

The general packing of the ions and the hydrogen-bond network is essentially identical with that found in the other Tutton's salts, that is, each water molecule forms two hydrogen bonds (Table 6) which range in length from 2.71 to 2.86 Å. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulfate groups, but one bond (to O(3) and O(4) of the same sulfate ion) is 'bifurcated'. In addition, there is a fairly close approach of the water octahedra along the *c* axis, the O(9)–O(9') distance being 3.00 Å for the vanadium, 3.03 Å for the iron, and 3.02 Å for the cobalt compound.

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The Crystal Structure of Bis-(*N*-isopropyl-3-ethylsalicylaldiminato)nickel

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The crystal structure of bis-(*N*-isopropyl-3-ethylsalicylaldiminato)nickel, Ni(C₁₂H₁₆NO)₂, has been determined from three-dimensional data collected on a single-crystal diffractometer with Cu *K*α radiation. The cell has dimensions *a* = 26.947, *b* = 19.883, and *c* = 8.820 Å, belongs to space group *Pbca*, and contains eight molecules. The structure consists of discrete molecules in which nickel(II) exhibits a distorted-tetrahedral coordination configuration. The dihedral angle between the plane defined by the Ni–N(1)–O(1) group and the plane defined by the Ni–N(2)–O(2) group is 85.3°.

Introduction

A striking example of the small energy difference between the diamagnetic and paramagnetic states of the nickel(II) ion has been provided by a series of ring-substituted salicylaldimine chelates of nickel(II). That is, Holm & Swaminathan (1963) have reported that for 3-substituted bis-(*N*-isopropylsalicylaldiminato)nickel chelates the magnetic moments are 3.28, 0, and 3.30 Bohr magnetons for the substituents hydrogen, methyl, and ethyl, respectively. Consistent with these magnetic moments, the coordination configuration of the 3-hydrogen chelate has indeed been shown to be tetrahedral (Fox, Oriolo, Lingafelter & Sacconi, 1964) and the coordination configuration of the 3-methyl chelate has been shown to be strictly planar (Braun & Linga-

felter, 1966). We have now completed the structural determination of the 3-ethyl chelate by three dimensional X-ray diffraction techniques.

Experimental

Bis-(*N*-isopropyl-3-ethylsalicylaldiminato)nickel was prepared by the method of Sacconi, Paoletti & Del Re (1957), using 3-ethylsalicylaldehyde which was prepared according to the general procedure of the Duff (1941) reaction. Final purification was accomplished by two recrystallizations from equal volumes of methanol and 2-butanol by slow evaporation at room temperature. The crystals were in the form of flat needles, lath-like on (100) and elongated along [001]. A crystal of dimensions 0.14 × 0.12 × 0.03 mm was used

in the determination of cell dimensions and in the collection of intensity data.

Cell dimensions were determined on a Picker X-ray diffractometer equipped with a General Electric goniostat, using Cu $K\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$). The cell dimensions with their standard deviations are

$$\begin{aligned} a &= 26.947 \pm 0.002 \text{ \AA} \\ b &= 19.883 \pm 0.001 \\ c &= 8.820 \pm 0.001 \end{aligned}$$

Systematic absences of $0kl$ for k odd, $h0l$ for l odd, and $hk0$ for h odd identified the space group as $Pbca$. The cell contains eight molecules: measured density 1.24 g.cm^{-3} , calculated density 1.235 g.cm^{-3} .

The intensity data were collected by the ω - 2θ scan method (Furnas, 1957) using nickel-filtered Cu $K\alpha$ radiation and a Picker diffractometer equipped with a scintillation counter, pulse-height discriminator, and a General Electric single-crystal goniostat. A suitable scan range for each reflection was calculated by the formula of Alexander & Smith (1964), scan range = $1.8 + 0.86(\tan \theta)$. Stationary background measurements were made at the start and finish of each scan. Of the 2016 reflections which were examined, only 1180 reflections had an intensity (I) greater than twice the standard deviation of the intensity ($2\sigma_I$), owing to the very small size of the crystal. These 1180 reflections ranged in intensity from 1 to 2500.

Four standard reflections were measured periodically to detect systematic changes during the course of the data collection. The scale factor determined by these standard reflections was essentially constant, with only a random variation of $\pm 1\%$ due primarily to counting statistics.

Structure determination

All calculations were carried out on an IBM 7094 computer with a set of programs written or adapted by Stewart (1964). Lorentz and polarization factors were applied and relative structure factors were calculated without correction for absorption. The atomic scattering factors used were those of Viervoll & Øgrim (1949) for nickel, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen, and carbon, and those from Table 2 of Stewart, Davidson & Simpson (1965) for hydrogen. No correction was made for anomalous dispersion.

