

Ambidentate Character of Oxime Groups in Metal Complexes. The Crystal Structure of (4-Methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II)

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The crystal structure of (4-methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II) has been determined by Patterson methods from 2582 independent reflexions, measured with Cu $K\alpha$ radiation on an automatic diffractometer. The structure was refined by least-squares methods to $R=2.9\%$. The monoclinic cell of dimensions $a=8.468$, $b=19.953$, $c=8.419$ Å, $\beta=107.66^\circ$ has 4 molecules per unit cell and space group $P2_1/c$. The analysis reveals that the former ligand is chelated to the nickel atom *via* its oximino nitrogen atom, and the latter ligand *via* its oximino oxygen atom in the essentially planar molecule.

Introduction

Oximes have found numerous applications in the sequestration of particular metal ions and the relationship between geometrical isomerism and chelating ability for oximes of vicinal diketones has been known for some time (Martell & Calvin, 1952). It has been generally accepted that the most stable metal complexes are formed when the chelate rings involve oximino-nitrogen-metal bonding, on the basis of the known geometrical configuration of the ligand molecule. However, two complexes (I) and (II) (Fig. 1) exhibiting ambidentate character of the oxime ligands have been described (Lacey, Macdonald, Shannon & Collin, 1970; Lacey, Macdonald, McConnell & Shannon, 1971) and X-ray crystallographic evidence was adduced in support of structure (II).

Because of the novel features involved in the two modes of attachment proposed for the ligands of (I), it was felt that a crystal structure determination would

provide confirmation of the results of p.m.r. and infrared spectroscopic studies (Lacey *et al.*, 1970). For a number of reasons which will be given later, crystals of (I) were unsuitable for X-ray investigation and the related compound (II) was synthesized. Crystals of this compound were satisfactory but the data used in the preliminary structure reported (Lacey *et al.*, 1971), although adequate to confirm the configuration, contained errors which limited the accuracy of final refinement. The reasons for these errors will also be described later. It was therefore decided to redetermine the intensity data and to carry out another refinement. The main features already reported were substantiated but the overall residual $R(=\sum|\Delta F|/\sum F_o)$ improved from 0.083 to 0.029, with marked reductions in standard deviations for all parameters.

It was believed that (II) was the first example reported of a metal chelate complex in which an oxime ligand has been shown by X-ray diffraction to involve chelation to the central metal atom *via* oximino-oxygen-metal bonding rather than oximino-nitrogen-metal bonding. It is now known that similar bonding was demonstrated almost simultaneously (Biagini Cingi, Chiesi Villa, Gaetani Manfredotti, Guastini & Nardelli, 1972) in the complex (3-hydroxyimino-4,9-dimethyl-5,8-diazadodeca-4,9-diene-2,11-dionato)copper (II).

Experimental

Bis-(4-iminopentane-2,3-dione 3-oximato)nickel(II), compound (I)

The red complex was obtained by the methods previously indicated (Lacey *et al.*, 1970).

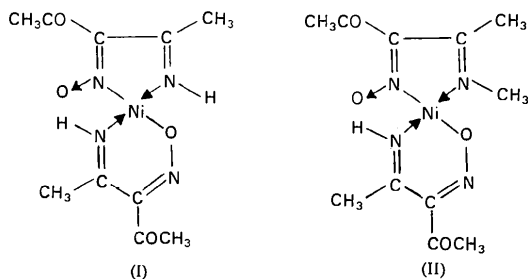


Fig. 1. I: *Bis*-(4-iminopentane-2,3-dione 3-oximato)nickel(II). II: (4-Methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II).

(4-Methyliminopentane-2,3-dione 3-oximato) (4-imino-pentane-2,3-dione 3-oximato)nickel(II), compound (II)

The orange-red complex was prepared as described in the preliminary communication (Lacey *et al.*, 1971). Suitable crystals for X-ray analysis were obtained by slow crystallization at room temperature from a chloroform-petroleum spirit mixture. The molecular ion composition is $C_{11}H_{16}N_4NiO_4$ by high-resolution mass spectroscopy. Found C: 40.5; H: 4.91; N: 17.4. $C_{11}H_{16}N_4NiO_4$ requires C: 40.4; H: 4.93; N: 17.1.

P.m.r. spectra were obtained on a Varian A60 spectrometer and mass spectra (70 eV) on a GEC-AEI MS902 spectrometer using the direct-insertion probe. Infrared spectra were obtained on a Perkin-Elmer 521 spectrometer, using CsBr disks.

X-ray intensity data were collected on a Siemens four-circle, single-crystal diffractometer, using Ni-filtered Cu $K\alpha$ radiation and a θ - 2θ scan. Each reflexion was scanned in steps of 0.1° , over a range which varied from 1° at low angles to 2.5° at 70. Counting rates exceeding the linearity range of the counter were reduced by the automatic insertion of calibrated absorbers. The time spent at each scanning step was automatically controlled to obtain approximately the same total count for each reflexion and thus approximately the same standard deviation. To prevent excessive counting for weak reflexions, an upper limit of 0.6 s was set for each step. Background was counted at each end of the scan range and averaged. After every 15 reflexions, a zero-check of all angular scales was made, followed by the measurement of a chosen 'standard reflexion', to check for any instrumental drift or deterioration of the crystal. No significant changes occurred.

