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A Redetermination of the Crystal and Molecular Structure of Nickel(II) Ethylmethylglyoxime*

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The crystal and molecular structure of bis-(2,3-pentanedionedioximate-*N,N'*)nickel(II) [or nickel(II) ethylmethylglyoxime] has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in the monoclinic system in space group $P2_1/c$ with two molecules per unit cell. Unit-cell parameters are: $a=4\cdot7471\pm0\cdot0005$, $b=11\cdot7409\pm0\cdot0030$, $c=11\cdot9895\pm0\cdot0020$ Å; $\beta=91\cdot611\pm0\cdot016°$. The structural analysis of the complex, based on all reflections out to 50° in 2θ with Mo $K\alpha$ radiation (final R value for 802 observed reflections of 4·8%) reveals an intramolecular hydrogen bond with an O---O distance of 2·454 Å. Bond distances in the five-membered chelate ring indicate significant delocalization of the two conjugated carbon–nitrogen double bonds.

Introduction

The *vic*-dioxime complexes of metal(II) ions have received considerable attention, not only because they are useful in the analysis of certain transition metals, but also because the solid complexes exhibit certain structural features which are of general interest. These features include short intramolecular hydrogen bonds and packing configurations which give rise to unusual optical properties.

The detailed study of such features and the correct explanation of these unusual optical properties are dependent on precise structural information. The structure of nickel(II) ethylmethylglyoxime [$Ni(EMG)_2$] was originally solved (Frasson & Panattoni, 1960) with two-dimensional film data. Infrared structural studies of the hydrogen bonding in several metal(II)-*vic*-dioximes by Caton & Banks (1967), together with a theoretical treatment of hydrogen bonding by Lippincott & Schroeder (1955), suggest that the intramolecular hydrogen bond in $Ni(EMG)_2$ is considerably longer than the reported value of 2·33 Å. We have therefore undertaken a redetermination of the crystal and molecular structure of $Ni(EMG)_2$.

Experimental

Crystal data:

$C_{10}H_{18}N_4O_4Ni$, $M=316\cdot99$ g.mole^{-1}, Monoclinic $P2_1/c$, $a=4\cdot7471\pm0\cdot0005$, $b=11\cdot7409\pm0\cdot0030$, $c=11\cdot9895\pm0\cdot0020$ Å, $\beta=91\cdot611\pm0\cdot016°$, $V=668\cdot0$ Å^3, $D_c=1\cdot58$ g.cm^{-3}, $Z=2$, $F(000)=332$, $T\simeq24°$, Mo $K\alpha$ ($\lambda=0\cdot7107$ Å), $\mu=14\cdot7$ cm^{-1}.

Two different modifications of $Ni(EMG)_2$ have been reported (Anex & Krist, 1967). One of these crystallizes in a monoclinic space group and has been designated the α form. The other crystallizes in an orthorhombic space group and has been designated the β form. A recent study by Egneus (1969) has shown that the α form is the more stable of the two and that crystallization from chloroform produces this modification alone. Crystals of $Ni(EMG)_2$ were prepared by precipitation of the complex from aqueous solution followed by recrystallization from a chloroform solution. This procedure was employed in order to insure that the crystals obtained would be of the α form.

A suitable crystal was selected and mounted in a thin-walled Lindemann glass capillary. Preliminary precession photographs exhibited *2/m* Laue symmetry, indicating a monoclinic space group. Systematic absences of $h0l$ for l odd and $0k0$ for k odd indicated the space group $P2_1/c$ (C_{2h}^5) in agreement with the previously reported determination. The unit-cell parameters and their standard deviations were obtained by a least-squares fit to 14 independent reflection angles whose centers were determined by left–right, top–bottom beam splitting on a previously aligned Hilger–Watts four circle diffractometer (Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å). Any error in the instrumental zero was eliminated by centering the reflection at both $+2\theta$ and -2θ.

