The density plotting program is slightly simpler than that for contours, and only requires storage of four rows at any one time. The value of *f* at one corner of a plotting element is taken as applying to the whole of that element. Density plots do not, in general, show the fine detail of contour plots, and the angularity of contours is no longer apparent. Their use is more for giving an immediate impression than for quantitative measurement.

Conclusion

The methods described could well be adapted to other small computers equipped with a similar display device. Experience has shown that the quality of the contours is quite adequate for resolving details of the order of one plotting unit – the examples shown were both from the same data, on a grid of 64 × 64 points. The time taken to plot one section is dependent on the plotting hardware and, in the case of density plotting, on the density required. The examples were each plotted in about four minutes, which compares well with other methods.

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The Crystal and Molecular Structure of Nickel-Glyoxime

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Nickel-glyoxime, $(H_2C_2N_2OOH)_2Ni$, crystallizes in the monoclinic system, prismatic class, with two molecules per unit cell and belongs to space group $P2_1/c$. Unit-cell parameters are: $a_0 = 4{\cdot}1961 \pm 0{\cdot}0009$, $b_0 = 7{\cdot}2005 \pm 0{\cdot}0014$, $c_0 = 12{\cdot}4039 \pm 0{\cdot}0021$ Å; $\beta = 91°4' \pm 1'$. The structural analysis of this complex, based on all the reflexions accessible with Cu $K\alpha$ radiation (final R value for 524 'observed' reflexions 3·9 %), shows that the Ni atom coordinates four N atoms in a plane, while the remainder of the molecule is planar only in first approximation. Only symmetry C_2 can be assigned to the Ni-glyoxime molecule; the existence of several intermolecular contacts between C and O atoms explains the departure from strict planarity. By a three-dimensional difference synthesis and from stereochemical considerations, it has also been possible to locate the hydrogen atoms satisfactorily. The intermolecular distance between two oxygen atoms bound by a hydrogen bond is $2{\cdot}453 \pm 0{\cdot}006$ Å, and the bond is likely to be of the symmetrical type. There is no appreciable contact between Ni and other atoms.

Continuing a program of studies on the crystal and molecular structure of glyoxime (Calleri, Ferraris & Viterbo, 1966) and its derivatives, the authors have carried out a structural study of the nickel-glyoxime complex and are now also investigating the structure of palladium-glyoxime.

Experimental

Preparation; optical and crystallographic data

The crystals of nickel-glyoxime, $Ni(H_2C_2N_2OOH)_2$, were obtained by recrystallization from nitrobenzene at 50 °C of the compound prepared by reaction between nickel(II) chloride and glyoxime in aqueous alcoholic solution, made slightly ammoniacal. The crystals so obtained are brick-red, of small dimensions and usually somewhat squat though always elongated in a preferential direction.

From Weissenberg photographs we deduced that nickel-glyoxime (NiG) crystallizes in the monoclinic system and, choosing the elongation direction as [100], we noticed that the systematically absent reflexions were: $h0l$ with l odd and $0k0$ with k odd, which unambiguously indicates that the compound belongs to the space group $P2_1/c$. The reciprocal unit-cell parameters, a^*, b^*, c^*, and β^* were refined by a least-squares procedure using 30 θ_{hkl} values, between 60° and 80°, measured with a single crystal on the diffractometer with Cu $K\alpha$ filtered radiation ($\lambda\alpha_1 = 1{\cdot}54050$ Å, $\lambda\alpha_2 = 1{\cdot}54434$ Å). The minimized function was:

$$d^*_{\text{meas}} - d^*_{\text{calc}} = \delta d^* = \sum_{i=1}^{4} \left(\frac{\partial d^*}{\partial x^*_i} dx^*_i \right), \qquad (1)$$

where x^*_i are the reciprocal-cell parameters. The following values, for the direct-cell parameters were obtained:

$$a_0=4{\cdot}1961\pm0{\cdot}0009\text{ Å};\quad b_0=7{\cdot}2005\pm0{\cdot}0014\text{ Å};$$
$$c_0=12{\cdot}4039\pm0{\cdot}0021\text{ Å};\quad \beta=91°4'\pm1'\,.$$

From measurements done with a two-circle goniometer we found the following forms: $a=\{100\}, b=\{010\}, c=\{001\}, d=\{011\}, e=\{112\}, f=\{212\}, g=\{11\bar{1}\}$. In most crystals the form $\{011\}$ predominates, seldom the form $\{001\}$. Fig. 1 illustrates the combination of all the forms found.

NiG crystals exhibit a cleavage parallel to $\{010\}$; on the cleavage face it was possible to measure an extinction angle of $\sim 20°$ with the elongation direction [100], while on face (011) this angle is $\simeq 37°$. Both (010) and (011) faces show a strong pleochroic effect; on these faces the crystals appear bright-red when observed in white light polarized in the direction forming the smaller angle with [100], while if the light vibrates in the other direction it is almost completely absorbed, even if the thickness of the crystal is very small. On face (001) there is practically no dichroism. The optic-axial plane is parallel to (010) and on the face (001) it is possible to observe the emergence of only one optic axis. In view of both the strong pleochroism and the deep colour of NiG crystals, it would appear rather wearisome to measure the refractive indices, and this was not attempted. Other physical data are: $V_c=374{\cdot}708$ Å^3; M.W. 232·834; $D_{\text{meas}}=2{\cdot}095$, $D_{\text{calc}}=2{\cdot}064$ g.cm^{-3}; Z=2; $F(000)=236$; linear absorption coefficient for Cu $K\alpha$ radiation: $\mu=36{\cdot}54$ cm^{-1}.