The scaled intensities were then corrected for Lorentz and polarization factors and for absorption (Coppens, Leiserowitz & Rabinovich, 1965). 2582 independent reflexions were measured, of which 268 were classed as unobserved. An unobserved reflexion was defined as one whose net count was less than 3σ where $\sigma = (\text{total count for this reflexion})^{1/2}$. Such reflexions were given intensity values of 3σ for purposes of refinement.

As mentioned earlier, a solution which refined to $R=0.083$ had been obtained with another set of data. At that time, some trouble was being experienced with the mounting of crystals, and the crystal in this case had been observed to have moved on two occasions, necessitating redetermination of the matrix from which the angular settings were generated. This was obviously the reason for the poor refinement and the intensity data were measured again. The structure refined quickly using the new data, commencing with the parameters from the first refinement.

The method of crystal mounting now used in this Laboratory is perhaps worthy of description. The mount has no angular adjustment, but can be moved laterally for centring by elastically bending a metal rod to which the crystal fibre is attached. This is achieved by set-screws through a cylinder, coaxial

with the rod, and the pressure is communicated through a ball-race which prevents torsional creep. Initially, crystals were mounted in any orientation on a glass fibre, using Araldite as an adhesive. Small movements of the crystal, almost entirely around the ϕ axis, were traced to residual strain in the glass fibre. Quartz fibres were more satisfactory in this regard, but occasional movements were observed, and this was attributed to slow contraction of the Araldite. Finally, complete stability was obtained using quartz tubes and a minimum of Araldite, so that the crystal was supported at 2 or more points around the circumference of the end of the tube.

Examination of complex (I)

Despite repeated attempts to grow suitable crystals of compound (I) from many solvents by many techniques, the habit was invariably long prismatic needles of cross-section less than 0.1 mm. Sometimes, long flat laths were seen, but these appeared to be rows of cohering tetragonal prisms. However, it is believed that data could have been obtained for a reasonably accurate structure determination: sets of Weissenberg photographs were produced with reflexions out to the Cu $K\alpha$ limit. The space group was $I4_1$, with $a=14.3$ and $c=6.1$ Å. The principal reason for not continuing with the structure was the evidence of disorder in the crystalline arrangement. In one region of reciprocal space, very small sharp spots surrounded by broad diffuse areas appeared at positions corresponding to half indices for both h and k , and were present at all levels about the c axis.

Interesting as this structure appeared, it was decided that its solution would still leave doubt as to the true nature of the ligand-metal bonding. Instead of a 5:6 chelate ring structure, one may have been able to postulate a partially ordered arrangement of 5:5 and 6:6 chelate ring systems. The closely related complex (II), on the other hand, crystallized readily in a suitable size for X-ray analysis and showed no evidence of disorder.

Crystal data for the second intensity data set for complex (II)

Condensed formula $C_{11}H_{16}N_4NiO_4$, F.W. 326.86 ($^{12}C=12.0000$). Red, well-formed long prisms.

Crystal used measured approximately $0.5 \times 0.25 \times 0.2$ mm.

Density, measured by flotation $D_m=1.6$ cm $^{-3}$; calculated for $Z=4$, $D_x=1.602$ g cm $^{-3}$.

Radiation used: Ni-filtered Cu $K\alpha$.

$\lambda(\text{Cu } K\alpha)=1.5418$ Å.

Linear absorption coefficient for Cu $K\alpha$,

$\mu=24.04$ cm $^{-1}$.

Cell parameters at 20°C for monoclinic cell from least-squares calculation using high-angle diffractometer measurements:

$a=8.468$ (4), $b=19.953$ (10), $c=8.419$ (4) Å, $\beta=107.66$ (5) $^\circ$;

Cell volume 1355.5 Å 3 .

Systematic absences $h0l$, $l=2n+1$; $0k0$, $k=2n+1$; thus determining the space group uniquely as $P2_1/c$.

Results and discussion

The structure of (II) was solved by Patterson methods, an unsharpened Patterson map revealing the Ni atom and most of the N and O atoms. A cycle of least squares followed by a difference synthesis revealed all non-hydrogen atoms. Refinement was by the method of least squares, using *ORFLS* (Busing, Martin & Levy, 1962) in which the quantity $\sum w(|F_o| - |F_c|)^2$ is minimized. The weights w were taken as $1/\sigma^2$ where the e.s.d. σ was determined from counting statistics. Using isotropic temperature factors, the agreement residual $R = \sum(|F_o| - |F_c|) / \sum |F_o|$ fell to 0.15 after two cycles.

Anisotropic temperature factors reduced R to 0.105, at which stage hydrogen positions were sought from a difference synthesis following a refinement cycle using only high-angle data ($\sin \theta/\lambda > 0.3$). The hydrogen atoms were located and included in the refinement but

it was at this stage that inconsistencies in the data were becoming obvious, and the refinement terminated at $R=0.083$.

Using the new set of data, an isotropic extinction parameter was included in the refinement based on the method of Zachariassen (1967). Anomalous dispersion was also allowed for by the use of two sets of scattering factors for both Ni and O, one representing f and $\Delta f'$ and the other $\Delta f''$, based upon the figures of Cromer (1965). Two cycles were sufficient to reduce R to 0.029, allowing positional parameters for the H atoms to vary, but keeping their temperature factors equal to those of the atom to which they are attached. The shifts at this time were less than the appropriate e.s.d. and further refinement was of little significance. The final positional and thermal parameters are given in Table 1 where the figures in parentheses are the e.s.d.'s. Table 2 shows the observed and calculated structure factors ($10 \times$ absolute scale).