For data collection, a crystal having approximate dimensions $0\cdot2\times0\cdot2\times0\cdot5$ mm was mounted in a glass capillary with **a** along the spindle axis. Data were collected at room temperature using a fully automated Hilger–Watts four circle diffractometer equipped with scintillation counter and interfaced with an SDS-910 computer in a real time mode. Two octants of data were recorded using Zr-filtered Mo $K\alpha$ radiation within a 2θ sphere of 50° ($\sin\theta/\lambda=0\cdot5947$). The θ–2θ step-scan technique, 0·01° per step counting for 0·4096 sec per step, was employed with a take-off angle of 4·5°. Variable step symmetric scan ranges were used with the number of steps for a given reflection determined as follows: $N=(50+2$ per $°\theta)$. Stationary-crystal stationary-counter background measurements were made by counting for one half the total scan time at each end of

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the scan. 1608 reflections were measured in this way.

As a general check on the electronic and crystal stability, the intensities of three standard reflections were measured periodically during the data collection. Monitoring options based on these standard counts were used to maintain crystal alignment and to stop the collection of data if standard counts fell below statistically allowed fluctuations. No decrease in any of the standards was observed during data collection.

The intensity data were corrected for Lorentz- polarization effects. The absorption coefficient, μ, is 14·68 cm^{-1}, and an absorption correction (Busing & Levy, 1957) was made using *ABCOR*;* the maximum and minimum transmission factors were 0·839 and 0·755 respectively. The estimated error in each intensity was calculated by $[\sigma(I)]^2=[C_t+C_b+(0{\cdot}05C_t)^2+(0{\cdot}05C_b)^2]$ where C_t and C_b are the total count and background count respectively. The individual values of F_o^2 from equivalent sets were then averaged to give 1397 independent F_o^2 values. The estimated standard deviation in each structure factor was calculated from the mean deviation of intensity by the method of finite differences (Williams & Rundle, 1964). The reciprocals of the structure factor variances were used as weights in the least-squares refinement.

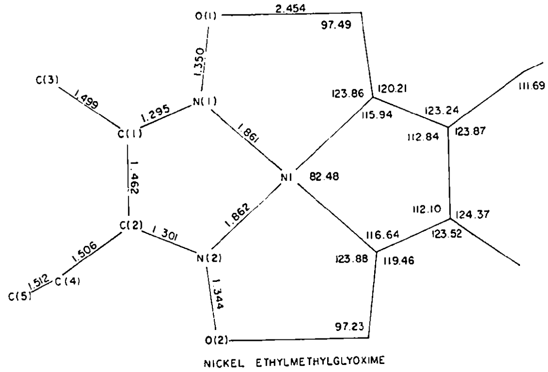

Fig. 1. Interatomic distances and angles in Ni(EMG)$_2$.

Solution and refinement of structure

Owing to the presence of only two molecules per unit cell, the metal atoms are restricted to the centers of symmetry. The positions of the remaining atoms except hydrogen were obtained from three-dimensional electron density difference maps and were refined by full-matrix least-squares techniques with isotropic thermal parameters to a conventional discrepancy index of

$$R=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}135,$$

and a weighted R index of

$$wR=[\sum w(|F_o|-F_c|)^2/\sum|F_o|^2]^{1/2}=0{\cdot}122\,.$$

The relativistic Dirac–Slater X-ray scattering factors for neutral atoms of Cromer & Waber (1965) were used with those of nickel modified for the real and imaginary parts of anomalous dispersion (Cromer, 1965). All unique data were used in the refinement.

At this point, anisotropic refinement of nickel and nitrogen atoms for two cycles gave a value for R of 0·115. The remaining atoms with the exception of the methyl carbon atoms, were next refined anisotropically, and two cycles gave values for R and wR of 0·104 and 0·094 respectively.

An electron density difference map was calculated and it revealed some rather diffuse peaks which could be interpreted as hydrogen atoms. Owing to the uncertainty in the positions of these atoms, however, their positions were calculated assuming tetrahedral methyl groups and a C–H distance of 1·08 Å. The methyl hydrogen atoms were placed as near as possible to the observed peaks in the difference map. The methylene hydrogen atoms were placed in the plane which bisects the C–C–C angle of the ethyl substituent, at an angle of 109·5° from one another. The hydroxyl hydrogen atom was placed midway between the oxygen atoms. All hydrogen atoms were assigned isotropic thermal parameters slightly larger than those of the atoms to which they are bound.

