1.47 (1.48) Å. for complex A (C) agree within experimental error with the average value of 1.44 Å. for the nickel complex. The average value of 1.46 Å. for the three metal complexes appears to be significantly longer than the average values of 1.36 and 1.38 Å. found for the open allylic fragment in $[(C_3H_5)PdCl]_2$.[25,26] These longer allylic bonds for the cyclobutenyl–metal complexes may be inherent in the strained four-membered carbon ring system and do not necessarily reflect a difference in the strength of interaction between the metal and the two types of allylic fragments present. This conclusion is supported by the average allylic C–C bond length of 1.41 Å. found[30] for the uncomplexed cyclobutenium cation in $[(C_6H_5)_4C_4Cl]^+SnCl_5^-$.

The average bond length of the allylic carbons to the phenyl carbons in complex A (C) is 1.46 (1.45) Å., whereas a bond length of 1.52 (1.54) Å. is observed between the cyclobutenyl tetrahedral carbon and its bonded phenyl carbon. The cyclobutenyl ring bond angles for the three metal complexes (Figure 4) are similar to those in the cyclobutenium ring, and all are reduced by equivalent amounts from the *ideal* strain-free values. For all four rings (Figure 4) the bonds from the ring carbons to the attached allylic ring substituents essentially bisect the external angles (*i.e.*, ~133 ± 8°). The small differences in bond lengths and angles for the metal-complexed cyclobutenyl systems compared to those for the planar cyclobutenium cation no doubt are due to the rigidity of the four-membered ring system.

Of interest also is a comparison of the directions of the lines perpendicular to the planes defined by the three bonding carbon neighbors of each of the allylic carbons. For an ideally trigonally hybridized carbon these lines define the direction of the p_π-type orbitals. A determination of the angles between these lines allows a qualitative estimate of the amount of electron delocalization retained in the cyclobutenyl system in complexes A and C and $[(CH_3)_4C_4C_5H_5]NiC_5H_5$. The results of such a calculation are given below for the three cyclobutenyl–metal systems

Angle	Complex A	Complex C	$[(CH_3)_4C_4C_5H_5]NiC_5H_5$
P_{C_3}–P_{C_2}	14.2°	15.4°	16.5°
P_{C_3}–P_{C_4}	16.0°	14.5°	16.4°
P_{C_2}–P_{C_4}	6.9°	4.9°	2.2°

Here P_{C_2} and P_{C_4} represent the perpendicular lines extending from the planes of attached carbons for the terminal allylic carbons and P_{C_3} the line from the central carbon. The results of these calculations again show the similarities in the three transition metal–cyclobutenyl systems. The small differences observed among corresponding angles are not significant. There is a symmetrical distortion of the σ-framework such that the normals through the terminal allylic carbons remain essentially parallel. It is concluded that considerable electron delocalization in the allylic portion of the cyclobutenyl ring is retained on forming these metal complexes.

Acknowledgments.—The authors are grateful to both the National Science Foundation and to the United States Atomic Energy Commission for their financial support of this work. W. O. wishes to thank Procter and Gamble for a one-year fellowship (1963–1964). We wish to extend special thanks to Dr. M. D. Glick and Miss Judith Coleman for their help in the refinement of these compounds. We also acknowledge the use of the IBM 704 computer at MURA (under the Atomic Energy Commission) and the use of the CDC 1604 computer at the Department of Computer Sciences (University of Wisconsin).

CONTRIBUTION FROM THE HERBERT JONES CHEMICAL LABORATORY,
THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS

The Structure of a Self-Condensation Product of *o*-Aminobenzaldehyde in the Presence of Nickel Ions[1]

BY EVERLY B. FLEISCHER AND EDWARD KLEM

Received November 16, 1964

The structure of the closed tridentate macrocyclic ligand nickel complex, tribenzo[*b,f,j*][1.5.9]triazacycloduodecinenickel nitrate, has been determined by X-ray diffraction. The nickel is in an octahedral configuration with the three nitrogens of the macrocyclic ligand occupying a face of the octahedron. Two waters and a nitrate fill the remainder of the positions. A second nitrate is not bound directly to the nickel but connected to the complex by a system of hydrogen bonds.

Introduction

This work was undertaken to determine the structure of the nickel complex of tribenzo[*b,f,j*][1.5.9]triazacycloduodecine (hereafter called TRI) with the composition $Ni(TRI)(H_2O)_2(NO_3)_2$ (see Figure 1). At the time this work was undertaken the structure of the TRI ligand and the details of the coordination around the nickel ion were not known.[2] Melson and

---

(1) This research was supported by a grant from the Public Health Service.