Intensity measurement

Intensities, on a relative scale, were measured by a General Electric manual three-circle diffractometer fitted with a proportional counter, krypton filled. The crystal used for the measurements ($0{\cdot}16\times0{\cdot}14\times0{\cdot}30$ mm) was mounted with its x axis parallel to the φ axis and integrated intensities were collected by the moving-crystal moving-counter technique with a scanning speed of 2° per minute. Background was measured for a $\frac{1}{2}°$ interval on both sides of each peak. It has been possible so to examine 833 reflexions, corresponding to 96% of those accessible with Cu $K\alpha$ radiation, of which about 200 had an intensity below the measurable minimum. Intensity values for independent reflexions have been deduced by arithmetic averaging of the measurements done twice for the points of half the reciprocal lattice.

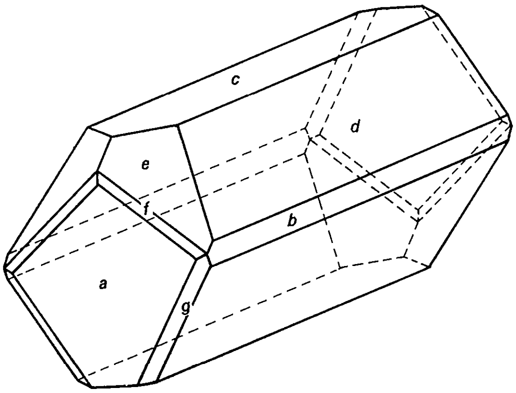

Fig. 1. Clinographic drawing of a nickel-glyoxime crystal showing all the forms observed.

Considering the small dimensions of our crystal, the absorption effect is, in our opinion, negligible, so that no absorption correction was used. Correction for the Lorentz-polarization effect was performed by standard formulae; the computation of atomic scattering factors was done by the expression of Forsyth & Wells (1959) taking the constants, for neutral atoms, from Moore (1963). In fact, some attempts to use corrections for the anomalous scattering of the nickel atom were not convincing; furthermore an experimental curve, drawn for that atom, agreed with the values of Moore with a $B=3{\cdot}5$ Å^2. Looking at the discrepancies between F_o and F_c we could infer also that the effect of secondary extinction was not appreciable.

Determination of the structure

Patterson and Fourier syntheses

In a unit cell of NiG there are two molecules and the two Ni atoms must be in special positions of symmetry $\bar{1}$. Since the section $b_0c_0\sin\beta$ has the largest area, it was reasonable to expect that the best resolved electron density projection was that along [100]. We therefore computed, along this direction, both a projection of the Patterson function and one of electron density with all positive F_{0kl}, including also the reflexions with $k+l$ odd to which Ni atoms do not contribute. The examination of these two projections permitted us to solve the structure, and with successive cycles of electron density projections and difference syntheses it was possible to reach $R=0{\cdot}121$ for $0kl$ reflexions, with a mean vibrational parameter $B=4$ Å^2.

The x coordinates were obtained from a three-dimensional Patterson synthesis and they were improved by difference projections along [100], reducing the R value for $h0l$ reflexions to 0·144. Despite this low value of R, the x coordinates were still rather inaccurate, owing to the overlappings which happen in the projection along [010], and consequently the values of bond lengths and angles were not acceptable. The molecule of NiG, however, showed clearly the typical configuration of similar complexes, *i.e.* with a nickel atom coordinating four nitrogen atoms in a plane (*cf.* Figs. 2–4).

Structure refinement

The results reached in successive stages of the refinement, by the least-squares method, are summarized in Table 1 with reference, for the numbering of atoms, to Fig. 2. The R value was reduced from 0·164 to 0·112 by a first cycle with isotropic vibrational parameters, using a full-matrix program (Sgarlata, 1965); using the same program with anisotropic vibrational parameters, we reached $R=0{\cdot}063$ and $R=0{\cdot}054$ after elimination of about 30 weak reflexions marked with an asterisk in Table 2. A third cycle did not give significant variations to parameters and also R remained unchanged. At this stage we tried to locate the hydrogen atoms by a three-dimensional difference synthesis, using the coordinates of $R=0{\cdot}112$; the peaks, where the hydrogen atoms bound to carbon atoms were to be expected, appeared rather diffuse so that we had to make use also of stereochemical considerations in locating them. Between the oxygen atoms O(1) and O(2) several ripples appeared, but it was impossible to use them for locating the hydrogen; considering the shortness of the distance between the above mentioned oxygen atoms ($2{\cdot}453 \pm 0{\cdot}006$ Å) we assumed that the hydrogen atom was midway and on the line joining the two oxygen atoms. In fact the assumption of a symmetrical hydrogen bond is in agreement with what can be deduced from the correlation diagram, between O---O and O–H distances, reported by Atoji & Rundle (1958) and from recent neutron diffraction studies (*cf. e.g.* Ellison & Levy, 1965). The introduction of the hydrogen atoms into the computation of structure factors, with an isotropic factor $B=3$ Å^2, reduced R to 0·048; the smallest improvement was actually effected by the hydrogen bound to the oxygen atoms. The full-matrix program employed for the first three least-squares cycles makes use of no weighting system, so that we completed the refinement with another program (Panattoni *et al.*, to be published), in which the system of normal equations is subdivided into partial systems of three and six equations, for coordinates and vibrational parameters respectively. We introduced the following weighting system:

$$W_{hkl}=\frac{1}{(3/|F_{\max}|)|F_o|^2+|F_o|+2|F_{\min}|} \quad \text{if } |F_o| \geq 2|F_{\min}| \quad (2)$$

$$W_{hkl}=a|F_o|^2 \quad \text{if} \quad |F_o|<2|F_{\min}|\,, \quad (3)$$

Table 1. *Bond distances after the refinement with isotropic B* ($R=0{\cdot}112$), *after the 'anisotropic' refinement without weighting system* ($R=0{\cdot}054$) *and final values* ($R=0{\cdot}039$)