Fig. 2 is a stereoscopic pair of projections of the molecule, prepared by the program *ORTEP* (Johnson,

Table 1. *Final positional ($\times 10^4$) and thermal ($\times 10^4$) parameters*

| | <i>x</i> | <i>y/B</i> | <i>z</i> | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₁₂ | <i>B</i> ₁₃ | <i>B</i> ₂₃ |
|-------|-----------|------------|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| N(1) | 2916 (0) | -35 (0) | 506 (0) | 110 (1) | 15 (0) | 96 (0) | 1 (0) | 14 (0) | 0 (0) |
| O(1) | 1142 (2) | -85 (1) | -1365 (2) | 154 (2) | 17 (0) | 117 (2) | -9 (1) | -8 (2) | 5 (1) |
| O(2) | -1136 (2) | -2202 (1) | -1546 (2) | 237 (3) | 23 (0) | 194 (3) | -25 (1) | 16 (2) | 3 (1) |
| O(3) | 5298 (2) | -384 (1) | 3449 (2) | 138 (2) | 20 (0) | 135 (2) | 5 (1) | -2 (2) | 11 (1) |
| O(4) | 6613 (2) | 1506 (1) | 4643 (2) | 270 (4) | 26 (0) | 178 (3) | -17 (1) | -21 (3) | -11 (1) |
| N(1) | 2652 (2) | -892 (1) | 1096 (2) | 128 (2) | 17 (0) | 109 (2) | 5 (1) | 12 (2) | 1 (1) |
| N(2) | 4744 (2) | 84 (1) | 2407 (2) | 107 (2) | 18 (0) | 111 (2) | 5 (1) | 21 (2) | 2 (1) |
| N(3) | 3329 (2) | 868 (1) | 89 (2) | 122 (2) | 17 (0) | 109 (2) | 5 (1) | 24 (2) | 4 (1) |
| N(4) | 183 (2) | -600 (1) | -1975 (2) | 145 (3) | 18 (0) | 117 (2) | -7 (1) | 10 (2) | -1 (1) |
| C(1) | 348 (2) | -1182 (1) | -1207 (2) | 122 (3) | 17 (0) | 111 (3) | 0 (1) | 31 (2) | -2 (1) |
| C(2) | -904 (2) | -1680 (1) | -2170 (2) | 149 (3) | 19 (0) | 145 (3) | -3 (1) | 36 (3) | -7 (1) |
| C(3) | -1885 (3) | -1518 (1) | -3923 (3) | 207 (5) | 25 (1) | 160 (4) | -12 (1) | -6 (3) | -10 (1) |
| C(4) | 1585 (2) | -1344 (1) | 383 (2) | 130 (3) | 16 (0) | 122 (3) | 5 (1) | 38 (2) | -1 (1) |
| C(5) | 1664 (3) | -2016 (1) | 1193 (3) | 183 (4) | 17 (0) | 174 (4) | 1 (1) | 13 (3) | 10 (1) |
| C(6) | 5343 (2) | 708 (1) | 2641 (2) | 109 (3) | 19 (0) | 127 (3) | -1 (1) | 25 (2) | 0 (1) |
| C(7) | 6648 (2) | 931 (1) | 4162 (2) | 144 (3) | 25 (1) | 126 (3) | -12 (1) | 23 (2) | 1 (1) |
| C(8) | 7981 (3) | 458 (1) | 5062 (3) | 118 (3) | 38 (1) | 137 (3) | -4 (1) | 2 (3) | 2 (1) |
| C(9) | 4511 (2) | 1146 (1) | 1251 (2) | 112 (3) | 18 (0) | 128 (3) | 1 (1) | 34 (2) | -1 (1) |
| C(10) | 5069 (3) | 1853 (1) | 1170 (3) | 167 (4) | 20 (1) | 190 (4) | -9 (1) | 25 (3) | 5 (1) |
| C(11) | 2436 (3) | 1236 (1) | -1425 (3) | 176 (4) | 21 (1) | 125 (3) | 6 (1) | 10 (3) | 10 (1) |

Table 1 (*cont.*)

Hydrogen atoms. Thermal parameters were taken equal to those of the atoms to which the hydrogen atoms are bonded.

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|------------|------------|------------|
| H(1) | -2273 (36) | -1118 (16) | -3993 (37) |
| H(2) | -1139 (40) | -1603 (16) | -4396 (38) |
| H(3) | -2654 (36) | -1853 (15) | -4359 (36) |
| H(4) | 1804 (33) | -2388 (13) | 475 (36) |
| H(5) | 600 (36) | -2111 (13) | 1407 (36) |
| H(6) | 2485 (35) | -2016 (13) | 2168 (38) |
| H(7) | 3355 (30) | -993 (12) | 2024 (31) |
| H(8) | 7596 (34) | 202 (16) | 5816 (37) |
| H(9) | 8902 (35) | 673 (15) | 5523 (34) |
| H(10) | 8258 (35) | 162 (15) | 4308 (39) |
| H(11) | 4553 (36) | 2131 (14) | 1586 (39) |
| H(12) | 6301 (35) | 1897 (12) | 1529 (36) |
| H(13) | 4927 (32) | 1965 (14) | 34 (37) |
| H(14) | 2122 (31) | 1661 (14) | -1209 (34) |
| H(15) | 3017 (34) | 1215 (14) | -2163 (34) |
| H(16) | 1445 (35) | 1020 (13) | -2046 (33) |