(2) G. L. Eichhorn and R. A. Latif, *J. Am. Chem. Soc.*, **76**, 5180 (1954); G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

TABLE I
OBSERVED F VALUES

H00 (2-16) 2331, 873, 810, 806, 869, 397, 473, 618/ H10 (1-16) 549, U, 618, 585, 214, 81, 52, 164, 535, 320, 380, 99, 114, 106, 188,
269/ H20 (0-16) 2224, 1184, 1369, 1301, 321, 472, 301, 968, 244, 551, 792, 752, 433, 72, 340, 144, 99/ H30 (1-16) 154, 67, 987, 311,
456, 435, 812, 423, 890, 431, 543, 71, 109, 211, 169, 178/ H40 (1-16) 1218, 404, 383, 260, 70, 845, 622, 1401, 749, 227, 516, 423, 489,
182, 384, 163/ H50 (1-15) 1001, 279, 283, 377, 305, 283, 852, 77, 72, 147, 81, 186, 311, U, U/ H60 (0-15) 182, 586, 383, 397, 82, 425,
U, 144, 359, 459, U, 351, 219, 556, 192, 296/ H70 (1-14) 272, 669, 327, 1215, 307, 705, 203, 687, U, U, 229, U, 104, 176/ H80 (0-14)
1203, 1530, 385, 614, 177, U, U, U, 139, 600, U, 434, 341, 324, 464/ H90 (1-13) 65, 223, 916, 190, 999, 356, 497, 302, 78, U, 66, 116,
U/ H, 10, 0 (0-12) 85, 463, 588, U, 246, 198, 148, U, 99, U, 406, 206, 634/ H, 11, 0 (1-11) 68, U, 473, 477, 625, 120, 847, U, 404,
325, 330/ H, 12, 0 (0-10) 272, U, 268, U, U, U, 166, 581, 170, 591, 136/ H, 13, 0 (1-8) 67, 93, U, 146, 288, 63, 143, 123/ H, 14, 0
(0-6) 201, 99, 138, U, 265, 334, 83/ H01 (2-16) 1572, 1411, 867, 349, 359, 667, 498, 293/ H11 (0-16) 258, 461, U, 458, 695, 607, U,
674, 991, 782, 439, 667, 178, 111, U, 172, 74/ H21 (1-16) 316, 1351, 1104, 670, 151, 463, 510, 366, 698, 175, 68, 761, 376, 752, 66,
242/ H31 (0-16) 1647, 314, 487, 642, 231, 460, 111, 314, 428, 723, 310, U, 279, U, 186, 234, 214/ H41 (0-16) 121, 304, 270, 281, 90,
493, 360, U, 845, 246, 140, 134, 377, 393, 265, 239, U/ H51 (0-16) 469, 1088, 125, 591, 504, 213, 671, 451, 254, 596, 747, 126, 85, 233,
74, 93, 181/ H61 (0-16) 819, 1077, 320, 644, U, 329, 457, 196, 192, 83, 254, 415, 545, 327, 421, U, 373, U/ H71 (0-15) 103, 786, 126,
83, 293, U, 801, 367, 442, 536, 372, 139, 114, 374, 83, 247/ H81 (0-15) 1155, 858, 470, 341, 296, 800, 258, 136, 263, U, 186, 395, 164,
347, 167, 198/ H91 (0-14) 219, 810, 187, 80, 312, 579, 526, 877, 380, 833, 288, 668, 186, 147, 122/ H 10, 0 (0-13) 822, 193, 897, U,
871, U, 259, 142, 118, 255, 282, 237, 404, 163/ H, 11, 1 (0-12) U, 167, 270, U, U, 183, U, 837, 734, 1067, 301, U, U/ H, 12, 1 (0-11)
374, 209, 203, 221, 169, U, 203, 240, 87, 244, 431, U/ H, 13, 1 (0-9) U, U, U, U, U, 361, 245, 951, 290, 716/ H, 14, 1 (0-7) 210, 84,
147, 168, U, 209, 157, 107/ H02 (2-16) 637, 2423, 821, 536, 217, 700, 714, 1445/ H12 (0-16) 1676, 2222, 488, 772, 862, 1266, 673, 385,
U, 766, 233, 674, U, 421, 152, U, 62/ H22 (0-16) 511, 413, 2410, 523, 681, 1512, 1064, 860, 426, 380, U, 209, 400, 424, 502, 726, 566/