	$R=0{\cdot}112$	$R=0{\cdot}054$	$R=0{\cdot}039$
C(1)–C(2)	1·46 Å	1·454 Å	1·435 ± 0·007 Å
C(1)–N(1)	1·29	1·305	1·303 ± 0·006
C(2)–N(2)	1·27	1·278	1·277 ± 0·007
N(1)–O(2)	1·36	1·347	1·343 ± 0·005
N(2)–O(3)	1·38	1·340	1·350 ± 0·005
O(1)–O(2)	2·42	2·438	2·453 ± 0·006
Ni —N(1)	1·87	1·857	1·868 ± 0·004
Ni —N(2)	1·89	1·882	1·880 ± 0·004
C(1)–H(1)	—	—	1·07
C(2)–H(2)	—	—	1·08
O(1)–H(3)	—	—	1·23
O(2)–H(3)	—	—	1·23

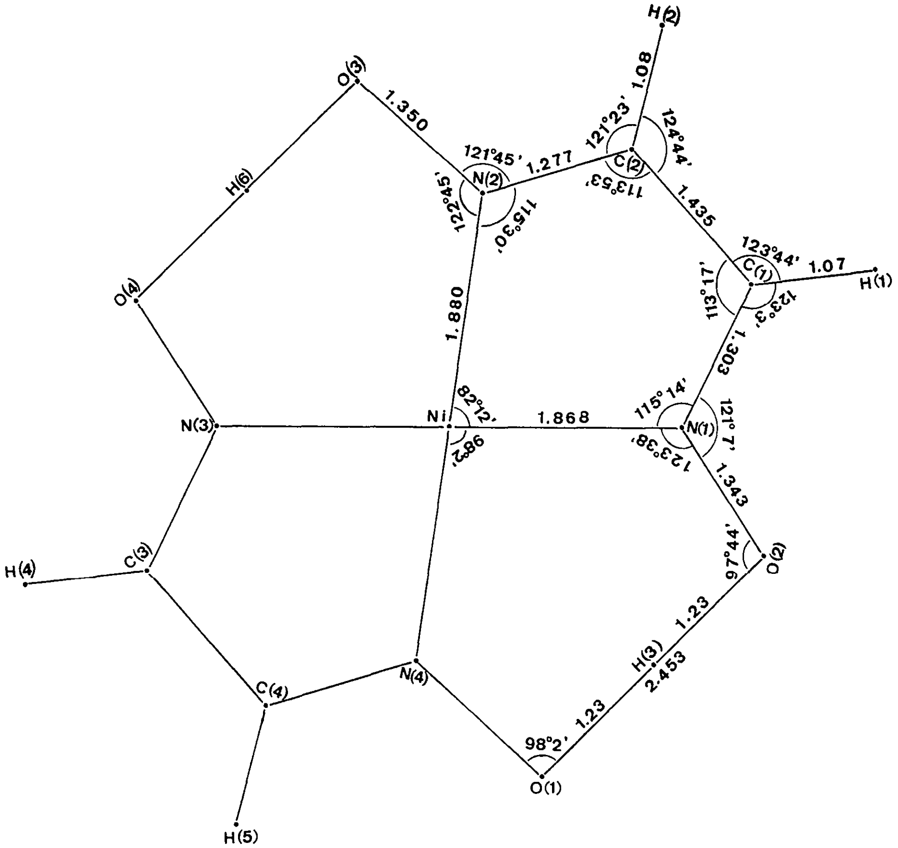

Fig. 2. Molecular bonds and angles.

where $|F_{\min}|=3{\cdot}3$ and $|F_{\max}|=80$; the constant a has been put equal to 0·00030 so that the two weighting functions coincide when $|F_o|=2|F_{\min}|$. After one cycle, followed by the elimination of a few very weak reflexions, we had $R=0{\cdot}041$; hydrogen atoms were included in the structure-factor calculations, though their parameters were not refined, with an isotropic vibrational parameter similar to that of the atoms to which they are bound. A second cycle reduced R to 0·039, but, since the variations of vibrational and positional parameters were now negligible, the refinement could be regarded as accomplished. In Table 2 the values of F_c computed with the use of the final parameters are compared with the observed structure factors, for all

Table 2. *Observed structure amplitudes and calculated structure factors*

(10 times the true values for the whole unit cell)