Since there are eight molecules in the cell of space group $Pbca$, no atoms are required to be in special positions. The positional parameters of the nickel atom in the eightfold general position were readily obtained from a three-dimensional Patterson synthesis. A series of Fourier syntheses enabled the positions of all 29 non-hydrogen atoms to be determined, and resulted in a reduction of R to 0.21. R is defined throughout as $\sum ||F_o| - |F_c|| / \sum |F_o|$, where the sums are over the unique, observed reflections only.

Further refinement was carried out with the full-matrix least squares program of Busing & Levy (1959)

as adapted in the UW crystallographic calculation system (Stewart, 1964). The function minimized was $\sum w(|F_o| - |F_c|)^2$. Initially, a weighting scheme based on counting statistics was used; that is, $1/w = 1/\sigma_F$ for unobserved reflections for which $F_c > F_o$ and for all observed reflections and $w = 0$ for unobserved reflections for which $F_c \leq F_o$. Here the unobserved reflections are the 302 reflections for which $I \leq 0$. Three cycles of least-squares refinement using individual anisotropic temperature factors reduced R to 0.158.

A three-dimensional ΔF synthesis at this stage revealed the positions of all 32 hydrogen atoms. After the introduction of these hydrogen atoms, three additional anisotropic cycles of refinement of the non-hydrogen atoms and two cycles of refinement of the hydrogen atoms with individual isotropic temperature factors reduced R to 0.109. During these and all subsequent least-squares calculations, the calculated structure factor contributions of the parameters not being refined were included as fixed contributions.

Two observations at this stage indicated desirable changes for the further refinements. First, many of the weak reflections had very large ΔF 's. Partially to eliminate the errors in the least-squares refinement which would be caused by such large ΔF 's, a change in the definition of an 'unobserved' reflection was made. That is, the 836 reflections for which $I \leq 2\sigma_I$ were coded unobserved and were assigned an intensity of $2\sigma_I$. In subsequent least-squares calculations the weights of these unobserved reflections were made zero when $F_c \leq F_o$. Secondly, it appeared that the strong reflections had unduly large weights. In order better to eliminate the errors which seemed inherent in the weighting scheme based on pure counting statistics, unit weights were used for all observed reflections and for unobserved reflections for which $F_c > F_o$.

Two cycles of refinement of the non-hydrogen atoms with individual isotropic temperature factors and one cycle with individual anisotropic temperature factors reduced R to 0.070. Because of the large number of variables involved, each anisotropic cycle of refinement of the non-hydrogen atoms was carried out in two stages: one stage refining their thermal parameters and one stage refining their positional parameters.

A change in the weighting scheme was then made to correspond to the plot of root-mean-square ΔF vs F_o , where the r.m.s. ΔF is calculated from all ΔF 's within a statistically large enough group of F_o 's. Considering the r.m.s. ΔF as an average standard deviation, the weighting scheme was taken as $1/w = 1/(5.55 - 0.078 F_o)$ for $F_o < 43$ for observed reflections and for unobserved reflections for which $F_c > F_o$ and $1/w = 1/(2.00 + 0.0047 F_o)$ for $F_o \geq 43$. Three cycles of refinement of the non-hydrogen atoms with anisotropic temperature factors reduced R to 0.060.

A final change in the weighting scheme was made to correspond to the plot of r.m.s. ΔF vs F_o shown in Fig. 1. One anisotropic cycle on the non-hydrogen atoms and two isotropic cycles on the hydrogen atoms,

using the weighting scheme $w=1/(7.05-0.115 F_o)$ for $F_o < 47$ and $w=1/(1.07+0.0127 F_o)$ for $F_o \geq 47$, did not change R from its final value of 0.060.

For the final cycle of non-hydrogen atom refinement, the average shift/error for positional and thermal parameters was 0.2, with a maximum of 0.7. For the final cycle of hydrogen atom refinement the average shift/error was 0.1, with a maximum of 0.5.

The final parameters and their estimated standard deviations are listed in Tables 1 and 2. Since it was

necessary to refine the atomic parameters in three stages because the 389 parameters greatly exceeded the 180-variable capacity of the full-matrix least squares program, the σ 's estimated by the least-squares program have been increased by empirically determined correction factors. The list of observed and calculated structure factors is given in Table 3. Examination of these structure factors by the method of Housty & Clastre (1957) did not show any detectable secondary extinction.

Table 1. Parameters of non-hydrogen atoms and their estimated standard deviations

Anisotropic thermal factors are of the form: $\exp[-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*]$.