Two cycles of refinement with hydrogen parameters

Table 1. *Final refined positional and anisotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

The β_{ij} are defined by: $T=\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$

Numbers in parentheses are standard deviations in the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	410 (5)	74 (1)	53 (1)	−21 (2)	30 (1)	−3 (1)
N(1)	−270 (8)	−1524 (4)	−414 (3)	331 (20)	79 (4)	67 (3)	−13 (7)	37 (7)	4 (3)
N(2)	2686 (9)	25 (4)	−1102 (3)	517 (23)	79 (4)	60 (3)	−19 (9)	30 (7)	1 (3)
O(1)	−2071 (9)	−2272 (3)	39 (3)	696 (25)	72 (3)	100 (3)	−52 (7)	76 (7)	−3 (3)
O(2)	4150 (8)	958 (3)	−1378 (3)	635 (23)	95 (3)	80 (3)	−51 (8)	82 (7)	−3 (2)
C(1)	1344 (11)	−1858 (4)	−1204 (4)	524 (27)	72 (4)	66 (4)	14 (10)	2 (9)	−1 (3)
C(2)	3101 (11)	−935 (4)	−1614 (4)	426 (26)	79 (5)	58 (4)	25 (9)	−4 (8)	−2 (3)
C(3)	1408 (13)	−3058 (5)	−1631 (5)	765 (39)	76 (5)	108 (5)	18 (12)	56 (12)	−12 (4)
C(4)	5087 (12)	−1060 (4)	−2563 (4)	515 (29)	103 (5)	75 (4)	22 (11)	49 (9)	−4 (4)
C(5)	3594 (15)	−893 (6)	−3682 (5)	920 (47)	159 (8)	74 (5)	56 (16)	17 (12)	−6 (5)

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* In addition to local programs written at this Laboratory, the authors wish to acknowledge the use of *ABCOR* (Busing & Levy, 1957), *ORTEP* (Johnson, 1965), *ORFFE* (Busing, Martin & Levy, 1964), *LCR*2 (Williams, 1964), and a local modification of *ORFLS* (Busing, Martin & Levy, 1962).

unvaried and anisotropic thermal parameters for all heavy atoms gave values for R and wR of 0·089 and 0·074 respectively. Hydrogen atom positions were then recalculated and two further cycles gave values for R and wR of 0·088 and 0·073 respectively.

A statistical analysis of $w\Delta^2$ where $\Delta^2=(|F_o|-|F_c|)^2$ as a function of scattering angle and magnitude of F_o revealed that the relative weighting scheme used was reasonable. An attempt to refine the positional and thermal parameters of the methyl hydrogen atoms was not entirely successful, but based on the refined C–H bond distances these hydrogen atoms were relocated with a C–H distance of 1·01 Å. During the final refinement, the positional and thermal parameters of all hydrogen atoms were calculated and not varied because the agreement between observed and calculated structure amplitudes seemed insensitive to these parameters. Two final cycles of refinement gave values for R and wR of 0·088 and 0·073 respectively. Two final cycles of refinement using 802 observed reflections (those with $F^2>3\sigma F^2$) gave values for R and wR of 0·048 and 0·060 respectively, with no significant shifts in the final refined parameters. A final electron density difference map revealed no peaks greater than 0·4 e.Å^{-3}. The final standard deviation for an observation of unit weight, $[\sum w\Delta^2/(NO-NV)]^{1/2}$, where NO is the number of observations (1397) and NV is the number of variables (88) was 1·26 electrons. During the final cycle, the largest shift in any parameter was less than 0·01 times its own σ.

Table 1 gives the final refined positional and thermal parameters for the heavy atoms along with their standard deviations as derived from the inverse matrix of the final least-squares refinement cycle. R.m.s. components of thermal displacement along the principal axes are given for the heavy atoms in Table 2. A list of all 1397 unique recorded and calculated structure amplitudes is found in Table 3.