1965), viewed along a direction lying in the (100) plane and making an angle of 60° with **b**. This shows clearly the near-planarity of the ring systems, and the slight twist of the acetyl groups. The least-squares planes for the five- and six-membered rings have respective sets of coefficients

$$A=0.8267 \quad B=-0.2729 \quad C=-0.7196 \quad D=1.7814$$

$$A=0.8066 \quad B=-0.3081 \quad C=-0.7253 \quad D=1.6897$$

in the equation $Ax + By + Cz + D = 0$, based on the crystallographic axes. These planes make an angle of slightly more than 2° with each other. The vibration ellipsoids representing 50% probability reveal nothing unexpected, the amplitudes of the ring atoms being slightly greater normal to the molecular plane and the peripheral acetyl groups showing greater amplitude and higher anisotropy than the tightly bound rings.

Table 2. Observed and calculated structure factors ($\times 10$)

| h | k | l | h ² | k ² | l ² | h ² +k ² | h ² +l ² | k ² +l ² | h ² +k ² +l ² | Observed | Calculated |
|-----|---|---|----------------|----------------|----------------|--------------------------------|--------------------------------|--------------------------------|--|----------|------------|
| 1 | 0 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 2 | 1.0 | 1.0 |
| 2 | 0 | 0 | 4 | 0 | 0 | 4 | 4 | 0 | 8 | 4.0 | 4.0 |
| 3 | 0 | 0 | 9 | 0 | 0 | 9 | 9 | 0 | 18 | 9.0 | 9.0 |
| 4 | 0 | 0 | 16 | 0 | 0 | 16 | 16 | 0 | 32 | 16.0 | 16.0 |
| 5 | 0 | 0 | 25 | 0 | 0 | 25 | 25 | 0 | 50 | 25.0 | 25.0 |
| 6 | 0 | 0 | 36 | 0 | 0 | 36 | 36 | 0 | 72 | 36.0 | 36.0 |
| 7 | 0 | 0 | 49 | 0 | 0 | 49 | 49 | 0 | 98 | 49.0 | 49.0 |
| 8 | 0 | 0 | 64 | 0 | 0 | 64 | 64 | 0 | 128 | 64.0 | 64.0 |
| 9 | 0 | 0 | 81 | 0 | 0 | 81 | 81 | 0 | 162 | 81.0 | 81.0 |
| 10 | 0 | 0 | 100 | 0 | 0 | 100 | 100 | 0 | 200 | 100.0 | 100.0 |
| 11 | 0 | 0 | 121 | 0 | 0 | 121 | 121 | 0 | 242 | 121.0 | 121.0 |
| 12 | 0 | 0 | 144 | 0 | 0 | 144 | 144 | 0 | 288 | 144.0 | 144.0 |
| 13 | 0 | 0 | 169 | 0 | 0 | 169 | 169 | 0 | 338 | 169.0 | 169.0 |
| 14 | 0 | 0 | 196 | 0 | 0 | 196 | 196 | 0 | 392 | 196.0 | 196.0 |
| 15 | 0 | 0 | 225 | 0 | 0 | 225 | 225 | 0 | 450 | 225.0 | 225.0 |
| 16 | 0 | 0 | 256 | 0 | 0 | 256 | 256 | 0 | 512 | 256.0 | 256.0 |
| 17 | 0 | 0 | 289 | 0 | 0 | 289 | 289 | 0 | 578 | 289.0 | 289.0 |
| 18 | 0 | 0 | 324 | 0 | 0 | 324 | 324 | 0 | 648 | 324.0 | 324.0 |
| 19 | 0 | 0 | 361 | 0 | 0 | 361 | 361 | 0 | 722 | 361.0 | 361.0 |
| 20 | 0 | 0 | 400 | 0 | 0 | 400 | 400 | 0 | 800 | 400.0 | 400.0 |
| 21 | 0 | 0 | 441 | 0 | 0 | 441 | 441 | 0 | 882 | 441.0 | 441.0 |
| 22 | 0 | 0 | 484 | 0 | 0 | 484 | 484 | 0 | 968 | 484.0 | 484.0 |
| 23 | 0 | 0 | 529 | 0 | 0 | 529 | 529 | 0 | 1058 | 529.0 | 529.0 |
| 24 | 0 | 0 | 576 | 0 | 0 | 576 | 576 | 0 | 1152 | 576.0 | 576.0 |