HKL	F_o	F_c
00L		
2	627	720
4*	122	154
6	420	427
8	201	210
10	240	239
12	187	188
14	122	117
01L		
1*	470	628
2	-223	-214
3*	55	100
4	200	183
5	563	552
6	132	122
7	392	385
8	-89	-86
9	221	215
10	-57	-56
11	132	129
13	34	31
15	79	74
02L		
0*	78	112
1*	-48	-57
2*	41	22
3	-80	-86
4	262	287
5*	59	48
6	330	340
7	23	16
8	154	161
9	-75	-72
10	163	160
13*	39	42
03L		
1	499	552
2	-128	-124
3*	150	190
4	-189	-177
5	221	241
6*	52	58
8	76	69
9	96	96
10	-44	-42
11	158	160
13	66	67
15	45	46
04L		
0	495	505
1*	-46	-30
2	251	272
3	-45	-38
4	299	319
5	41	42
6	314	319
7*	51	40
8	107	100
9	-62	-62
10	141	141
11	-50	-48
12	119	122
14	51	50
05L		
1	130	134
3	189	202
4	42	42
5	306	314
7	151	148
8	-68	-77
9	105	98
10	-58	-53
11	108	105
13*	37	31
06L		
0	105	104
2	107	105
3	-43	-48
4	137	134
5*	-56	-49
10	79	74
12	47	44
07L		
1	74	69
2*	37	32
3	65	64
4	-39	-41
5	83	84
08L		
0	84	81
1	33	35
2	55	49
3	35	34
4	71	65
6	88	85
09L		
1	61	62
3	42	38
10L		
0	536	534
2	839	888
-2	121	127
4*	82	119
-4	520	502
6	353	345
-6	416	414
8	430	417
-8	369	367
10	131	126
-10	126	126
12	100	93
-12	119	119
14*	53	46
-14	120	122
11L		
0	-304	-270
1	655	703
-1*	92	127
2	-754	-753
-2	-72	-67
3	577	582
-3	449	451
4	-300	-262
-4*	60	49
5	93	98
-5	322	340
6	85	72
-6	-53	-49
7	311	309
-7	297	305
9	195	195
-9	226	229
-10	142	146
11	103	101
12	-43	-44
-12	94	98
13	80	79
-13	104	104
14*	43	53
15	42	44
-15	73	75
12L		
0	196	221
1	207	186
-1	-200	-189
2	540	563
-2	465	492
-3	162	150
4	179	193
-4	391	410
5	-80	-68
-5	309	274
6	79	88
-6*	32	37
7*	-49	-41
8	192	195
-8	211	226
9	-62	-57
-9	-73	-74
10	137	140
-10	103	100
11	-50	-49
12	93	99
-12	34	27
14	44	42
12L (contd.)		
-14	100	103
13L		
0	214	206
1	342	349
2	245	226
-2	-113	-110
3	300	306
-3	384	406
4	49	46
5	147	168
-5	158	169
6	42	40
7	246	256
-7	161	171
8	93	96
-8	-113	-110
9	133	135
-9	218	221
-10	-94	-104
11	89	85
-11	83	83
12	-28	-26
13	70	64
-13	83	84
14*	41	49
14L		
0	165	169
1	-95	-94
-1	-91	-87
2	307	312
-2	190	211
3	-118	-106
-3	-120	-117
4	198	215
-4	290	300
-5	-82	-81
6	275	284
-6	192	195
7	108	107
-7	-110	-113
8	168	161
-8	213	216
9	64	63
-9*	-52	-46
-10	125	127
-11	37	33
12	78	79
-12	66	62
-14	44	39
15L		
1	167	173
-1	183	196
2	-84	-73
-2	-32	-25
3	178	186
-3	299	313
4	-54	-51
-4	105	106
5	136	133
-5	119	109
6	-49	-52
-6	50	43
7	134	132
-7	57	49
8	-64	-63
9	54	51
-9	112	112
11	74	68
-11*	63	54
-13	45	41
16L		
0	79	75
2	108	103
-2	203	208
3	26	24
4	105	100
-4	138	137
-5	53	48
6	84	80
7	-48	-49
8	65	65
-8	65	59
10	59	55
16L (contd.)		
-10	74	74
17L		
1	56	52
-1*	45	31
3	97	94
-3	96	92
-4	-73	-81
5	99	93
-5	64	64
-6	-40	-43
7	78	78
-7	67	68
8	29	28
-9	76	77
18L		
0	68	62
2	69	66
-2	60	60
-3	-35	-35
4*	38	34
-4	74	72
6	56	52
-6	56	55
19L		
1	47	49
-1	49	49
20L		
0	238	236
2	100	104
-2	382	369
4	101	111
-4	359	355
-6	402	396
8	188	187
-8*	-38	-43
10	173	174
-10	-44	-45
12	51	48
-12	151	152
-14	48	49
21L		
0	163	149
1	259	258
-1	336	338
2*	-54	-43
-2*	148	115
3	516	486
-3*	115	143
4	-96	-85
-4	251	220
5	292	284
-5	241	249
7	49	54
-7	292	294
8	-61	-62
9	160	152
-9	68	64
10	-64	-60
-10	71	73
11	95	99
-11	144	144
13	49	47
-13	91	102
-14*	-18	-23
22L		
0	282	292
1	109	103
-1	-41	-39
2	357	353
-2	353	357
3	-62	-60
-3	128	121
4	605	594
-4	111	120
5	-109	-101
6	208	208
-6	331	327
-7	-87	-81
8	121	113
-8	265	271
9	42	38
22L (contd.)		
10	160	159
-10	138	138
12	73	74
-12	134	129
14	49	51
23L		
0	33	35
1	124	132
-1	419	435
2*	86	74
3	150	145
-3	331	334
-4	-103	-101
5	181	184
-5	260	261
-6	-148	-143
7	146	150
-7	230	228
8	92	96
-8	-66	-67
9	168	181
10	44	45
11	92	92
-11	79	75
13	46	43
-13	74	71
24L		
0	229	237
1	96	96
-1	-63	-62
2	106	108
-2	188	197
4	114	113
-4	54	57
6	90	88
-6	145	149
-7	-39	-41
8	88	84
-8	70	67
-10	60	53
12	28	25
-12	79	79
25L		
0	83	83
1	104	101
-1	179	183
-2	33	27
3	138	134
-3	36	35
4	-50	-47
-4	105	101
5	148	148
6	-22	-26
7	78	74
-7	118	121
8	-41	-42
9	43	38
-9	98	96
-11	74	73
26L		
0	122	117
-2	204	208
3*	-29	-24
4	113	113
-4	94	88
-5*	-42	-48
6	112	112
-6	97	97
8	86	88
-8	101	98
10	65	66
-10	48	47
27L		
1	77	75
-1	127	134
-2	-31	-34
3	66	63
-3	87	84
4	37	33
-4	-55	-64
5	73	68
-5	61	60
28L		
0*	65	57
2*	53	47
-2*	38	31
4*	38	32
30L		
0	109	116
2	242	234
4	166	157
-4	298	291
6	173	164
-6	109	110
8	57	60
10*	40	30
-10	156	159
12	42	36
-12	66	70
31L		
1	246	242
-1	134	137
2	74	70
-2	128	126
3	173	171
-3	230	229
4	72	71
5	203	193
-5	276	270
6	94	93
-6	-147	-152
7	105	99
-7	46	44
-8	-69	-74
9	51	49
-9	125	125
11	93	95
-11	115	112
-13*	35	28
32L		
0	278	269
1	71	71
-1*	-34	-27
2	173	171
-2	252	255
-3	-61	-59
4	196	191
-4	315	312
5	-79	-82
-5	-78	-74
6	198	200
-6	173	169
8*	61	73
-8	113	110
-9	41	41
10	109	111
-10	125	122
12	86	100
-12	49	42
33L		
0*	-43	-31
1	219	225
-1	151	151
2	78	76
-2	40	33
3	124	124
-3	145	146
-4	-32	-35
5	157	160
-5	185	185
6	-104	-110
-6	29	30
7	138	143
-7*	74	64
9	68	64
-9	107	103
11	55	49
-11	78	76
12*	-46	-21
34L		
0	152	158
-1	110	109
2	162	163
3	55	54
-3	60	64
34L (contd.)		
-4	85	81
-5	-32	-32
6	80	77
-6	83	80
-7	-46	-50
8	60	60
-8	63	60
-9*	-34	-30
-10	93	96
35L		
0	47	42
1	127	124
-1	103	99
-2*	-29	-24
-3	76	77
-4	-51	-49
5*	52	40
-6	-48	-50
7	76	76
-7	76	70
9	42	47
-9	66	63
36L		
0	131	129
1	30	32
-1	-37	-39
2	67	62
-2	104	103
-3	-46	-50
4	51	50
-4	88	85
6	86	86
-6	76	71
-8	73	69
37L		
1	104	103
-1	62	60
3	58	58
5	43	42
-5	37	34
40L		
2	122	113
-2	195	179
4	154	148
-4	191	192
6	129	127
-6	85	84
8	107	111
-8	124	123
10*	32	28
41L		
1	95	91
-1	160	162
2	69	68
-2*	-33	-26
3	131	131
-3	204	204
-4	-52	-49
5	94	89
-6*	-42	-52
7	78	74
-7	72	71
9	46	44
-9	89	91
42L		
0	114	118
2	100	99
-2	174	183
4	102	103
-4*	60	43
-5	-36	-34
6	69	66
8	34	32
-8	108	110
-10	40	42
43L		
0	-95	-104
1	48	44
-1*	53	42
-2	29	26
43L (contd.)		
3	105	107
-3	104	105
5	78	84
-5	80	80
6	-34	-37
7	76	83
-7*	107	83
8*	-37	-45
-9	65	61
44L		
0	75	66
2	118	120
-2	95	95
4	53	48
-4	99	103
-6	63	67
-8	57	53
45L		
0	40	43
1	90	101
-1	80	83
-2	-37	-39
3	81	86
-3	69	68
-4	-32	-31
-5*	42	34
-6	-31	-31
46L		
0*	36	30
2	55	53
-2	27	26
50L		
0	117	120
2	83	83
-2	95	101
4*	80	88
-4	59	59
-6	66	65
51L		
1	63	64
-1	105	117
3	33	29
-3	47	46
5*	55	65
-5	52	53
52L		
0*	64	74
1*	-36	-42
-2	47	49
-3*	-27	-35
4	27	24
-4	18	15
53L		
1	46	53
-1	57	60
-2*	-32	-42
-3	31	29