	Positional parameter $\times 10^4$			Thermal parameter $\times 10$					
	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	3529 (1)	3945 (1)	4272 (1)	45 (1)	55 (1)	60 (1)	2 (1)	0 (1)	-2 (1)
O(1)	4048 (1)	3850 (2)	2842 (5)	22 (2)	45 (3)	54 (3)	5 (2)	6 (2)	3 (3)
O(2)	2848 (1)	3805 (2)	3976 (5)	29 (2)	44 (3)	51 (3)	2 (2)	12 (2)	-10 (3)
N(1)	3839 (2)	3323 (3)	5748 (7)	50 (3)	36 (3)	33 (3)	1 (3)	2 (3)	-1 (3)
N(2)	3452 (2)	4867 (3)	5039 (6)	36 (3)	41 (3)	48 (3)	3 (3)	-5 (3)	-6 (3)
C(1)	4628 (2)	3244 (3)	4375 (8)	43 (4)	26 (4)	40 (4)	0 (3)	2 (4)	3 (4)
C(2)	4487 (2)	3586 (3)	3040 (8)	24 (3)	24 (4)	41 (4)	-10 (3)	8 (4)	-3 (3)
C(3)	4840 (2)	3637 (3)	1865 (9)	29 (4)	46 (5)	46 (5)	1 (3)	-7 (4)	1 (4)
C(4)	5311 (3)	3390 (4)	2093 (10)	34 (4)	40 (4)	54 (5)	-11 (4)	12 (4)	-1 (4)
C(5)	5448 (3)	3073 (4)	3416 (11)	42 (4)	58 (5)	63 (6)	13 (4)	0 (4)	7 (5)
C(6)	5119 (3)	2994 (4)	4518 (10)	60 (5)	42 (4)	46 (5)	11 (4)	-12 (4)	0 (4)
C(7)	4294 (3)	3121 (4)	5615 (10)	54 (4)	35 (4)	50 (5)	8 (3)	-15 (5)	1 (4)
C(8)	3552 (3)	3053 (4)	7057 (9)	61 (4)	49 (5)	35 (4)	17 (4)	-1 (5)	-4 (4)
C(9)	3233 (4)	2483 (8)	6520 (15)	70 (6)	78 (7)	57 (7)	-2 (7)	14 (6)	6 (6)
C(10)	3253 (5)	3584 (7)	7779 (15)	105 (8)	84 (8)	54 (7)	6 (7)	35 (6)	4 (6)
C(11)	4677 (3)	3960 (6)	394 (12)	55 (6)	80 (7)	57 (7)	19 (6)	33 (6)	4 (7)
C(12)	5028 (6)	3957 (8)	-836 (20)	110 (8)	107 (10)	93 (10)	41 (9)	18 (9)	36 (10)
C(21)	2543 (3)	4826 (3)	5133 (7)	43 (4)	45 (5)	32 (4)	8 (4)	-1 (4)	-1 (3)
C(22)	2480 (2)	4189 (3)	4418 (8)	30 (3)	48 (5)	34 (4)	-2 (3)	1 (4)	14 (4)
C(23)	1985 (2)	3968 (4)	4192 (9)	41 (4)	61 (5)	54 (4)	0 (4)	-3 (4)	-16 (5)
C(24)	1595 (3)	4376 (5)	1707 (11)	37 (4)	102 (6)	63 (6)	1 (4)	1 (4)	9 (5)
C(25)	1688 (3)	4974 (5)	5443 (10)	40 (4)	96 (6)	55 (6)	22 (4)	16 (4)	1 (5)
C(26)	2135 (3)	5182 (4)	5651 (10)	53 (4)	62 (5)	45 (4)	19 (4)	12 (5)	5 (5)
C(27)	3030 (3)	5112 (4)	5345 (9)	62 (5)	45 (4)	45 (5)	5 (4)	-11 (4)	-13 (4)
C(28)	3890 (3)	5313 (4)	5270 (10)	55 (4)	47 (5)	50 (5)	0 (4)	-18 (4)	-17 (4)
C(29)	4079 (5)	5564 (8)	3779 (16)	115 (9)	101 (10)	55 (8)	-68 (7)	-3 (7)	2 (7)
C(30)	4275 (5)	4979 (6)	6194 (18)	62 (5)	51 (7)	109 (10)	-14 (5)	-28 (7)	-16 (6)
C(31)	1892 (3)	3312 (6)	3425 (13)	28 (5)	87 (7)	71 (8)	-9 (5)	3 (5)	5 (6)
C(32)	1819 (6)	2740 (8)	4481 (23)	120 (9)	85 (10)	140 (10)	-25 (9)	-16 (9)	28 (9)