Table 2. *R.m.s. component of thermal displacement* (Å) *along principal axis R*

	$R=1$	$R=2$	$R=3$
Ni	0·1848 (12)	0·2126 (17)	0·2398 (13)
N(1)	0·1764 (60)	0·2322 (61)	0·2378 (53)
N(2)	0·2005 (55)	0·2308 (66)	0·2530 (56)
O(1)	0·2064 (50)	0·2449 (46)	0·3146 (51)
O(2)	0·1995 (50)	0·2489 (46)	0·3062 (49)
C(1)	0·2189 (93)	0·2223 (69)	0·2476 (71)
C(2)	0·2035 (64)	0·2109 (72)	0·2453 (69)
C(3)	0·2192 (73)	0·2706 (75)	0·3114 (78)
C(4)	0·2056 (70)	0·2607 (67)	0·2714 (74)
C(5)	0·2299 (74)	0·3036 (84)	0·3521 (86)

Results and discussion

Interatomic distances and angles with standard deviations are given in Table 4 and illustrated in Fig. 1. The standard deviations in the distances and angles were calculated using the variance–covariance matrix and *ORFFE*, and include errors in the lattice constants. The present study reveals a much longer hydrogen bond than was previously reported. The latest value of 2·454 Å is in much better agreement with the distance

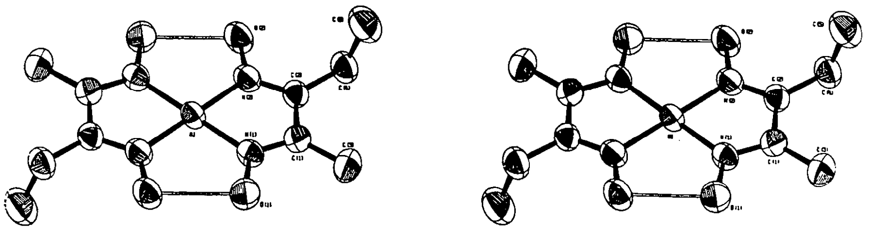

Fig. 2. Stereo illustration of a molecule of Ni(EMG)$_2$ with thermal ellipsoids scaled to enclose 50% probability.

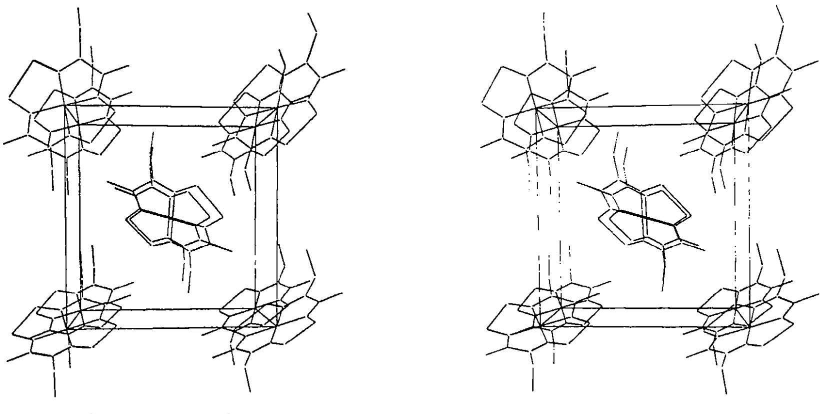

Fig. 3. Stereo view, along **a**, of the crystal packing of Ni(EMG)$_2$.

expected from existing correlations of OH stretching frequencies with O---O distance. Statistical comparisons of chemically equivalent bonds reveal no significant differences and suggest that the hydrogen bond is symmetrical. The bond distances in this complex agree well with their equivalents in other oximes, *vic*-dioximes and metal(II)-*vic*-dioxime complexes.