592 observed reflexions; the final R value for all these reflexions is 0·053 (R=0·039 for 524 reflexions used in the latter stages of refinement). 'Unobserved' reflexions are not reported; F_c values corresponding to these reflexions have been computed at several stages, but practically all the values were below the observable minimum.

Final parameters

Final fractional coordinates and vibrational anisotropic parameters are listed in Table 3; the latter are the result of the refinement of B_{ij} coefficients of the function:

$$\exp\left(-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right). \tag{4}$$

The significant figures of standard deviations are reported below the values of the corresponding parameters. Standard deviations, particularly of bond lengths and angles, are satisfactorily small. The presence of a heavy atom causes the standard deviation for the light atoms to be greater than that which could be expected from the low R value.

In order to present the anisotropy of thermal vibration it is useful to refer the vibrational ellipsoids to their own principal axes, *i.e.* in the form:

Table 3. *Final fractional coordinates and vibrational parameters with (below) the significant figures of the standard deviations*

	x/a_0	y/b_0	z/c_0	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0·1348	0·3362	0·0848	3·52	3·63	3·90	−0·45	−0·51	0·01
	12	8	4	21	23	23	20	18	21
C(2)	−0·0844	0·2513	0·1573	3·02	4·73	3·47	0·31	0·19	−0·19
	11	9	4	22	25	23	19	18	20
N(1)	0·1973	0·2326	0·0017	2·98	3·61	3·30	−0·88	−0·28	1·03
	9	6	3	17	19	18	15	14	16
N(2)	−0·1736	0·0887	0·1288	2·31	3·79	2·77	0·08	0·38	0·65
	9	6	3	14	18	16	15	12	15
O(1)	0·3819	0·0106	−0·1872	3·65	5·62	3·70	−0·68	1·69	0·60
	8	6	2	15	20	15	19	12	18
O(2)	0·3959	0·2911	−0·0749	4·71	5·53	3·96	−2·80	0·98	1·00
	9	6	3	19	23	17	17	15	16
Ni	0	0	0	3·14	4·37	3·77	−0·42	0·27	0·61
				3	4	4	5	3	5
H(1)	0·228	0·474	0·095	3·50	3·50	3·50	—	—	—
H(2)	−0·174	0·316	0·229	3·50	3·50	3·50	—	—	—
H(3)	0·389	0·151	−0·131	4·50	4·50	4·50	—	—	—

