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

BY R. L. BRAUN AND E. C. LINGAFELTER

*Department of Chemistry, University of Washington, Seattle, Washington 98105, U.S.A.*

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The crystal structure of bis-(*N*-isopropyl-3-ethylsalicylaldiminato)palladium, Pd(C<sub>12</sub>H<sub>16</sub>NO)<sub>2</sub>, 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*2<sub>1</sub>/*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 ( $\lambda = 0\cdot71069$  Å). The cell dimensions with their standard deviations are

$$\begin{aligned} a &= 10\cdot672 \pm 0\cdot002 \text{ \AA} \\ b &= 13\cdot063 \pm 0\cdot002 \\ c &= 7\cdot998 \pm 0\cdot001 \\ \beta &= 98\cdot09 \pm 0\cdot01^\circ. \end{aligned}$$

Systematic absences of *0k0* for *k* odd and *h0l* for *h* odd identified the space group as *P*2<sub>1</sub>/*a*. The cell contains two molecules: measured density 1·47 g.cm<sup>-3</sup>, calculated density 1·465 g.cm<sup>-3</sup>.

The intensity data were collected by the  $\omega$ -2 $\theta$  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  $\theta$ ). Stationary background measurements were made at the start and finish of each scan. Of the 2061 reflections which were examined within the limit-

ing Cu  $K\alpha$  sphere, 1556 reflections had an intensity ( $I$ ) greater than twice the standard deviation of the intensity ( $2\sigma_I$ ). These 1556 reflections ranged in intensity from 1 to 18,000. The remaining 505 reflections were coded 'unobserved' and were assigned an intensity of  $2\sigma_I$  for later least-squares refinement.

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  $\pm 0.5\%$  due primarily to counting statistics. These periodic scale factors were not applied.

### 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 Thomas & Umeda (1957) for palladium, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen, and carbon, and those from Table II of Stewart, Davidson & Simpson (1965) for hydrogen. No correction was made for anomalous dispersion.

Since there are two molecules in the cell of space group  $P2_1/a$ , the palladium atoms are required to be at centers of symmetry. A three-dimensional Fourier synthesis was calculated, using phases determined by the palladium atoms at (0,0,0) and  $(\frac{1}{2}, \frac{1}{2}, 0)$ . Such a Fourier synthesis shows mirror planes in  $(x, 0, z)$  and  $(x, \frac{1}{2}, z)$ . Another three-dimensional Fourier synthesis phased on the palladium atom and on a nitrogen atom arbitrarily selected from the mirror-related pair at 2 Å from the palladium atom destroyed the pseudo-mirror planes. This and a third Fourier synthesis enabled the positions of all 15 non-hydrogen atoms to be determined and resulted in a reduction of  $R$  to 0.15.  $R$  is defined throughout as  $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ , 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  $\Sigma w(|F_o| - |F_c|)^2$ , where  $w=1$  for observed reflections and for unobserved reflections for which  $F_c > F_o$  and  $w=0$  for unobserved reflections for which  $F_c \leq F_o$ . Three cycles of least-squares refinement using individual isotropic temperature factors followed by one cycle using individual anisotropic temperature factors reduced  $R$  to 0.046. Introduction of all 16 hydrogen atoms, which had been clearly located from a three-dimensional  $\Delta F$  synthesis, reduced  $R$  to 0.039. Two more cycles of refinement of the non-hydrogen atoms with anisotropic temperature factors and four cycles of refinement of the hydrogen atoms with individual isotropic temperature factors reduced  $R$  to 0.024. During these and all subsequent least-squares calculations, the calculated structure factor contributions of the parameters not being refined were included as fixed contributions.