A significant feature of the complex is the delocalization of the two carbon–nitrogen double bonds through the carbon–carbon bond in the chelate ring. Similar

Table 3. *Observed and calculated structure amplitudes*

H	K	FO	FC
L = 14			
0	0	67	59
0	1	43	2
0	2	75	67
L = 13			
0	0	0	0
1	0	0	0
2	0	0	0
0	1	92	75
1	1	64	69
2	1	76	69
0	2	0	-13
1	2	41	39
2	2	0	-23
0	3	119	108
1	3	141	131
0	4	43	-32
1	4	41	35
0	5	38	33
L = 12			
0	0	109	105
1	0	94	98
2	0	80	76
0	1	0	-18
1	1	0	4
2	1	41	-26
0	2	112	103
1	2	139	133
2	2	109	96
0	3	0	-31
1	3	60	58
2	3	30	-13
0	4	135	122
1	4	178	160
2	4	94	79
0	5	20	10
1	5	18	4
2	5	0	-3
0	6	57	37
1	6	79	80
0	7	0	18
L = 11			
0	0	0	0
1	0	22	0
2	0	0	0
3	0	0	0
0	1	158	145
1	1	149	138
2	1	89	91
3	1	65	70
0	2	12	8
1	2	12	-25
2	2	44	-39
3	2	27	34
0	3	203	186
1	3	168	164
2	3	85	81
3	3	54	54
0	4	81	74
1	4	41	61
2	4	13	-13
3	4	35	4
0	5	131	123
1	5	175	168
2	5	78	83
0	6	28	-29
1	6	17	-22
2	6	0	1
0	7	76	69
1	7	91	81
2	7	24	40
0	8	50	-24
1	8	28	14
L = 10			
0	0	95	94
1	0	219	214
2	0	74	76
3	0	66	61
0	1	38	36
1	1	105	-103
2	1	30	-19
3	1	46	39
0	2	170	160
1	2	186	177
2	2	117	113
3	2	84	85
0	3	98	88
1	3	52	-46
2	3	6	20
3	3	38	37
0	4	325	319
1	4	156	159
2	4	96	89
3	4	82	72
0	5	67	59
1	5	0	-5
2	5	0	2
3	5	23	10
0	6	176	169
1	6	98	87
2	6	50	57
3	6	46	54
0	7	48	-42
1	7	29	35
2	7	27	12
0	8	124	112
1	8	100	99
2	8	33	29
0	9	19	-23
1	9	27	32
L = 9			
0	0	0	0
1	0	0	0
2	0	14	0
3	0	0	0
4	0	32	0
0	1	236	228
1	1	263	261
2	1	50	42
3	1	87	83
4	1	78	52
0	2	71	-79
1	2	47	-42
2	2	56	52
3	2	42	75
4	2	22	-24
0	3	227	227
1	3	142	139
2	3	151	145
3	3	148	152
4	3	97	104
0	4	31	23
1	4	36	-27
2	4	0	16
3	4	16	-19
0	5	344	345
1	5	116	116
2	5	99	101
3	5	78	72
0	6	38	26
1	6	0	20
2	6	28	31
3	6	0	20
0	7	112	115
1	7	26	41
2	7	60	66
3	7	63	73
0	8	16	-14
1	8	0	29
2	8	0	-15
0	9	142	125
1	9	121	112
2	9	34	43
0	10	0	9
1	10	30	-5
L = 8			
0	0	611	591
1	0	154	157
2	0	98	101
3	0	78	74
4	0	59	65
0	1	81	-76
1	1	84	-86
2	1	5	15
3	1	0	0
4	1	11	0
0	2	275	272
1	2	113	108
2	2	168	172
3	2	176	179
4	2	101	101
0	3	19	-22
1	3	0	18
2	3	52	53
3	3	36	-40
4	3	0	-13
0	4	242	238
1	4	223	221
2	4	138	129
3	4	150	150
4	4	81	79
0	5	53	62
1	5	23	-4
2	5	20	9
3	5	0	19
4	5	17	22
0	6	123	116
1	6	123	124
2	6	93	94
3	6	91	94
0	7	15	-22
1	7	31	35
2	7	19	12
3	7	29	31
0	8	151	152
1	8	73	67
2	8	73	71
3	8	81	77
0	9	34	7
1	9	14	-11
2	9	15	-37
0	10	164	148
1	10	73	79
2	10	81	70
0	11	0	6
1	11	0	7
L = 7			
0	0	70	0
1	0	0	0
2	0	16	0
3	0	20	0
4	0	11	0
0	1	422	407
1	1	96	93
2	1	172	177
3	1	141	134
4	1	89	90
0	2	19	18
1	2	121	-127
2	2	44	54
3	2	114	-120
4	2	19	9
0	3	230	236
1	3	251	253
2	3	288	289
3	3	217	220
4	3	87	80
0	4	53	-49
1	4	0	4
2	4	113	107
3	4	38	-4
4	4	43	50
0	5	182	184
1	5	143	149
2	5	90	89
3	5	121	118
4	5	40	51
0	6	84	74
1	6	64	50
2	6	35	-23
3	6	0	47
4	6	29	-7
0	7	114	97
1	7	104	108
2	7	146	144
3	7	114	112
0	8	46	-42
1	8	33	20
2	8	33	-34
3	8	25	32
0	9	200	197
1	9	86	89
2	9	95	90
3	9	80	83
0	10	24	2
1	10	0	-34
2	10	31	3
0	11	96	[illegible]
1	11	42	29
0	12	28	33
L = 6			
0	0	550	543
1	0	219	211
2	0	70	76
3	0	159	157
4	0	34	56
5	0	63	60
0	1	82	-77
1	1	27	21
2	1	108	-109
3	1	65	-65
4	1	0	3
5	1	28	-28
0	2	151	150
1	2	200	197
2	2	369	362