Table 4. *Vibrational parameters of the principal axes of vibration with the values of the angles φ which these axes make with the normal to the molecular plane*

	i	q_i (Å^2)	r.m.s.d. (Å)	g_{i1}	g_{i2}	g_{i3}	φ
C(1)	1	0·959	0·220	−0·386	0·381	−0·411	34°30′
	2	1·217	0·248	−0·476	0·192	0·844	90
	3	0·740	0·193	0·790	0·522	0·345	55 30
C(2)	1	0·987	0·224	0·185	0·192	0·969	55 45
	2	1·208	0·247	0·153	0·963	−0·216	68
	3	0·735	0·193	−0·971	0·188	0·120	42 30
N(1)	1	0·741	0·194	−0·671	0·283	−0·704	13
	2	1·301	0·257	−0·376	0·666	0·633	77 30
	3	0·559	0·168	0·639	0·690	−0·322	87 30
N(2)	1	0·704	0·189	−0·411	0·551	−0·738	25 30
	2	1·067	0·232	0·129	0·824	0·555	86 30
	3	0·541	0·165	0·902	0·133	−0·383	64 30
O(1)	1	1·402	0·266	−0·680	0·160	−0·735	18 30
	2	1·470	0·273	−0·076	0·955	0·284	73 30
	3	0·483	0·156	0·729	0·249	−0·616	82 30
O(2)	1	1·294	0·256	0·394	0·225	0·902	47 30
	2	1·999	0·318	−0·635	0·768	0·068	42
	3	0·388	0·140	0·665	0·600	−0·425	87
Ni	1	0·978	0·222	−0·480	0·550	−0·697	21
	2	1·256	0·252	−0·095	0·742	0·660	89
	3	0·721	0·191	0·872	0·383	−0·279	69

$$\sum_{i=1}^{3} q_i\Big(\sum_{j=1}^{3} g_{ij}h_ja_j^*\Big)^2 , \qquad (5)$$

where q_i are the three principal vibrational semi-axes (in Å^2) and g_{ij} are their direction cosines with respect to the reciprocal unit-cell axes. The values of q_i and g_{ij} for NiG, together with the root-mean-square displacements (r.m.s.d.) along the three principal directions of vibration, are listed in Table 4. Table 4 also gives the values of the angle φ which the principal axes of vibration make with the normal to the molecular plane [*cf.* equation (6)]. The final bond lengths and bond angles are given in Tables 1 and 5 respectively and also in the Fig. 2.

Table 5. *Molecular bond angles*

C(2)–C(1)–N(1)	113°	7′	±30′
C(1)–C(2)–N(2)	113	53	±28
C(1)–N(1)–O(2)	121	7	±26
C(1)–N(1)–Ni	115	14	±20
N(2)–Ni —N(1)	82	12	±10
O(3)–N(2)–Ni	122	45	±19
C(2)–N(2)–O(3)	121	45	±24
C(2)–N(2)–Ni	115	30	±20
O(2)–N(1)–Ni	123	38	±19
C(2)–C(1)–H(1)	123	44	
N(1)–C(1)–H(1)	123	3	
N(2)–C(2)–H(2)	121	23	
C(1)–C(2)–H(2)	124	44	
N(4)–O(1)–H(3)	98	2	
N(1)–O(2)–H(3)	97	44	

Description and discussion of the structure

The best mean plane for the NiG molecule referred to the crystallographic axes (Schomacher, Waser, Marsh & Bergman, 1959), has the following equation in fractional coordinates:

$$3{\cdot}1945x-2{\cdot}7930y+6{\cdot}2670z=0 , \qquad (6)$$

i.e. the molecule at the origin is roughly parallel to $(1\bar{1}2)$. Table 6 shows how, despite the fact that the distances of atoms from this plane are all under 0·02 Å, application of the t test (Cruickshank & Robertson, 1953) leads to the conclusion that all the atoms except N(1) and N(2) are significantly out of the plane (see the values of $t_0=d/\sigma$ in Table 6). Furthermore the quantity $\chi^2=\Sigma\,(d/\sigma)^2=84{\cdot}27$, indicates that the mol-