| 25 | 0 | 0 | 625 | 0 | 0 | 625 | 625 | 0 | 1250 | 625.0 | 625.0 |
| 26 | 0 | 0 | 676 | 0 | 0 | 676 | 676 | 0 | 1352 | 676.0 | 676.0 |
| 27 | 0 | 0 | 729 | 0 | 0 | 729 | 729 | 0 | 1458 | 729.0 | 729.0 |
| 28 | 0 | 0 | 784 | 0 | 0 | 784 | 784 | 0 | 1568 | 784.0 | 784.0 |
| 29 | 0 | 0 | 841 | 0 | 0 | 841 | 841 | 0 | 1682 | 841.0 | 841.0 |
| 30 | 0 | 0 | 900 | 0 | 0 | 900 | 900 | 0 | 1800 | 900.0 | 900.0 |
| 31 | 0 | 0 | 961 | 0 | 0 | 961 | 961 | 0 | 1922 | 961.0 | 961.0 |
| 32 | 0 | 0 | 1024 | 0 | 0 | 1024 | 1024 | 0 | 2048 | 1024.0 | 1024.0 |
| 33 | 0 | 0 | 1089 | 0 | 0 | 1089 | 1089 | 0 | 2178 | 1089.0 | 1089.0 |
| 34 | 0 | 0 | 1156 | 0 | 0 | 1156 | 1156 | 0 | 2312 | 1156.0 | 1156.0 |
| 35 | 0 | 0 | 1225 | 0 | 0 | 1225 | 1225 | 0 | 2450 | 1225.0 | 1225.0 |
| 36 | 0 | 0 | 1296 | 0 | 0 | 1296 | 1296 | 0 | 2592 | 1296.0 | 1296.0 |
| 37 | 0 | 0 | 1369 | 0 | 0 | 1369 | 1369 | 0 | 2738 | 1369.0 | 1369.0 |
| 38 | 0 | 0 | 1444 | 0 | 0 | 1444 | 1444 | 0 | 2888 | 1444.0 | 1444.0 |
| 39 | 0 | 0 | 1521 | 0 | 0 | 1521 | 1521 | 0 | 3042 | 1521.0 | 1521.0 |
| 40 | 0 | 0 | 1600 | 0 | 0 | 1600 | 1600 | 0 | 3200 | 1600.0 | 1600.0 |
| 41 | 0 | 0 | 1681 | 0 | 0 | 1681 | 1681 | 0 | 3362 | 1681.0 | 1681.0 |
| 42 | 0 | 0 | 1764 | 0 | 0 | 1764 | 1764 | 0 | 3528 | 1764.0 | 1764.0 |
| 43 | 0 | 0 | 1849 | 0 | 0 | 1849 | 1849 | 0 | 3698 | 1849.0 | 1849.0 |
| 44 | 0 | 0 | 1936 | 0 | 0 | 1936 | 1936 | 0 | 3872 | 1936.0 | 1936.0 |
| 45 | 0 | 0 | 2025 | 0 | 0 | 2025 | 2025 | 0 | 4050 | 2025.0 | 2025.0 |
| 46 | 0 | 0 | 2116 | 0 | 0 | 2116 | 2116 | 0 | 4232 | 2116.0 | 2116.0 |
| 47 | 0 | 0 | 2209 | 0 | 0 | 2209 | 2209 | 0 | 4418 | 2209.0 | 2209.0 |
| 48 | 0 | 0 | 2304 | 0 | 0 | 2304 | 2304 | 0 | 4608 | 2304.0 | 2304.0 |
| 49 | 0 | 0 | 2401 | 0 | 0 | 2401 | 2401 | 0 | 4802 | 2401.0 | 2401.0 |
| 50 | 0 | 0 | 2500 | 0 | 0 | 2500 | 2500 | 0 | 5000 | 2500.0 | 2500.0 |
| 51 | 0 | 0 | 2601 | 0 | 0 | 2601 | 2601 | 0 | 5202 | 2601.0 | 2601.0 |
| 52 | 0 | 0 | 2704 | 0 | 0 | 2704 | 2704 | 0 | 5408 | 2704.0 | 2704.0 |
| 53 | 0 | 0 | 2809 | 0 | 0 | 2809 | 2809 | 0 | 5618 | 2809.0 | 2809.0 |
| 54 | 0 | 0 | 2916 | 0 | 0 | 2916 | 2916 | 0 | 5832 | 2916.0 | 2916.0 |
| 55 | 0 | 0 | 3025 | 0 | 0 | 3025 | 3025 | 0 | 6050 | 3025.0 | 3025.0 |
| 56 | 0 | 0 | 3136 | 0 | 0 | 3136 | 3136 | 0 | 6272 | 3136.0 | 3136.0 |
| 57 | 0 | 0 | 3249 | 0 | 0 | 3249 | 3249 | 0 | 6502 | 3249.0 | 3249.0 |
| 58 | 0 | 0 | 3364 | 0 | 0 | 3364 | 3364 | 0 | 6740 | 3364.0 | 3364.0 |
| 59 | 0 | 0 | 3481 | 0 | 0 | 3481 | 3481 | 0 | 6982 | 3481.0 | 3481.0 |
| 60 | 0 | 0 | 3600 | 0 | 0 | 3600 | 3600 | 0 | 7230 | 3600.0 | 3600.0 |
| 61 | 0 | 0 | 3721 | 0 | 0 | 3721 | 3721 | 0 | 7482 | 3721.0 | 3721.0 |
| 62 | 0 | 0 | 3844 | 0 | 0 | 3844 | 3844 | 0 | 7740 | 3844.0 | 3844.0 |
| 63 | 0 | 0 | 3969 | 0 | 0 | 3969 | 3969 | 0 | 8002 | 3969.0 | 3969.0 |