3	2	265	260
4	2	80	78
0	3	221	-216
1	3	177	183
2	3	22	-25
3	3	35	-53
4	3	36	46
0	4	291	290
1	4	251	253
2	4	253	260
3	4	110	115
4	4	88	92
0	5	24	26
1	5	40	41
2	5	19	22
3	5	59	60
4	5	56	48
0	6	96	91
1	6	129	130
2	6	185	188
3	6	80	85
4	6	47	52
0	7	68	70
1	7	15	5
2	7	40	36
3	7	24	5
4	7	45	-48
0	8	136	127
1	8	152	149
2	8	154	157
3	8	105	109
0	9	0	-21
1	9	98	-95
2	9	0	2
3	9	28	16
0	10	138	128
1	10	72	62
2	10	70	72
3	10	86	83
0	11	35	24
1	11	46	39
2	11	32	41
0	12	77	67
1	12	0	33
L = 5			
0	0	0	0
1	0	22	0
2	0	20	0
3	0	0	0
4	0	0	0
5	0	0	0
0	1	287	276
1	1	118	125
2	1	451	448
3	1	169	177
4	1	77	77
5	1	50	63
0	2	221	-221
1	2	48	30
2	2	346	-352
3	2	41	42
4	2	23	-29
5	2	0	-21
0	3	245	245
1	3	336	324
2	3	330	327
3	3	161	165
4	3	56	67
5	3	59	65
0	4	58	63
1	4	277	296
2	4	32	14
3	4	100	107
4	4	80	8
0	5	164	181
1	5	322	335
2	5	160	159
3	5	163	150
4	5	101	103
0	6	75	76
1	6	112	-109
2	6	46	56
3	6	0	6
4	6	41	31
0	7	136	128
1	7	221	226
2	7	172	181
3	7	98	108
4	7	50	43
0	8	28	-20
1	8	50	-42
2	8	60	80
3	8	78	-81
4	8	0	-16
0	9	164	153
1	9	132	124
2	9	143	137
3	9	64	64
0	10	0	-7
1	10	0	-4
2	10	27	30
3	10	0	19
0	11	0	17
1	11	34	28
2	11	139	124
0	12	0	2
1	12	42	43
2	12	0	-8
0	13	109	85
L = 4			
0	0	37	32
1	0	429	412
2	0	472	453
3	0	78	72
4	0	197	178
5	0	95	90
0	1	19	18
1	1	426	-408
2	1	299	-285
3	1	0	-20
4	1	17	-26
5	1	36	-9
0	2	34	55
1	2	519	514
2	2	470	485
3	2	144	143
4	2	71	76
5	2	76	66
0	3	76	-68
1	3	69	71
2	3	49	34
3	3	59	61
4	3	55	-64
5	3	17	-11
0	4	443	444
1	4	341	306
2	4	147	151
3	4	174	175
4	4	40	81
5	4	89	[illegible]
0	5	114	107
1	5	61	67
2	5	82	85
3	5	71	86
4	5	47	42
0	6	218	207
1	6	203	202
2	6	216	224
3	6	194	200
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2	7	44	-41
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3	7	78	70
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2	11	100	104
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2	10	94	93
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2	1	12	0
3	1	45	56
4	1	31	17
0	2	151	160
1	2	200	205
2	2	177	171
3	2	164	161
4	2	98	101
0	3	84	-88
1	3	91	97
2	3	0	9
3	3	42	9
0	4	301	319
1	4	87	85
2	4	128	129
3	4	153	150
0	5	58	-59
1	5	48	-55
2	5	14	-29
3	5	0	-1
0	6	158	169
1	6	0	13
2	6	100	97
3	6	123	123
0	7	51	62
1	7	0	-3
2	7	22	17
0	8	113	112
1	8	79	92
2	8	71	69
0	9	25	23
1	9	0	-14
L = -11			
0	0	0	0
1	0	24	0
2	0	0	0
3	0	0	0
0	1	140	145
1	1	95	100
2	1	86	79
3	1	126	116
0	2	0	-8
1	2	85	87
2	2	51	-51
3	2	26	43
0	3	181	186
1	3	169	168
2	3	199	199
3	3	156	160
0	4	73	-76
1	4	17	29
2	4	30	-15
3	4	26	25
0	5	117	123
1	5	22	24
2	5	92	84
3	5	109	103
0	6	30	29
1	6	28	-45
2	6	0	-1
0	7	54	69
1	7	47	55
2	7	104	106
0	8	0	24
1	8	0	-11
L = -12			
0	0	99	105
1	0	80	73
2	0	59	57
3	0	89	89
0	1	32	18
1	1	40	-36
2	1	0	6
3	1	0	17
0	2	93	103
1	2	116	121
2	2	151	152
3	2	132	128
0	3	47	31
1	3	6	3
2	3	0	22
0	4	116	122
1	4	102	102
2	4	122	128
0	5	30	-10
1	5	26	-18
2	5	0	-3
0	6	42	37
1	6	28	35
0	7	47	-18
1	7	10	8
L = -13			
0	0	0	0
1	0	0	0
2	0	35	0
0	1	70	75
1	1	96	88
2	1	75	71
0	2	0	13
1	2	39	-43
2	2	0	1
0	3	110	108
1	3	112	113
2	3	146	136
0	4	0	37
1	4	49	33
0	5	41	33
1	5	62	76
L = -14			
0	0	41	59
1	0	39	44
0	1	26	-2
1	1	0	-37
0	2	78	67