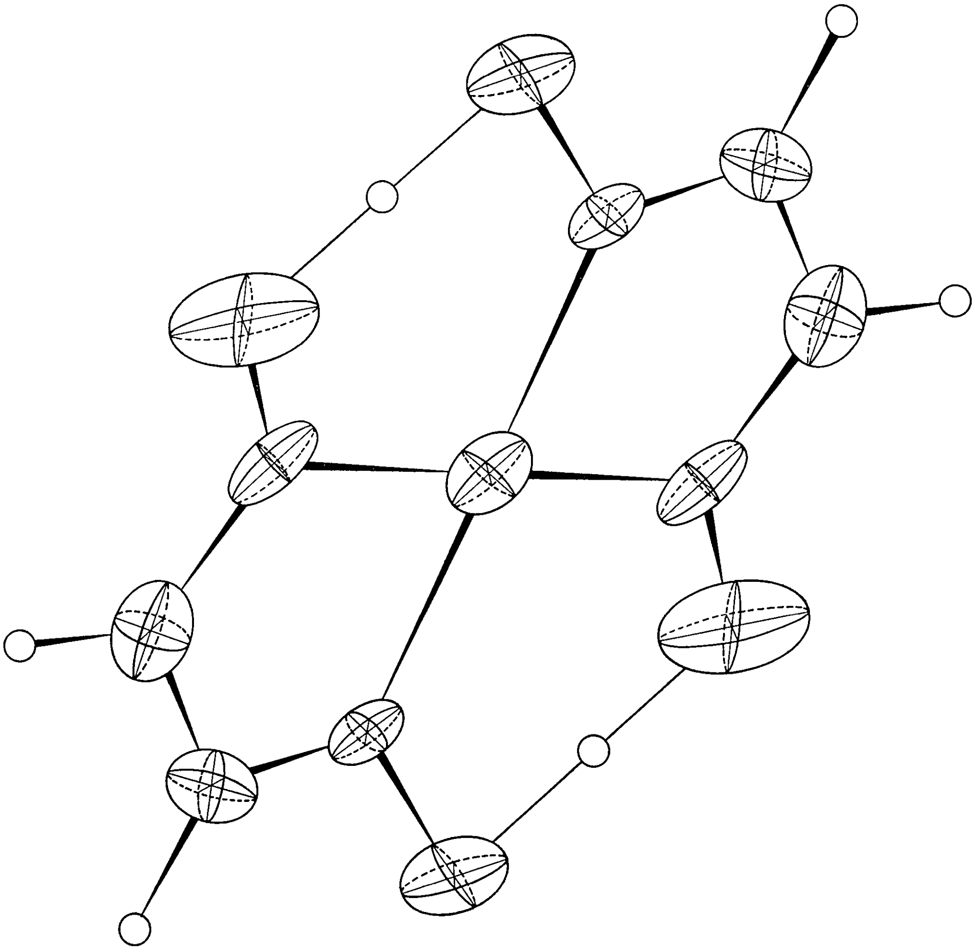

Fig. 3. Clinographic projection, along the x axis, of the molecule at the origin. The ellipsoids are not drawn in perspective and in scale, only their axes are.

ecule is significantly non-planar; while the coordination group of Ni with four nitrogen atoms is significantly planar, the remaining atoms, involved in intermolecular contacts as explained below, are probably out of plane (6).

Apart from the non-planarity of the molecule discussed above, considering that the hydrogen bond O(1)–H(3)–O(2) is most likely to be symmetrical, one could expect the NiG molecule to have symmetry D_{2h}, but that is not so. Looking at Table 1 it is easy to see that the bonds which should be equal in length if the symmetry were D_{2h} are actually not equal. Statistical tests show that the N–O bonds are not significantly different, while the difference between the Ni–N bonds is possibly and that between C=N bonds is highly significant. We must conclude that the symmetry of the NiG molecule is probably only C_2 and the loss of ideal symmetry is most probably to be ascribed to intermolecular contacts (see below).

Bond lengths C–C and C=N are comparable to those we found for glyoxime; also in NiG there is an important degree of conjugation between C=N bonds, since the C–C bond has about 20% of double-bond character. N–O bonds in NiG are appreciably

Table 6. *Distances (d) of atoms from the mean plane* (6), *with their standard deviations*

	d	σ	$\|d/\sigma\|$
C(1)	0·0230 Å	0·0051	4·51
C(2)	0·0143	0·0050	2·86
N(1)	−0·0087	0·0038	2·29
N(2)	0·0049	0·0038	1·29
O(1)	0·0172	0·0033	5·21
O(2)	−0·0177	0·0038	4·66
Ni	0·0000	—	—

$\chi^2 = 84{\cdot}27$

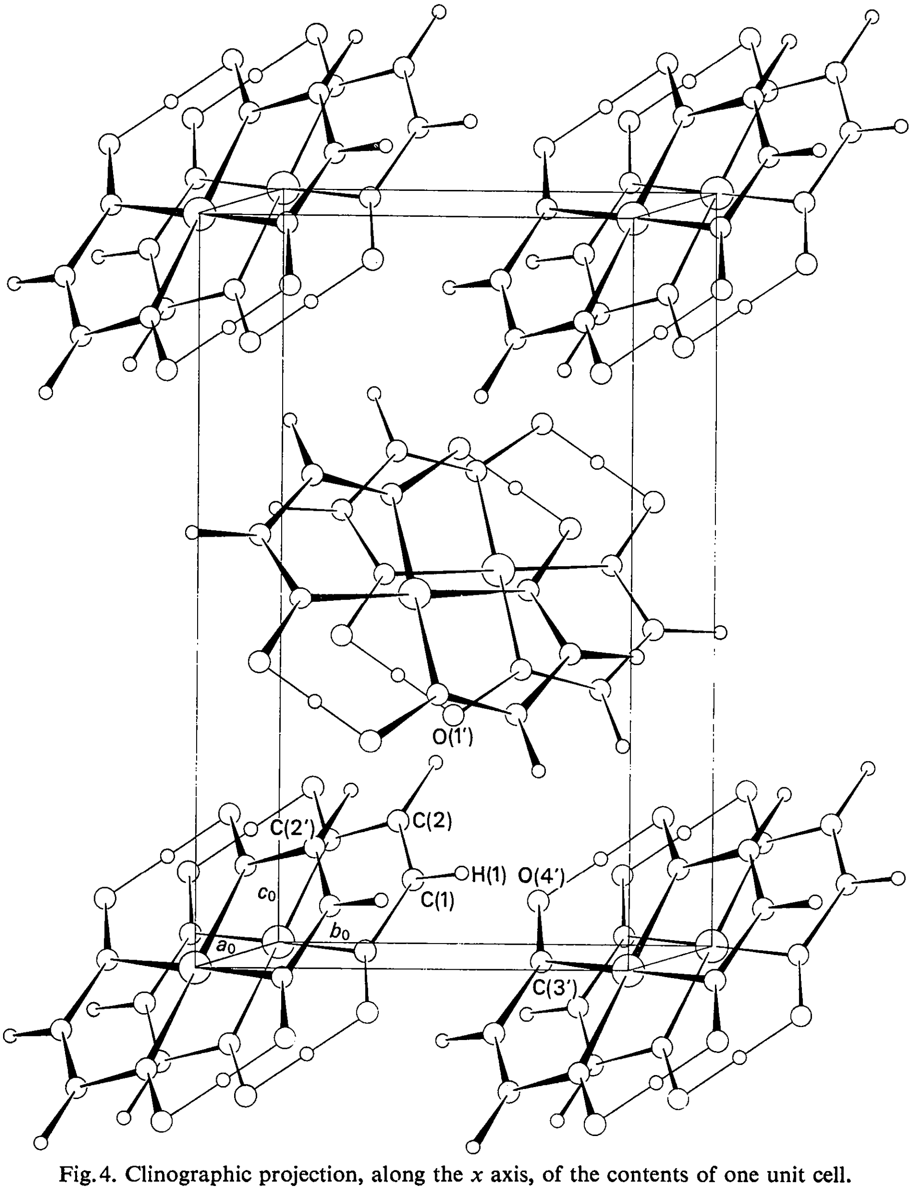

Fig. 4. Clinographic projection, along the x axis, of the contents of one unit cell.