Table 2. Parameters of hydrogen atoms and their estimated standard deviations

	Positional $\times 10^3$			Thermal		Positional $\times 10^3$			Thermal
	x/a	y/b	z/c	B		x/a	y/b	z/c	B
H(4)	548 (2)	341 (3)	136 (7)	2 (1)	H(24)	130 (2)	426 (4)	460 (9)	6 (2)
H(5)	576 (2)	291 (3)	353 (8)	4 (1)	H(25)	139 (2)	520 (3)	589 (9)	7 (2)
H(6)	519 (2)	285 (3)	546 (8)	4 (1)	H(26)	221 (2)	561 (3)	601 (8)	5 (1)
H(7)	442 (2)	284 (3)	618 (7)	2 (1)	H(27)	303 (2)	550 (3)	575 (8)	4 (1)
H(8)	382 (2)	291 (3)	786 (8)	5 (2)	H(28)	378 (2)	566 (3)	581 (9)	4 (1)
H(91)	348 (3)	218 (3)	615 (8)	5 (2)	H(291)	381 (3)	581 (4)	307 (10)	8 (2)
H(92)	303 (3)	229 (4)	742 (9)	7 (2)	H(292)	436 (3)	589 (4)	382 (10)	9 (2)
H(93)	301 (2)	265 (4)	590 (10)	6 (2)	H(293)	413 (3)	528 (5)	326 (10)	10 (3)
H(101)	339 (3)	391 (4)	799 (10)	8 (2)	H(301)	414 (3)	476 (4)	712 (9)	9 (2)
H(102)	301 (3)	379 (4)	696 (10)	8 (2)	H(302)	438 (3)	468 (4)	568 (10)	9 (2)
H(103)	302 (3)	348 (4)	865 (10)	5 (2)	H(303)	454 (3)	531 (4)	650 (9)	7 (2)
H(111)	438 (2)	374 (3)	-44 (8)	4 (1)	H(311)	157 (3)	336 (3)	273 (8)	6 (2)
H(112)	460 (2)	437 (3)	84 (9)	7 (2)	H(312)	217 (3)	320 (4)	262 (8)	3 (1)
H(121)	494 (3)	427 (5)	-152 (11)	14 (3)	H(321)	171 (3)	234 (5)	377 (12)	13 (3)
H(122)	539 (3)	416 (4)	-32 (11)	16 (4)	H(322)	211 (3)	269 (5)	473 (11)	13 (3)
H(123)	512 (3)	350 (5)	-139 (11)	13 (3)	H(323)	148 (4)	281 (5)	513 (11)	12 (3)

Table 3. Observed and calculated structure factors
Columns are h, 10F_o, and 10F_c. Unobserved reflections are marked with *.

Table with multiple columns containing numerical data for observed and calculated structure factors. The table is organized into groups by Miller indices (h, k, l) and includes observed (F_o) and calculated (F_c) values. Unobserved reflections are marked with an asterisk (*).

Discussion

The crystal consists of discrete molecules. The projection of atomic coordinates on (001), shown in Fig. 2, illustrates the pseudo-tetrahedral coordination configuration about the nickel atom.

Least-squares equations for selected planes within the molecule are listed in Table 4. The salicyaldimine groups are quite planar, only C(7) (0.06 Å), O(1) (0.07 Å), C(27) (0.08 Å), and O(2) (0.06 Å) lying slightly but significantly out of the plane defined by the benzene ring. As in many salicyaldimine chelates, the nickel atom is found to be significantly out of the plane defined by the salicyaldimine group, lying 0.30 Å out of the plane in one case and 0.22 Å in the other. Various dihedral angles between the least-squares planes illustrate several important features of this structure. First, the dihedral angle between the coordination plane defined by atoms Ni, O(1), and N(1) and the coordination plane defined by atoms Ni, O(2), and N(2) can be taken as a measure of the flattening of the coordination tetrahedron. This angle is 85.3°, compared with the corresponding angle of 81.5° in bis-(*N*-isopropylsalicyaldiminato)nickel (Fox, Orioli, Lingafelter & Sacconi, 1964) and 60° in bis-(*N*-isopropylsalicyaldiminato)copper (Orioli & Sacconi, 1966). Secondly the average dihedral angle between an isopropyl group and its salicyaldimine residue is 90°, significantly greater than the value of 79° found for this angle in the planar chelate bis-(*N*-isopropyl-3-methylsalicyaldiminato)nickel (Braun & Lingafelter, 1966). This movement of the isopropyl group in the planar chelate from the perpendicular position in the tetrahedral chelate may be a reflection of the appreciable steric interaction involving the isopropyl group in the planar chelate. Finally, the dihedral angle of 6.0° between the plane of the benzene ring and the plane defined by atoms C(3), C(11), and C(12) is very different from the corresponding angle of 84.0° between the plane of the benzene ring and the plane defined by atoms C(23), C(31), and C(32). This may illustrate the effect of crystal packing forces on the rotational freedom about the C(3)–C(11) and C(23)–C(31) bonds. The corresponding single independent angle in bis-(*N*-isopropyl-3-ethylsalicyaldiminato)palladium (Braun & Lingafelter, 1967) is 87.1°.