Table 4. *Interatomic distances and angles*

Distances			
Ni—N(1)	1·861 (4) Å	Ni—N(2)	1·862 (4) Å
N(1)–O(1)	1·350 (5)	N(2)–O(2)	1·344 (5)
N(1)–C(1)	1·295 (6)	N(2)–C(2)	1·301 (5)
C(1)–C(2)	1·462 (7)	C(4)–C(5)	1·512 (8)
C(1)–C(3)	1·499 (7)	C(2)–C(4)	1·506 (7)
	O(1)–O(2′)	2·454 (5)	
Angles			
Ni—N(1)–O(1)	123·9 (3)°	Ni—N(2)–O(2)	123·9 (3)°
Ni—N(1)–C(1)	116·6 (3)	Ni—N(2)–C(2)	115·9 (3)
N(1)–O(1)–O(2)′	97·2 (3)	N(2)–O(2)–O(1)′	97·5 (3)
O(1)–N(1)–C(1)	119·5 (4)	O(2)–N(2)–C(2)	120·2 (4)
N(1)–C(1)–C(2)	112·1 (4)	N(2)–C(2)–C(1)	112·8 (4)
N(1)–C(1)–C(3)	123·5 (5)	N(2)–C(2)–C(4)	123·2 (4)
C(3)–C(1)–C(2)	124·4 (5)	C(4)–C(2)–C(1)	123·9 (4)
C(2)–C(4)–C(5)	111·7 (5)	N(1)–Ni—N(2)	82·5 (2)