Considering the root-mean-square  $\Delta F$  as an average standard deviation, a weighting scheme for further

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

	Positional parameter $\times 10^3$			Thermal parameter
	$x/a$	$y/b$	$z/c$	$B$
H(4)	-226 (3)	87 (2)	657 (4)	4 (1)
H(5)	-77 (3)	219 (3)	710 (5)	5 (1)
H(6)	55 (3)	256 (3)	514 (4)	4 (1)
H(7)	131 (3)	223 (3)	272 (4)	4 (1)
H(8)	180 (3)	148 (3)	-111 (5)	4 (1)
H(91)	247 (4)	305 (3)	-74 (6)	7 (1)
H(92)	105 (4)	306 (3)	-64 (5)	7 (1)
H(93)	208 (4)	319 (3)	99 (6)	7 (1)
H(101)	375 (4)	154 (3)	32 (5)	7 (1)
H(102)	342 (4)	157 (3)	207 (6)	7 (1)
H(103)	323 (4)	57 (4)	103 (5)	7 (1)
H(111)	-247 (3)	-100 (3)	351 (4)	5 (1)
H(112)	-304 (3)	-60 (2)	513 (4)	4 (1)
H(121)	-464 (4)	-51 (4)	293 (6)	7 (1)
H(122)	-440 (5)	50 (5)	377 (7)	10 (1)
H(123)	-389 (6)	18 (4)	174 (8)	11 (1)

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 $\times 10^2$					
	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Pd	0	0	0	255 (1)	249 (1)	314 (1)	-10 (1)	53 (1)	-16 (1)
O	-1138 (2)	72 (1)	1767 (2)	319 (7)	328 (8)	357 (7)	-51 (7)	117 (6)	-60 (7)
N	950 (2)	1269 (2)	938 (3)	276 (8)	265 (9)	323 (9)	-43 (7)	48 (7)	-17 (7)
C(1)	-111 (2)	1431 (2)	3466 (3)	320 (11)	283 (10)	333 (10)	26 (8)	56 (8)	4 (8)
C(2)	-1012 (2)	643 (2)	3127 (3)	294 (10)	282 (10)	316 (10)	70 (8)	62 (8)	18 (8)
C(3)	-1853 (3)	454 (2)	4338 (3)	351 (12)	319 (10)	378 (11)	57 (9)	106 (9)	31 (9)
C(4)	-1755 (3)	1049 (2)	5771 (4)	471 (14)	437 (14)	380 (12)	35 (11)	188 (11)	1 (11)
C(5)	-874 (3)	1830 (3)	6088 (4)	575 (16)	459 (14)	359 (12)	17 (13)	139 (11)	-95 (12)
C(6)	-64 (3)	2012 (2)	4964 (4)	449 (13)	345 (11)	385 (11)	-17 (12)	72 (9)	-56 (11)
C(7)	776 (3)	1689 (2)	2340 (3)	341 (11)	284 (10)	342 (11)	-50 (9)	24 (8)	-42 (8)
C(8)	1967 (3)	1706 (2)	49 (4)	369 (12)	374 (12)	396 (12)	-130 (9)	129 (10)	-65 (10)
C(9)	1919 (4)	2864 (3)	-87 (6)	627 (21)	417 (16)	599 (19)	-168 (15)	230 (17)	25 (15)
C(10)	3227 (4)	1325 (4)	897 (7)	378 (16)	708 (25)	813 (26)	-24 (16)	201 (16)	87 (21)
C(11)	-2830 (3)	-393 (3)	4046 (4)	411 (14)	406 (13)	472 (14)	-18 (11)	187 (11)	21 (11)
C(12)	-4052 (4)	-41 (4)	3014 (7)	473 (18)	648 (20)	821 (18)	-130 (14)	42 (15)	12 (18)

least-squares refinement was taken from a plot of r.m.s. ΔF vs F\_0 to be |w|=1/(0.70-0.0053 F\_0) for unobserved reflections for which F\_c > F\_0 and for observed reflections and w=0 for unobserved reflections for which F\_c ≤ F\_0. The final value of R=0.023 was then

reached in two cycles of anisotropic refinement of the non-hydrogen atoms and four cycles of isotropic refinement of the hydrogen atoms. All reflections with sin θ/λ > 0.48 were omitted during the refinement of the hydrogen atoms. In the final cycle of non-hydrogen

Table 3. Observed and calculated structure factors. Columns are h, 10|F\_o|, and 10F\_c. Unobserved reflections are marked with\*.