| 64 | 0 | 0 | 4096 | 0 | 0 | 4096 | 4096 | 0 | 8270 | 4096.0 | 4096.0 |
| 65 | 0 | 0 | 4225 | 0 | 0 | 4225 | 4225 | 0 | 8542 | 4225.0 | 4225.0 |
| 66 | 0 | 0 | 4356 | 0 | 0 | 4356 | 4356 | 0 | 8820 | 4356.0 | 4356.0 |
| 67 | 0 | 0 | 4489 | 0 | 0 | 4489 | 4489 | 0 | 9102 | 4489.0 | 4489.0 |
| 68 | 0 | 0 | 4624 | 0 | 0 | 4624 | 4624 | 0 | 9390 | 4624.0 | 4624.0 |
| 69 | 0 | 0 | 4761 | 0 | 0 | 4761 | 4761 | 0 | 9682 | 4761.0 | 4761.0 |
| 70 | 0 | 0 | 4900 | 0 | 0 | 4900 | 4900 | 0 | 9980 | 4900.0 | 4900.0 |
| 71 | 0 | 0 | 5041 | 0 | 0 | 5041 | 5041 | 0 | 10282 | 5041.0 | 5041.0 |
| 72 | 0 | 0 | 5184 | 0 | 0 | 5184 | 5184 | 0 | 10590 | 5184.0 | 5184.0 |
| 73 | 0 | 0 | 5329 | 0 | 0 | 5329 | 5329 | 0 | 10902 | 5329.0 | 5329.0 |
| 74 | 0 | 0 | 5476 | 0 | 0 | 5476 | 5476 | 0 | 11220 | 5476.0 | 5476.0 |
| 75 | 0 | 0 | 5625 | 0 | 0 | 5625 | 5625 | 0 | 11542 | 5625.0 | 5625.0 |
| 76 | 0 | 0 | 5776 | 0 | 0 | 5776 | 5776 | 0 | 11870 | 5776.0 | 5776.0 |
| 77 | 0 | 0 | 5929 | 0 | 0 | 5929 | 5929 | 0 | 12202 | 5929.0 | 5929.0 |
| 78 | 0 | 0 | 6084 | 0 | 0 | 6084 | 6084 | 0 | 12540 | 6084.0 | 6084.0 |
| 79 | 0 | 0 | 6241 | 0 | 0 | 6241 | 6241 | 0 | 12882 | 6241.0 | 6241.0 |
| 80 | 0 | 0 | 6400 | 0 | 0 | 6400 | 6400 | 0 | 13230 | 6400.0 | 6400.0 |
| 81 | 0 | 0 | 6561 | 0 | 0 | 6561 | 6561 | 0 | 13582 | 6561.0 | 6561.0 |
| 82 | 0 | 0 | 6724 | 0 | 0 | 6724 | 6724 | 0 | 13940 | 6724.0 | 6724.0 |
| 83 | 0 | 0 | 6889 | 0 | 0 | 6889 | 6889 | 0 | 14302 | 6889.0 | 6889.0 |
| 84 | 0 | 0 | 7056 | 0 | 0 | 7056 | 7056 | 0 | 14670 | 7056.0 | 7056.0 |
| 85 | 0 | 0 | 7225 | 0 | 0 | 7225 | 7225 | 0 | 15042 | 7225.0 | 7225.0 |
| 86 | 0 | 0 | 7396 | 0 | 0 | 7396 | 7396 | 0 | 15420 | 7396.0 | 7396.0 |
| 87 | 0 | 0 | 7569 | 0 | 0 | 7569 | 7569 | 0 | 15802 | 7569.0 | 7569.0 |
| 88 | 0 | 0 | 7744 | 0 | 0 | 7744 | 7744 | 0 | 16190 | 7744.0 | 7744.0 |
| 89 | 0 | 0 | 7921 | 0 | 0 | 7921 | 7921 | 0 | 16582 | 7921.0 | 7921.0 |
| 90 | 0 | 0 | 8100 | 0 | 0 | 8100 | 8100 | 0 | 16980 | 8100.0 | 8100.0 |
| 91 | 0 | 0 | 8281 | 0 | 0 | 8281 | 8281 | 0 | 17382 | 8281.0 | 8281.0 |
| 92 | 0 | 0 | 8464 | 0 | 0 | 8464 | 8464 | 0 | 17790 | 8464.0 | 8464.0 |
| 93 | 0 | 0 | 8649 | 0 | 0 | 8649 | 8649 | 0 | 18202 | 8649.0 | 8649.0 |
| 94 | 0 | 0 | 8836 | 0 | 0 | 8836 | 8836 | 0 | 18620 | 8836.0 | 8836.0 |
| 95 | 0 | 0 | 9025 | 0 | 0 | 9025 | 9025 | 0 | 19042 | 9025.0 | 9025.0 |
| 96 | 0 | 0 | 9216 | 0 | 0 | 9216 | 9216 | 0 | 19470 | 9216.0 | 9216.0 |
| 97 | 0 | 0 | 9409 | 0 | 0 | 9409 | 9409 | 0 | 19902 | 9409.0 | 9409.0 |
| 98 | 0 | 0 | 9604 | 0 | 0 | 9604 | 9604 | 0 | 20340 | 9604.0 | 9604.0 |
| 99 | 0 | 0 | 9801 | 0 | 0 | 9801 | 9801 | 0 | 20782 | 9801.0 | 9801.0 |
| 100 | 0 | 0 | 10000 | 0 | 0 | 10000 | 10000 | 0 | 21230 | 10000.0 | 10000.0 |