effects have been observed in the glyoxime complexes of Ni(II) (Calleri, Ferraris & Viterbo, 1967*a*; Murmann & Schlemper, 1967), Pd(II) (Calleri, Ferraris & Viterbo, 1967*b*) and Pt(II) (Ferraris & Viterbo, 1969) and in dimethylglyoxime (Hamilton, 1961).

With the exception of the ethyl group and O(1) the molecule is planar. The equation of the best mean plane through the planar portion of the molecule and the deviations of all atoms from the plane are given in Table 5. The nearest O(1) contact (3·37 Å) is with the C(2) atom of the molecule displaced in the **a** direction.

Table 5. *Distances of all atoms from the best mean plane through those atoms for which t values are given*

$$3{\cdot}284\,x-2{\cdot}753\,y+7{\cdot}952\,z=0{\cdot}0^*$$

	d	σ	t†
Ni	0·0000 Å	0·0001 Å	0·00
N(1)	0·0016	0·0041	0·40
N(2)	−0·0009	0·0037	0·23
O(1)	−0·0242	0·0035	
O(2)	0·0033	0·0036	0·92
C(1)	−0·0041	0·0051	0·81
C(2)	−0·0078	0·0050	1·55
C(3)	0·0071	0·0057	1·26
C(4)	−0·0757	0·0054	
C(5)	−1·5017	0·0072	

$\chi^2=5{\cdot}71$ for $\nu=4$

* The equation given is for the molecule at the origin and is given in fractional coordinates referred to the crystallographic axes.

† $t=d/\sigma$; $\chi^2=\sum t^2$.

An indication of the directions and r.m.s. amplitudes of vibration for the non-hydrogen atoms is provided by Fig. 2. A critical examination of the thermal parameters reveals nothing unusual or unexpected in the thermal motion of these atoms. The motion of the atoms in the chelate ring is more nearly isotropic than that of the atoms bound to the ring. The motion of the terminal carbon atom of the ethyl group reflects a significant contribution from a wagging of the entire group. The motion of the carbon and oxygen atoms which are bound to the chelate ring is considerably more restricted in a direction parallel to the bonds joining them to the ring. The motion of the oxygen atoms is suggestive of a non-linear hydrogen bond, and this may well be the case, as both of the N–O–O angles are considerably smaller than the 104·5° H–O–H angle in water.

Calculation of interatomic distances corrected for thermal motion assuming a riding model does not significantly change bond distances in the chelate ring, but does result in an increase of about 0·02 Å in the bonds external to the ring.

As an aid to visualization of the crystal packing, Fig. 3 provides a perspective view, along **a***, of a unit cell and those molecules which contribute to its contents. The molecules in adjacent layers are separated by a distance of 3·286 Å. The packing is such that the nickel atom of one molecule lies approximately above an oxygen atom in an adjacent molecule.

The results of this investigation and a study of nickel(II) dimethylglyoxime [$\mathrm{Ni(DMG)_2}$], which will soon be reported, lead us to believe that reports of OHO hydrogen bonds with O---O distances less than about 2·4 Å should be treated with suspicion. [A 2·42 Å O---O distance has been found in a neutron diffraction study of the related bis(2-amino-2-methyl-3-butanone oximato) nickel(II) chloride monohydrate by Schlemper, Hamilton & La Placa (1971).] The available structural information on OHO hydrogen bonds indicates that oxygen–oxygen repulsions make improbable any shorter O---O distances.

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