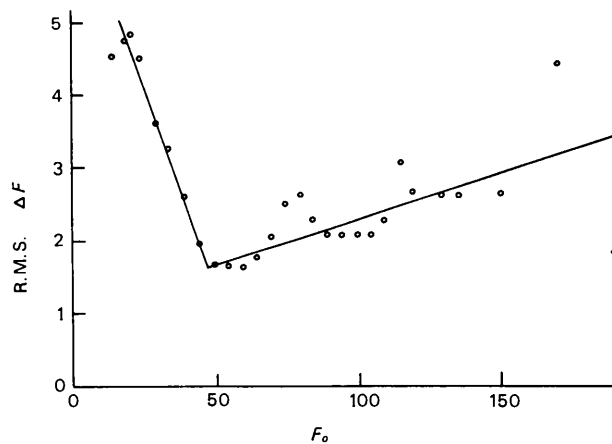


Fig. 1. Root-mean-square ΔF vs F_o at $R=0.06$.

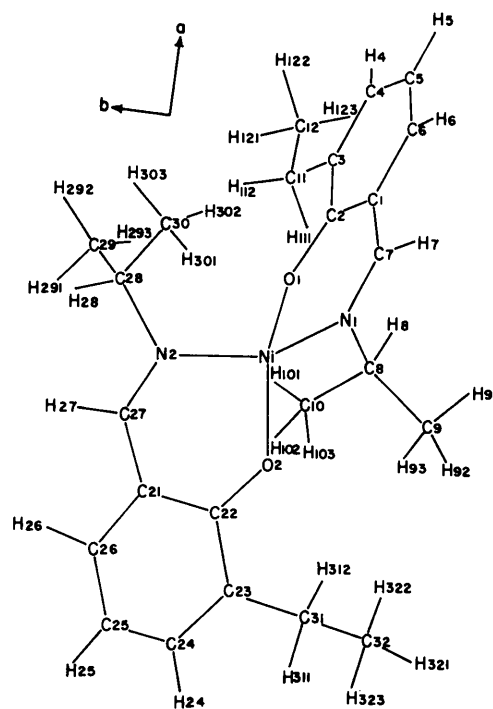


Fig. 2. Projection of one molecule on (001).

Table 4. Coefficients of least-squares plane equations, $A(x/a) + B(y/b) + C(z/c) = D^*$

Plane	A	B	C	D
Coordination (1)	13.004	15.278	3.707	12.199
Coordination (2)	-2.130	-7.016	8.223	-0.006
Benzene (1)	7.853	17.388	3.420	10.779
Benzene (2)	-0.861	9.371	-7.774	0.291
Salicyaldimine (1)	7.984	17.214	3.557	10.831
Salicyaldimine (2)	-1.092	8.992	-7.858	0.029
Isopropyl (1)	-2.900	8.981	-7.811	-3.801
Isopropyl (2)	6.209	17.437	3.719	13.640
C(3)–C(11)–C(12)	9.773	17.461	2.750	11.593
C(23)–C(31)–C(32)	26.497	-3.607	-0.119	3.777

* D = origin-to-plane distance in Å.

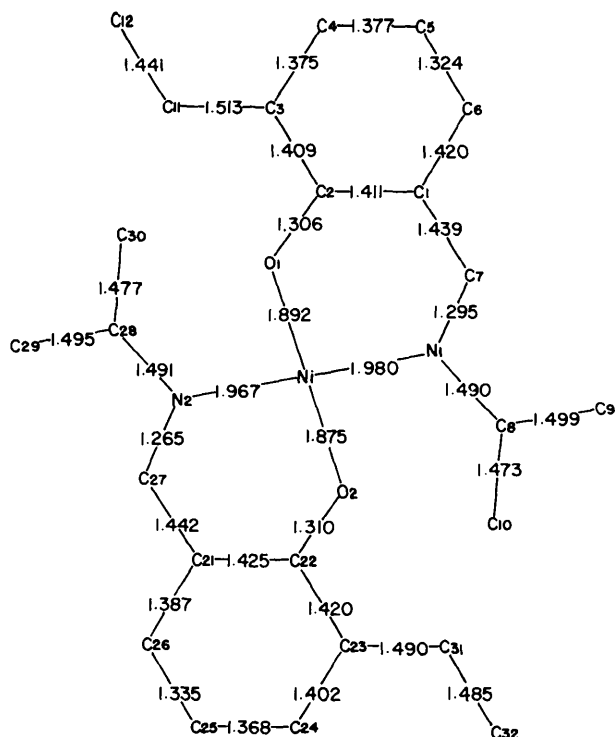


Fig. 3. Bond distances. Average values of the estimated standard deviations (Å) are: Ni-O, 0.004; Ni-N, 0.006; O-C, 0.007; N-C, 0.010; C-C, 0.013.