Fig. 3 shows the atom numbering used, and also assigns numbers to the bonds for use in Tables 3 and 4 which give bond distances and angles. The only hydrogen atom shown is H(7), the imino hydrogen, represented only as a small sphere since its thermal parameters were not determined but maintained equal to those of N(1). This hydrogen atom is of interest because of the possibility of its forming an intramolecular hydrogen bond with O(3). It could not be substituted by a methyl group, although this may be due purely to steric hindrance. The Ni-N(1)-H(7) angle of 111.5° , compared with 117.2° for C(4)-N(1)-H(7), is consistent with some bonding to O(3), since the e.s.d.'s

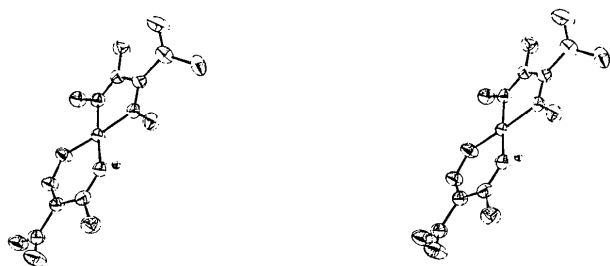


Fig. 2. Stereoscopic pair of projections of molecule. The vibrational ellipsoids represent 50% probability.

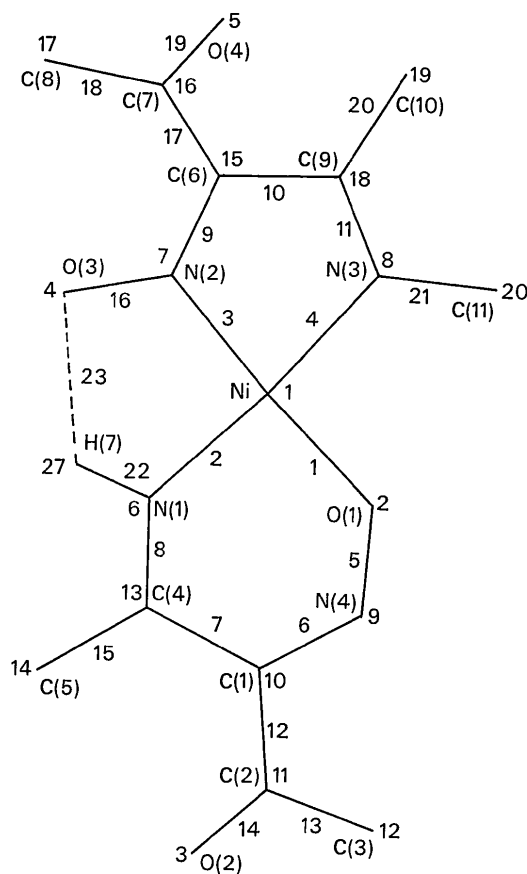


Fig. 3. Atom and bond numbering system used.

for these angles are about 1.5° . A recent three-dimensional neutron study of salicylic acid (Bacon & Jude, 1972) has established hydrogen positions with an e.s.d. of 0.006 \AA , and provides accurate figures for angles and distances in an intramolecular hydrogen bond. The figures obtained by Bacon & Jude are 2.606 and 0.957 \AA for the O-H...O and O-H distances respectively, and 145° for the O-H...O angle. These are to be compared with 2.696 \AA , 0.85 \AA and 126° in the present work. Although the location of the hydrogen atom in this X-ray determination is much less precise than in the neutron study the similarities suggest that an internal hydrogen bond has been formed.

Table 3. *Interatomic distances and standard deviations* (\AA)

The numbering scheme for the bond lengths is shown in Fig. 3.

| | | | |
|----|-----------|----|------------|
| 1 | 1.819 (1) | 13 | 1.492 (3) |
| 2 | 1.813 (2) | 14 | 1.210 (2) |
| 3 | 1.872 (1) | 15 | 1.497 (2) |
| 4 | 1.888 (1) | 16 | 1.269 (2) |
| 5 | 1.313 (2) | 17 | 1.482 (2) |
| 6 | 1.315 (2) | 18 | 1.490 (3) |
| 7 | 1.463 (2) | 19 | 1.220 (2) |
| 8 | 1.288 (2) | 20 | 1.496 (2) |
| 9 | 1.336 (2) | 21 | 1.466 (2) |
| 10 | 1.458 (2) | 22 | 0.850 (23) |
| 11 | 1.292 (2) | 23 | 2.103 (24) |
| 12 | 1.498 (2) | | |

Table 4. *Interatomic angles and standard deviations* ($^\circ$)

The numbering scheme for the angles is shown in Fig. 3.

| | | | |
|--------|-----------|--------|------------|
| 1, 2 | 92.7 (1) | 16, 9 | 122.7 (1) |
| 1, 3 | 175.9 (1) | 9, 10 | 111.8 (1) |
| 1, 4 | 92.5 (1) | 9, 17 | 123.9 (2) |
| 2, 3 | 91.4 (1) | 17, 10 | 124.4 (2) |
| 2, 4 | 174.8 (1) | 17, 19 | 118.8 (2) |
| 3, 4 | 83.5 (1) | 17, 18 | 120.0 (2) |
| 5, 6 | 122.5 (1) | 19, 18 | 121.2 (2) |
| 6, 12 | 111.5 (2) | 10, 20 | 121.3 (2) |
| 6, 7 | 125.8 (2) | 10, 11 | 115.1 (2) |
| 12, 13 | 118.8 (2) | 20, 11 | 123.5 (2) |
| 12, 14 | 121.2 (2) | 11, 21 | 121.2 (2) |
| 13, 14 | 120.1 (2) | 11, 4 | 114.4 (1) |
| 7, 15 | 122.4 (2) | 21, 4 | 124.4 (1) |
| 7, 8 | 118.4 (2) | 2, 22 | 111.5 (16) |
| 15, 8 | 119.2 (2) | 8, 22 | 117.2 (16) |
| 8, 2 | 131.3 (1) | 23, 22 | 126.4 (21) |
| 1, 5 | 129.2 (1) | 16, 23 | 88.3 (6) |
| 12, 7 | 122.7 (2) | | |
| 3, 16 | 122.2 (1) | | |
| 3, 9 | 115.0 (1) | | |