Table with 3 main columns: h, 10|F\_o|, and 10F\_c. The table contains a grid of numerical values for various h values (e.g., 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000).

atom refinement the average shift/error for positional and thermal parameters was 0.03, with a maximum of 0.21. In the final cycle of hydrogen atom refinement the average shift/error was 0.03 with a maximum of 0.43.

The final parameters and their estimated standard deviations are listed in Tables 1 and 2. The  $\sigma$ 's were obtained by simultaneous refinement of all parameters except those of C(12), H(121), H(122), and H(123), using full data for non-hydrogen  $\sigma$ 's and limited data for hydrogen  $\sigma$ 's. For the four omitted atoms, which exceeded the capacity of the full-matrix least-squares program,  $\sigma$ 's were obtained by application of an empirical correction factor. 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.

### Discussion

The crystal consists of discrete molecules. Fig. 1 shows the projection of atomic coordinates on (010). Since the palladium atom is at a center of symmetry, it has strictly planar coordination.

Bond lengths and angles involving the heavy atoms are shown in Fig. 2 and the C-H distances are listed in Table 4. The Pd-N bond length of 2.031 Å agrees well with the values of 2.030 and 2.043 Å in bis(ethylenediamine)palladium(II) chloride (Wiesner & Lingafelter, 1966), 2.022 Å in bis-(2,2'-dipyridyliminato)palladium (Freeman & Snow, 1965), and 2.01 Å in bis-(*N*-n-butylsalicylaldiminato)palladium (Frasson, Panattoni & Sacconi, 1964). The Pd-O bond length of 1.991 Å agrees well with the values of 2.00 Å in palladium(II) oxide (Pauling & Huggins, 1934) and 2.00 Å in bis-(*N*-n-butylsalicylaldiminato)palladium (Frasson, Panattoni & Sacconi, 1964).

Table 4. Carbon-hydrogen bond distances and their e.s.d.'s

C(4)-H(4)	0.92 (4) Å	C(10)-H(101)	0.83 (5) Å
C(5)-H(5)	0.93 (4)	C(10)-H(102)	0.98 (5)
C(6)-H(6)	0.97 (4)	C(10)-H(103)	0.99 (5)
C(7)-H(7)	0.92 (4)	C(11)-H(111)	1.00 (4)
C(8)-H(8)	0.96 (4)	C(11)-H(112)	0.97 (4)
C(9)-H(91)	0.88 (5)	C(12)-H(121)	0.87 (5)
C(9)-H(92)	1.00 (4)	C(12)-H(122)	1.03 (6)
C(9)-H(93)	0.96 (5)	C(12)-H(123)	1.09 (6)

The C-C bonds of the salicylaldimine residue again have the trend which has been found for the average bond lengths of eight salicylaldimine chelates (Lingafelter & Braun, 1966); namely, the interatomic distances C(3)-C(4), C(4)-C(5), and C(5)-C(6) are less than 1.386 Å, while the interatomic distances C(1)-C(2), C(2)-C(3), C(6)-C(1), and C(1)-C(7) are greater than 1.409 Å. The small average standard deviation of 0.005 Å for a C-C bond in this heavy metal chelate illustrates the good precision which can be achieved with diffractometer data, even with the use of Mo K $\alpha$  radiation without balanced filters.