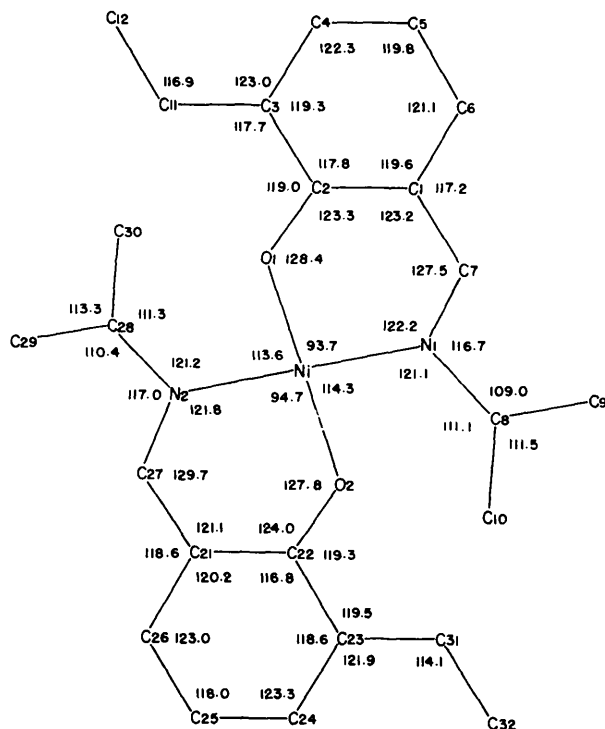


Fig. 4. Bond angles. Average values of the estimated standard deviations (°) are: O-Ni-O, O-Ni-N, N-Ni-N, 0.2; Ni-O-C, Ni-N-C, 0.4; N-C-C, O-C-C, C-N-C, C-C-C, 0.7.

Bond lengths and angles involving the heavy atoms are shown in Figs. 3 and 4 and carbon-hydrogen distances are listed in Table 5. The average Ni-O and Ni-N distances of 1.884 and 1.974 Å agree well with the corresponding average distances of 1.896 and 1.970 Å in the related tetrahedral chelate bis-(*N*-isopropylsalicylaldiminato)nickel (Fox, Orioli, Lingafelter & Sacconi, 1964). The average Ni-O distance is 0.047 Å longer and the average Ni-N distance is 0.054 Å longer than the corresponding distances of 1.837 and 1.920 Å in the planar chelate bis-(*N*-isopropyl-3-methylsalicylaldiminato)nickel (Braun & Lingafelter, 1966), reflecting the decreased strength of the σ coordination bonds (Pauling, 1960) and possibly less favorable $d\pi$ - $p\pi$ interaction in the tetrahedral chelates. The intrachelate angles of 93.7° for O(1)-Ni-N(1) and 94.7° for O(2)-Ni-N(2) are appreciably smaller than the normal tetrahedral angle of 109°28'. This may be partially or entirely caused by the constraints imposed by the chelating agent.

Table 5. C-H bond distances and their *e.s.d.*'s

C(4)-H(4)	0.79 (6) Å	C(24)-H(24)	0.83 (7) Å
C(5)-H(5)	0.90 (6)	C(25)-H(25)	0.95 (7)
C(6)-H(6)	0.90 (7)	C(26)-H(26)	0.94 (6)
C(7)-H(7)	0.82 (6)	C(27)-H(27)	0.86 (6)
C(8)-H(8)	1.05 (6)	C(28)-H(28)	0.89 (7)
C(9)-H(91)	0.95 (7)	C(29)-H(291)	1.07 (9)
C(9)-H(92)	1.03 (8)	C(29)-H(292)	1.00 (8)
C(9)-H(93)	0.89 (8)	C(29)-H(293)	0.73 (9)
C(10)-H(101)	0.77 (8)	C(30)-H(301)	0.99 (8)
C(10)-H(102)	1.05 (8)	C(30)-H(302)	0.80 (8)
C(10)-H(103)	1.02 (8)	C(30)-H(303)	1.01 (8)
C(11)-H(111)	1.16 (7)	C(31)-H(311)	1.06 (7)
C(11)-H(112)	0.93 (7)	C(31)-H(312)	1.05 (7)
C(12)-H(121)	0.91 (9)	C(32)-H(321)	1.06 (10)
C(12)-H(122)	1.14 (9)	C(32)-H(322)	0.82 (9)
C(12)-H(123)	1.05 (10)	C(32)-H(323)	1.09 (10)