shorter than in glyoxime, but in the former compound oxygen atoms are partially ionized and consequently they cause a mesomeric effect on N–O bonds, which explains this shortening. An analogous correspondence does not seem to be verified between the similar compound dimethylglyoxime and its complexes with transition metals; however it is to be remarked that most of the investigations carried out on these complexes were based on partial three-dimensional data.

Fig. 3 shows the clinographic projection, along the x axis, of the molecule at the origin; the vibrational ellipsoids are represented on an arbitrary scale, although the lengths q_i of semi-axes (*cf.* Table 4) are on the same scale. As can be seen, the anisotropy of vibration of the atoms is considerable. From the values of the angle φ (Table 4) between the normal to the plane (6) and the axes of the ellipsoids, it can be seen that one of the principal directions of vibration is practically always in the molecular plane. The direction of greatest vibration for C and N atoms is sensibly parallel to the C=N bond direction, as can be seen in Fig. 3 and as can also be calculated. In fact, the angles between the directions of greatest vibration of C(1) and N(1) atoms and the direction of the C(1)=N(1) bond are respectively ~26° and ~13°; similarly for C(2), N(2) and the C(2)=N(2) bond the above mentioned angles are ~30° and ~20°. Vibrational ellipsoids for O(1) and O(2) atoms are different from each other, and to O(1) a quasi-revolution ellipsoid has to be allocated, while the ellipsoid belonging to O(2) is strongly anisotropic. One can also recognize, however, in the direction of the O(1)–O(2) bond, a vibrational component which is strong and of the same order of magnitude for both atoms and thus seems to indicate that O(1) and O(2) are equally concerned in the formation of the hydrogen bond. Finally, it is to be noted that the vibrational ellipsoid associated with the Ni atom is so orientated as to have equal components along its bond directions.

Table 7. *Principal intermolecular distances*

C(1)–O(1′)	3·19 Å
C(1)–C(2′)	3·44
C(1)–C(3′)	3·34
C(1)–O(4′)	3·33
C(2)–O(1′)	3·22
H(1)–O(4′)	2·34

In Fig. 4 the content of one unit-cell is illustrated in clinographic projection along the x axis. Some intermolecular contacts between the atoms of the asymmetric unit and surrounding molecules occur and the shortest intermolecular distances are listed in Table 7 with reference to Fig. 4. Such contacts are remarkable, especially those occurring between O(1′) and C(1), C(2); they can very well justify the loss of ideal symmetry D_{2h} by the molecnle. The distances between C(1) and O(4′) and between H(1) and O(4′) seem also to suggest the existence of a weak interaction of type C–H---O; such a contact could explain the different behaviour of oxygen with regard to thermal vibration. In conclusion, all the atoms, except those of the coordination group around Ni, take part in intermolecular contacts and this fact explains the departure from strict planarity of NiG molecules. The atoms approaching Ni at the origin from surrounding molecules are oxygen atoms O(3) and O(4) of the molecule with a translation of a_0 [Ni–O(3), 3·45; Ni–O(4), 3·40 Å] and oxygen atoms O(1) and O(2) of the molecule with a translation of $-a_0$ [Ni–O(1), 3·45; Ni–O(2), 3·40 Å). According to the van der Waals radii stated in the literature, these do not seem to be genuine contacts.

The computations were done by Olivetti ELEA 6001 computers; we are very indebted to Prof. F. Sgarlata of Rome for having computed for us the three-dimensional Patterson and difference syntheses by his own programs.

Riassunto. La Ni-gliossima, $(H_2C_2N_2OOH)_2Ni$, cristallizza nel sistema monoclino, classe monoclino prismatica con due molecole per cella elementare ed appartiene al gruppo spaziale $P2_1/c$. Le costanti reticolari sono:

$$a_0 = 4{,}1961 \pm 0{,}0009;\ b_0 = 7{,}2005 \pm 0{,}0014\ \text{Å};$$
$$c_0 = 12{,}4039 \pm 0{,}0021\ \text{Å};\ \beta = 91°4' \pm 1'\ .$$

Lo studio strutturale di questo complesso, basato su tutti i riflessi misurabili con la radiazione Cu $K\alpha$ (R finale per 524 riflessi 'osservati' è risultato 3,9%), ha permesso di vedere che il nichelio coordina planarmente quattro atomi di azoto mentre il resto della molecola è planare solo in prima approssimazione. Alla molecola della Ni-gliossima viene assegnata la simmetria C_2; l'esistenza di diversi contatti intermolecolari tra atomi di carbonio e di ossigeno spiega perché le molecole non sono veramente piane. Per mezzo di una sintesi differenza tridimensionale, e con l'aiuto di considerazioni stereochimiche, è stato possibile collocare anche gli atomi di idrogeno. La distanza tra i due atomi di ossigeno di una stessa molecola, collegati da un legame idrogeno, risulta 2,453 ± 0,006 Å; questo legame idrogeno, è, con ogni verosimiglianza, del tipo simmetrico. Gli atomi di nichelio non sono interessati in alcun contatto intermolecolare.

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