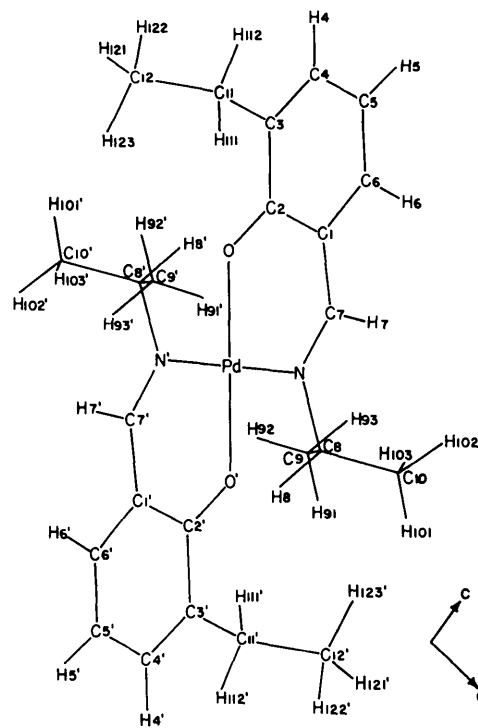


Fig. 1. Projection on (010).

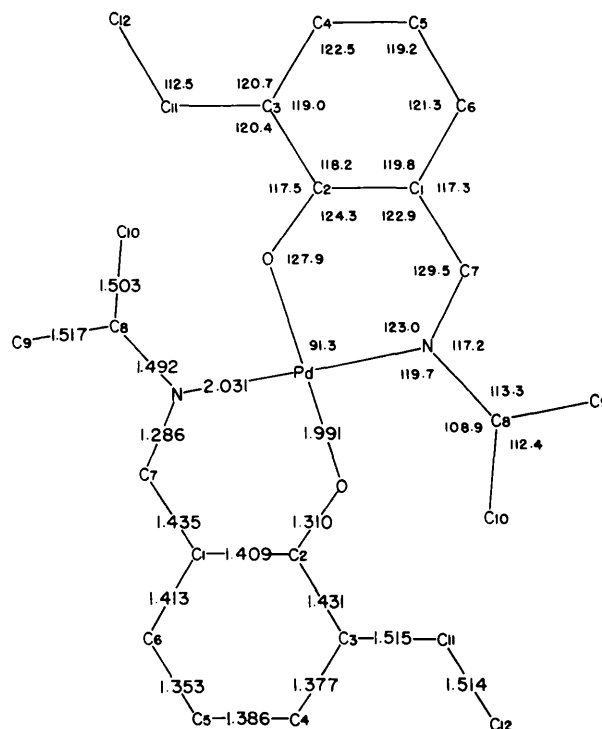


Fig. 2. Interatomic distances and angles. Average values of the estimated standard deviations are: Pd-O, Pd-N, 0.002 Å; O-C, N-C, 0.003 Å; C-C, 0.004 Å; O-Pd-N, 0.1°; Pd-O-C, 0.2°; O-C-C, N-C-C, C-C-C, 0.3°.

Least-squares equations for selected planes within the molecule and the angles between these planes are listed in Tables 5 and 6. The effective 'step' of 0.42 Å between the parallel salicylaldimine planes of the molecule is appreciably less than the step of 0.76 Å in the related planar nickel chelate, 3-M-Ni. In addition, while atoms N and C(7) in the latter nickel chelate were found to have large deviations (0.187 and 0.170 Å, respectively) from the plane of the benzene ring, in this case the deviations of these two atoms are significantly less (0.024 and 0.007 Å respectively). Thus the entire salicylaldimine group is quite closely planar.

Table 5. Coefficients of least-squares plane equations

Plane	$A(x/a) + B(y/b) + C(z/c) = D^*$			
	A	B	C	D*
Coordination	-5.939	7.497	-4.130	0
Benzene	-6.317	8.493	-3.106	0.210
Salicylaldimine	-6.286	8.529	-3.107	0.213
Isopropyl	-4.875	0.684	7.546	-0.806
C(3)-C(11)-C(12)	-5.089	3.397	7.186	4.214

\* D = origin-to-plane distance (Å).