Because of the high thermal parameters of the terminal carbon atoms in the isopropyl and ethyl groups, the accuracy of the bond lengths within these groups should not be considered as good as their precision of 0.01 to 0.02 Å. For example, the four internal bond lengths of the isopropyl groups average only 1.486 Å, considerably less than the normal length of a C(sp^3)-C(sp^3) bond. The apparent C(11)-C(12) bond length of 1.441 Å in one ethyl group is particularly affected by the high thermal motion. This bond length, when averaged over thermal motion (Busing & Levy, 1964) with C(12) riding on C(11), is lengthened to 1.467 Å and, with C(11) and C(12) moving independently, is lengthened to 1.614 Å. The joint thermal motion of these two atoms thus appears to be somewhat more independent than a simple riding motion.

Examination of the non-bonded intramolecular distances, listed in Table 6, substantiates the conclusion that the close intramolecular contacts involving the isopropyl group which were observed in the planar chelate bis-(*N*-isopropyl-3-methylsalicylaldiminato)nic-

kel (Braun & Lingafelter, 1966) are indeed relieved by distortion toward a tetrahedral configuration. For example, the short H(8)---O' distance of 2.20 Å in the planar chelate has increased to 4.51 Å for H(28)---O(1) and 4.66 Å for H(8)---O(2) and the short H(7)---H(93) distance of 2.2 Å has increased to >2.9 Å. Furthermore, there does not appear to be any unfavorable steric interaction between the ethyl and isopropyl groups. There is, however, some indication of unfavorable steric interaction between the benzene ring and the ethyl group which is essentially in the plane of the benzene ring. That is, the distances of 2.54 Å for C(12)---H(4) and 2.1 Å for H(122)---H(4) are appreciably less than the sums of the van der Waals radii, 3.2 and 2.4 Å, respectively.

Examination of the intermolecular contact distances shows no unreasonable values, the shortest distances being 2.5 Å for H---H, 2.62 Å for O---H, 3.54 Å for N---H, 2.87 Å for C(sp²)---H, 3.03 Å for C(sp³)---H,

3.61 Å for C(sp²)---C(sp²), 3.68 Å for C(sp²)---C(sp³), and 3.67 Å for C(sp³)---C(sp³).

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Table 6. Intramolecular distances (Å)

	C(9)	H(91)	H(92)	H(93)	C(10)	H(101)	H(102)	H(103)
C(7)	3.23	2.92	4.10	3.60	3.51	3.57	3.89	4.42
H(7)	3.30	2.9	4.0	3.8	3.75	3.8	4.3	4.5
H(8)	2.15	2.3	2.5	2.8	2.03	2.3	2.9	2.5
O(2)	3.61	4.13	4.31	2.89	3.56	3.83	2.67	4.20
C(31)	4.82	*	*	3.94	*	*	4.45	*
H(311)	*	*	*	5.0	*	*	*	*
H(312)	4.71	*	*	3.8	*	*	4.6	*
C(32)	4.25	4.84	4.27	3.44	*	*	4.42	*
H(321)	4.78	*	4.8	4.0	*	*	*	*
H(322)	3.44	4.0	3.5	2.6	4.46	*	3.8	4.5
H(323)	4.92	*	4.8	4.2	*	*	4.8	*
	C(29)	H(291)	H(292)	H(293)	C(30)	H(301)	H(302)	H(303)
C(27)	3.27	3.22	4.13	3.50	3.45	3.46	3.74	4.21
H(27)	3.31	3.2	4.0	3.7	3.53	3.6	4.0	4.1
H(28)	1.97	2.4	2.4	2.5	1.93	2.4	2.5	2.2
O(1)	3.51	3.95	4.23	2.88	3.76	4.20	3.12	4.54
C(11)	4.66	4.95	4.96	3.94	*	*	4.94	*
H(111)	*	*	*	4.5	*	*	*	*
H(112)	3.79	4.1	4.1	3.1	4.95	*	4.4	*
C(12)	*	*	*	*	*	*	*	*
H(121)	*	*	*	*	*	*	*	*
H(122)	*	*	*	*	*	*	*	*
H(123)	*	*	*	*	*	*	*	*
	C(11)	H(111)	H(112)	C(12)	H(121)	H(122)	H(123)	
O(1)	2.75	3.04	2.54	4.19	4.61	4.60	4.77	
C(28)	*	*	4.74	*	*	*	*	
H(28)	*	*	*	*	*	*	*	
H(4)	2.58	3.4	3.1	2.54	3.4	2.1	2.6	
	C(31)	H(311)	H(312)	C(32)	H(321)	H(322)	H(323)	
O(2)	2.80	3.71	2.50	3.52	4.23	3.06	4.30	
C(8)	*	*	*	*	*	4.46	*	
H(8)	*	*	*	*	*	*	*	
H(24)	2.68	2.6	3.6	3.34	4.1	3.8	3.0	
	C(28)	H(28)	N(1)					
O(1)	3.64	4.51	2.826					
	C(8)	H(8)	N(2)					
O(2)	3.64	4.66	2.827					

