of the orange-red $\text{NiHL}_2\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ consists of $[\text{Ni}(\text{HL})\text{L}]^+$ complex ions, uncoordinated water molecules and chloride ions. A stereoscopic view of the molecular packing is shown in Fig. 5. The nickel(II) atom is found to have a square-planar coordination environment stabilized by an intramolecular hydrogen bridge between the *cis* oxime oxygen atoms.

In our study on the amino-amidoxime complexes in aqueous solution, a corresponding orange-red species was readily obtained with ligand 2, too.¹ This complex evidently has a structure closely similar to that above. Not surprisingly, no such complex was found with ligand 3: the steric requirements of the two methyl groups on the amino nitrogen atoms and on the other hand, the oxygen–oxygen repulsion do not allow, without considerable strain in the molecule, a square-planar complex with a strong intramolecular hydrogen bond between the *cis* oxime oxygen atoms.¹

Comparison of the bond distances and angles given in Table 4 and Fig. 6 with those in the octahedral structure of the same ligand (Fig. 3

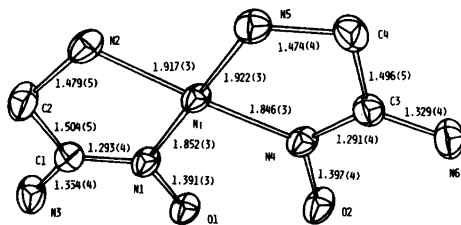


Fig. 6. ORTEP drawing of the complex ion $[\text{Ni}(\text{HL})\text{L}]^+$, $\text{HL}=\text{I}$, showing bond lengths (Å).

and Table 4) reveals some marked differences. The most significant changes occur in the Ni–N(oxime) and Ni–N(amine) bonds, which are considerably shorter in the four-coordinate than in the six-coordinate structure. This contraction is accompanied by pertinent opening in the intrachelate N–Ni–N angle. Another obvious difference is between the geometries of the oxime groups: the N–O distances are shorter and the C–N–O angles larger in the square-planar complex than in the octahedral complex. These alterations are expected from the different electronic state of nickel and the different function of the oxime groups in these two structures.

With oxime ligands the diamagnetic square-planar complexes are far more common than the octahedral structures and a great number of them have been characterized by X-ray or neutron diffraction methods. The geometry of the present complex generally agrees with the published results. Thus the average Ni–N(amine) distance 1.920(4) Å is normal and comparable to that observed in other studies, *e.g.* 1.908(1) Å in bis(2-amino-2-methyl-3-butanone oximate)nickel(II) chloride.¹¹

The Ni–N(oxime) distance is fairly constant in all the square-planar complexes. The smallest value in any structure yet reported seems to be 1.839(1) Å, which was observed with a tetradentate amine-oxime ligand.¹² The usual values are somewhat greater, varying between 1.86 and 1.88 Å; a mean value of 1.87 Å for several complexes containing this bond has recently been reported.¹³ Though rather short the Ni–N(oxime) bonds 1.846(3) and 1.852(3) Å

found here are not uncommon in view of these results.

The oxime N–O bond distance is more sensitive to minor variations in the structure than the Ni–N(oxime) bond, for the observed range for this bond is 1.313(7)–1.403(7) Å.^{13–16} Interestingly, all the longer distances (1.360(7)–1.403(7) Å) appear in complexes where the amidoxime group is present: with glyoxime and its alkylated derivatives, for example, distances are considerably shorter: between 1.34 and 1.35 Å.^{17–19} The N–O bond lengths 1.391(3) and 1.397(4) Å found in this study are longish, but in good agreement with those found in other amidoximate structures.

The intramolecular hydrogen bonded O...O distance in the complex, 2.489(3) Å, is in the range observed in comparable structures.^{20,21} When the O...O distance approaches 2.40 Å a symmetric hydrogen bond is often proposed.²⁰ Although the positions of hydrogen atoms refined with X-ray diffraction data cannot be considered reliable, the O–H distances obtained here for this bond, 0.98(7) and 1.62(7) Å, together with the value of the O–H–O angle 145(6)°, strongly support the existence of an asymmetric hydrogen bond in the structure. The significantly unequal C–N–O angles [114.8(2) and 116.3(2)°] in the complex probably point to the same conclusion.

Square-planar dioximate complexes of the nickel triad are known to prefer stacked structures in the solid state, and a direct electronic M–M interaction may be present.^{22,23} In this structure the arrangement of the complex units is such that the nickel(II) atom lies nearly perpendicularly above and below the amide nitrogen atoms N3 and N6 of the adjacent molecules

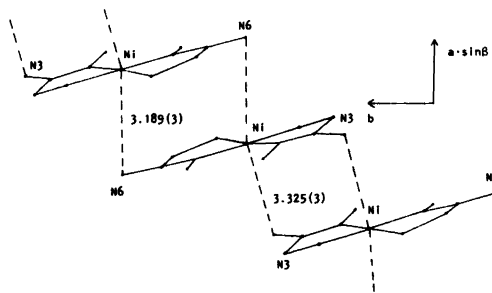


Fig. 7. Schematic projection of a part of the stack in $[\text{Ni}(\text{HL})\text{L}]^+$, $\text{HL}=1$.

(Table 4). The $\text{N3}^{\text{II}}-\text{Ni}$ and $\text{N6}^{\text{III}}-\text{Ni}$ distances are relatively short: 3.325(3) and 3.189(3) Å, respectively. This packing pattern, shown in the schematic representation in Fig. 7, is quite similar to the M–L–M form of stacking found earlier in bis(oxamide oximate)nickel(II)–oxamide oxime¹⁴ and in bis(oxamide oximate)cobalt(II)–oxamide oxime,²⁴ and it may indicate some bonding interaction between metal and axial nitrogen atoms.

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Received September 1, 1983.