Table 6. Angles between least-squares planes

Plane (1)	Plane (2)	Angle
Coordination	Benzene	8.6°
Coordination	Salicylaldimine	8.7
Salicylaldimine	Benzene	0.2
Salicylaldimine	Isopropyl	83.1
Benzene	Isopropyl	83.2
Benzene	C(3)-C(11)-C(12)	87.1

The non-bonded intramolecular steric interactions which cause a species of tetrahedral configuration to appear in equilibrium (Holm & Swaminathan, 1963) with a species of planar configuration for solutions of bis-(*N*-isopropyl-3-alkylsalicylaldiminato)nickel chelates have been described in detail from the crystal struc-

ture of 3-M-Ni (Braun & Lingafelter, 1966). Further confirmation of these steric interactions is given by the non-bonded intramolecular distances listed in Table 7. That is, the unfavorable steric interactions involving the hydrogen atoms of the isopropyl group are again evident, particularly in the distances of 2.19 Å for H(8)---O', compared with the sum of the van der Waals radii of 2.6 Å (Pauling, 1960), and the distance of 2.1 Å for H(7)---H(93), compared with the radii sum of 2.4 Å. In the planar chelate 3-M-Ni these distances were 2.20 and 2.2 Å, respectively, while in the tetrahedral chelate 3-E-Ni they were >4.51 and >2.9 Å, respectively.

The most important result of this structure determination is the characterization of the steric interactions between the 3-alkyl substituent and the *N*-isopropyl group. This is important in examining the apparent increase in the stability of the tetrahedral species of the nickel chelates in toluene solution (Holm & Swaminathan, 1963) as the 3-substituent is changed from hydrogen to methyl to ethyl. Although Holm & Swaminathan (1963) reported that metal chelate scale models indicate unfavorable interaction in a planar structure between the isopropyl group and the 3-substituent, only slight steric interaction between these groups is found in the crystal structures. Table 8 summarizes the non-bonded intramolecular contacts between these two groups for the three 3-alkyl chelates whose structures are known: 3-M-Ni, 3-E-Ni, and 3-E-Pd. The two independent distances in 3-E-Ni are listed separately because of the marked difference in the positions of the two 3-ethyl groups.

Examining first the contacts involving atom C(11), it is seen that the C(11)---C(9') distances are normal in the tetrahedral and planar chelates. Although the C(11)---C(10') distances of 3.71 Å in 3-M-Ni and 4.10 Å in 3-E-Pd are quite close to the radii sum of

Table 7. Intramolecular distances (Å)

The primed atoms are related to the unprimed atoms by the center of symmetry.								
	C(9)	H(91)	H(92)	H(93)	C(10)	H(101)	H(102)	H(103)
C(7)	2.878	3.71	3.02	2.71	3.042	3.77	2.86	3.29
H(7)	2.56	3.4	2.9	2.1	2.92	3.6	2.5	3.4
H(8)	1.98	2.2	2.2	2.8	2.06	2.2	2.9	2.4
O'	4.110	4.36	4.19	4.84	3.391	3.70	4.22	3.04
C(11')	4.717	4.42	4.96	*	4.101	3.80	*	4.03
H(111')	3.77	3.5	4.0	4.7	3.53	3.2	4.5	3.6
H(112')	*	4.9	*	*	4.89	4.5	*	4.9
C(12')	*	4.74	*	*	3.762	3.35	4.66	3.54
H(121')	4.99	4.5	*	*	3.76	3.2	4.6	3.7
H(122')	*	*	*	*	4.75	4.3	*	4.4
H(123')	4.77	4.6	*	*	3.04	2.8	3.9	2.6
	C(11)	H(111)	H(112)	C(12)	H(121)	H(122)	H(123)	
O	2.807	2.55	3.70	3.400	4.05	4.07	2.94	
C(8')	3.920	3.11	4.68	4.149	4.27	*	3.62	
H(8')	3.08	2.2	3.8	3.56	3.8	4.5	3.2	
H(4)	2.62	3.5	2.3	3.42	4.0	3.0	4.1	
	C(8')	H(8')	N					
O	2.815	2.19	2.875					

\* Distance is greater than 5.0 Å.