The projection of the unit-cell contents down the b axis, shown in Fig. 4, reveals alternating sheets of molecules oppositely inclined to the b axis. The impression that the molecules lie in the $(10\bar{1})$ plane is misleading, because of the long b axis. In fact the molecules lie close to the $(11\bar{1})$ and $(\bar{1}11)$ planes. There is no evidence of intermolecular hydrogen bonds, the closest approach distance between non-hydrogen atoms being 3.51 \AA .

Further characterizations of (I) and (II) were obtained by p.m.r., infrared and mass spectrometry. There were no significant ion contributions in the mass spectrum of (II) at m/e 312 and m/e 340, confirming that (II) was not an equimolar mixture of (I) (molecular ion m/e 312, based on $Ni=58$) and bis(4-methylimino-pentane-2,3-dione 3-oximato)nickel(II) (molecular ion m/e 340), and that it did not disproportionate prior to electron impact in the ion source. The p.m.r. spectrum of (II) ($CDCl_3$, 35°) exhibited five methyl resonances (δ 2.35, quartet, J 0.8 Hz; δ 2.40, singlet; δ 2.55, singlet; δ 2.55 doublet, J 1.2 Hz; δ 3.15, quartet, J 0.8 Hz) and one imino proton resonance (δ 8.88, broad), consistent with the conclusion that (II) in solution is a single complex and is not a mixture of linkage isomers. Analogous deductions have been made from the p.m.r. spectrum of (I) (Lacey *et al.*, 1970). There is therefore no immediate evidence to indicate that (II) assumes a different structure in solution from that in the crystal. The proton chemical shifts of the (4-iminopentane-2,3-dione 3-oximato) ligand of (II) are closely similar to those reported for one of the non-equivalent ligands of (I) (Lacey *et al.*, 1970), supporting the proposition that these ligands exhibit the same mode of chelation to their respective nickel atoms.

The infrared spectrum of (II) was similar to that reported for (I) (Lacey *et al.*, 1970), providing further evidence that their structures are formally related. There were two distinct regions for $\nu_{C=O}$ in the 1600–1700 cm^{-1} portion of each spectrum [1684(*vs*)/1671(*vs*) and 1646(*vs*)/1635(*sh*) cm^{-1} for (I), 1684(*vs*) and 1653(*vs*) cm^{-1} for (II)] as would be expected for structures in which one acetyl group is attached to a five-membered chelate ring and the other is attached to a six-membered chelate ring. Also, ν_{N-H} (3164 cm^{-1}) in the spectrum of (II) was at lower frequency than that observed for bis-(4-aminopent-3-en-2-onato)nickel(II) (3280 cm^{-1}), consistent with the presence of intramolecular hydrogen bonding in (II) as indicated by the crystallographic data.

Nickel(II) chelate complexes related to (II) have been reported recently and analogous structures have been suggested (Bose & Patel, 1972; Bose, 1972; Bose, Sharma & Patel, 1973). The reaction of palladium(II) with these types of ligands usually leads to symmetrical complexes (White, 1971; Sharma, Bose & Patel, 1972; Bose *et al.*, 1973) but mixed-ligand complexes arise when bulky sec-alkylimino or arylimino groups are incorporated in the molecule (Sharma *et al.*, 1972). Finally, chelate linkage isomers of (3-hydroxyimino-4,9-dimethyl-5,8-diazadodeca-4,9-diene-2,11-dionato)nickel(II) have been separated and characterized (Lacey, Macdonald & Shannon, 1973).

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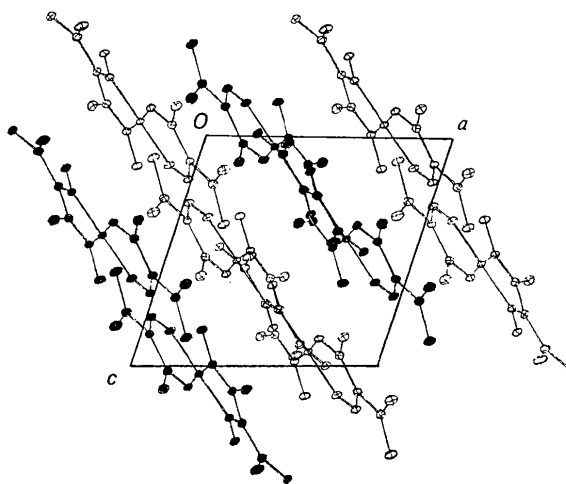


Fig. 4. Projection down the b axis. Molecules with full atoms and open atoms are oppositely inclined to the b axis, lying close to the $(1\bar{1}1)$ and $(11\bar{1})$ planes respectively. The overlapped molecules are related by diad screw axes through $(\frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{3}{2})$.

Committee, which has made possible the purchase and maintenance of the X-ray diffractometer equipment.

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