* Distance is greater than 5.0 Å.

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The Crystal Structure of Bis-(*N*-isopropyl-3-ethylsalicylaldiminato)palladium

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The crystal structure of bis-(*N*-isopropyl-3-ethylsalicylaldiminato)palladium, Pd(C₁₂H₁₆NO)₂, has been determined from three-dimensional data collected on a single-crystal diffractometer with Mo *K*α radiation. The cell has dimensions *a* = 10.672, *b* = 13.063, and *c* = 7.998 Å, belongs to space group *P*2₁/*a*, and contains two molecules. The structure consists of discrete molecules in which palladium(II) has strictly planar coordination configuration. The molecular structure shows the steric factors which cause the tetrahedral configuration to appear for the corresponding nickel(II) chelate.

Introduction

It has been shown (Holm & Swaminathan, 1963) that 3-substituted bis-(*N*-isopropylsalicylaldiminato)nickel chelates exist in a conformational equilibrium between a planar species and a tetrahedral species in toluene solution. In the crystalline state, however, these chelates exhibit a striking alternation in coordination configuration as the 3-substituent is changed from hydrogen to methyl to ethyl. That is, consistent with the magnetic moments reported by Holm & Swaminathan (1963), the coordination configurations have been shown to be tetrahedral for the 3-hydrogen chelate (Fox, Orioli, Lingafelter & Sacconi, 1964), planar for the 3-methyl chelate (3-M-Ni: Braun & Lingafelter, 1966), and tetrahedral for the 3-ethyl chelate (3-E-Ni: Braun & Lingafelter, 1967). The molecular structure of the planar chelate 3-M-Ni has shown the steric factors which cause the tetrahedral configuration to appear for *N*-isopropylsalicylaldimine chelates. In order to examine the intramolecular steric interactions of the planar 3-ethyl chelate, we have now completed the crystal structure determination of bis-(*N*-isopropyl-3-ethylsalicylaldiminato)palladium (3-E-Pd) by three-dimensional X-ray diffraction techniques.

Experimental

Bis-(*N*-isopropyl-3-ethylsalicylaldiminato)palladium was prepared by the method of Sacconi, Paoletti & Del Re (1957), using 3-ethylsalicylaldehyde which was

prepared according to the general procedure of the Duff (1941) reaction. Final purification was accomplished by two recrystallizations from equal volumes of chloroform and ligroin by slow evaporation at room temperature. The crystal used for determination of cell dimensions and collection of intensity data was a well-defined rhomb, tabular on (001) and bounded by {011}, approximate dimensions 0.25 × 0.20 × 0.12 mm.

Cell dimensions were determined on a Picker X-ray diffractometer equipped with a General Electric goniostat, using Mo *K*α radiation ($\lambda = 0.71069$ Å). The cell dimensions with their standard deviations are

$$\begin{aligned} a &= 10.672 \pm 0.002 \text{ \AA} \\ b &= 13.063 \pm 0.002 \\ c &= 7.998 \pm 0.001 \\ \beta &= 98.09 \pm 0.01^\circ \end{aligned}$$

Systematic absences of *0k0* for *k* odd and *h0l* for *h* odd identified the space group as *P*2₁/*a*. The cell contains two molecules: measured density 1.47 g.cm⁻³, calculated density 1.465 g.cm⁻³.

The intensity data were collected by the ω -2 θ scan method (Furnas, 1957), using zirconium-filtered Mo *K*α radiation and a Picker diffractometer equipped with a scintillation counter, pulse-height discriminator, and a General Electric single-crystal goniostat. A suitable scan range for each reflection was calculated by the formula of Alexander & Smith (1964), scan range = 1.8 + 1.0(tan θ). Stationary background measurements were made at the start and finish of each scan. Of the 2061 reflections which were examined within the limit-