Table 8. *Intramolecular contacts between the N-isopropyl group and the 3-alkyl substituent (Å)*

C(11)	Tetrahedral		Planar	
	3-E-Ni I	3-E-Ni II	3-M-Ni	3-E-Pd
C(11)---C(8')	*	*	3.77	3.92
C(11)---C(9')	4.66	4.82	4.79	4.72
C(11)---C(10')	*	*	3.71	4.10
Minimum between H[C(11)]---H(8')	4.74	*	2.3	2.2
Minimum between H[C(11)]---H[C(9')]	3.1	3.8	3.5	3.5
Minimum between H[C(11)]---H[C(10')]	4.4	4.6	2.8	3.2
C(12)				
C(12)---C(8')	*	*		4.15
C(12)---C(9')	*	4.25		*
C(12)---C(10')	*	*		3.76
Minimum between H[C(12)]---H(8')	*	*		3.2
Minimum between H[C(12)]---H[C(9')]	*	2.6		4.5
Minimum between H[C(12)]---H[C(10')]	*	3.8		2.6

\* Greater than 5.0 Å.

4.0 Å, neither of these contacts is seriously close, since the H---H distances between C(11) and C(10') are >2.8 Å for 3-M-Ni and >3.2 Å for 3-E-Pd, well above the radii sum of 2.4 Å. The only evidence of unfavorable steric interaction in the planar chelates involving atom C(11) is found in the C(11)---C(8') contact. That is, the C(11)---C(8') distances of 3.77 Å in 3-M-Ni and 3.92 Å in 3-E-Pd are slightly less than the radii sum of 4.0 Å. This intramolecular contact may indeed be of some steric importance, since the H(111)---H(8') distances of 2.3 and 2.2 Å in these two planar chelates are also slightly less than the radii sum of 2.4 Å.

Examining next the contacts involving atom C(12), it is seen that the C(12)---C(8') distances and the C(12)---C(9') distances are normal in both 3-E-Ni and 3-E-Pd, but that the C(12)---C(10') distance in 3-E-Pd is 3.76 Å, slightly less than the radii sum of 4.0 Å. This is probably not a seriously close contact, since the minimum H---H distance between the C(12) methyl group and the C(10') methyl group is 2.6 Å between H(123) and H(103'), well above the radii sum of 2.4 Å. In view of the absence of any seriously close intramolecular contacts involving the 3-substituent, it is likely that the steric interactions indicated for a planar structure by the scale models are in actuality somewhat alleviated by the sizable step between the parallel salicylaldimine residues.

Even though the intramolecular contacts involving the 3-substituent are not seriously close, they are close enough in the planar chelates to severely restrict free rotation of the methyl and ethyl groups. Among these chelates, the entropy increase which would be achieved by the increased rotational freedom of the 3-substituent when the coordination configuration is changed from planar to tetrahedral would likely follow the sequence

hydrogen < methyl < ethyl. Thus, the increasing stability of the tetrahedral species in solution as the 3-substituent is changed from hydrogen to methyl to ethyl would be explained by an entropy effect.

Examination of the intermolecular contact distances shows only one which requires comment: the distance of 3.619 Å between C(12) and C(10) is less than the sum of the radii for two methyl groups, 4.0 Å. This apparently close intermolecular contact is explicable in terms of the high thermal parameters of C(10) and C(12). The remaining distances are normal, the closest intermolecular contacts being 2.5 Å for H---H, 2.98 Å for O---H, 3.56 Å for N---H, 2.90 Å for C(sp<sup>2</sup>)---H, 3.13 Å for C(sp<sup>3</sup>)---H, 3.536 Å for C(sp<sup>2</sup>)---C(sp<sup>2</sup>), 3.735 Å for C(sp<sup>2</sup>)---C(sp<sup>3</sup>).

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