H32 (0-16) 145, 431, 596, 103, 129, 101, 250, 842, 115, 769, 271, 245, 204, 386, U, 81, 141/ H42 (0-16) 270, 878, 708, 1144, 752, 700,
374, 683, 1887, 417, 807, U, 138, 327, U, 409 U/ H52 (0-16) 202, 363, 258, 1061, 352, 232, 478, U, 231, 596, 320, 267, 416, 315, U, 65,
U/ H62 (0-16) 437, 810, 515, 1065, 163, 420, 431, 104, 420, 86, 71, 231, U, 368, 89, 290, 208/ H72 (0-16) 478, 1070, 704, 199, 201,
336, 353, 218, 747, 103, 445, 118, 476, 156, 130, 115, U/ H82 (0-15) 181, 74, 445, 680, 556, 441, 422, 467, 447, 112, U, U, U, 241, 167,
358/ H92 (0-14) U, 352, U, 114, 354, 65, 327, 388, 450, 948, 358, 404, 166, 204, 65/ H, 10, 2 (0-13) 432, 110, 699, 530, 478, 423,
816, 68, 362, 267, U, 95, U, 63/ H, 11, 2 (0-12) 88, 308, U, U, 67, 206, 483, 842, 290, 741, U, 193, 347/ H, 12, 2 (0-11) 420, U, 502,
102, 673, 150, 504, U, 196, 593, 185/ H, 13, 2 (0-9) 87, 95, 118, 177, 192, 290, 166, 388, U, 348/ H03 (2-16) 600, 1064, 1300, 591,
394, 222, 785, 1207/ H13 (0-16) 417, 466, 793, U, 12, 225, 528, 827, U, 978, 280, 563, 325, 800, 201, 66/ H23 (0-16) 250, 143, 217,
826, 1127, 564, 725, 794, 474, 204, 236, 73, U, 371, 99, 260, 583/ H33 (0-16) 118, 333, 697, 315, 670, 1226, 85, 940, 430, 678, 331,
422, 580, 262, 122, 255, 313/ H43 (0-16) 705, 920, 559, 886, 667, 1138, 629, 643, 650, 488, 93, 345, 399, 306, U, 556, 247/ H53 (0-16)
883, 347, 139, 382, 198, U, 157, 594, 340, 78, 376, 190, 374, 147, 327, 129, 92/ H63 (0-16) 411, 459, U, 730, 536, 668, 110, 612, 218,
422, 193, U, 302, 167, 192, 353, U/ H73 (0-16) 991, 184, 417, 226, 318, U, 309, 106, 548, 179, 554, 82, 449, 172, 296, 140, 109/ H83
(0-15) 334, 126, 386, 454, 480, 432, 273, 216, 99, 386, 138, 282, 367, U, 336, 211/ H93 (0-14) 297, 538, 129, 191, 226, 208, 87, 162,
240, 87, 549, 542, 199, 145, 345/ H, 10, 3 (0-13) 93, 241, 378, 340, 611, U, 424, U, U, 346, 187, U, 160, U/ H, 11, 3 (0-12) 196, 410,
116, 234, 270, 141, 200, 272, 133, 151, 84, 419, 70/ H, 12, 3 (0-10) 421, U, 721, 287, 667, 84, 164, 227, 335, 596, 134/ H, 13, 3 (0-8)
357, 395, U, 185, U, 185, 167, 441, 102/ H04 (0-16) 20, 63, 386, 405, 855, 193, 185, U, 230/ H14 (0-16) 70, 1408, 392, 269, 172, 456,
332, 138, 199, 493, 433, 871, U, 605, U, 312, 83/ H24 (0-16) 297, 613, U, 470, 630, 590, 784, 217, 459, U, U, 78, 250, 124, 282, 100/
H34 (0-16) 805, 360, 715, 62, 494, 144, 162, U, 455, 277, 308, 425, 402, 280, 229, 269, 125/ H44 (0-16) 96, 351, 278, 225, 662, 463,
445, 928, 967, 464, 193, 280, U, 123, 114, 8, 63/ H54 (0-16) 715, 125, 553, 196, 269, 141, 182, 728, 731, 404, 852, U, 543, 125, 322,
157, 172/ H64 (0-16) 495, 156, 619, 520, 127, 810, 67, 844, 271, 671, 274, 239, 102, U, 188, 167, 200/ H74 (0-15) 561, 277, 248, 198,
155, 345, 135, 403, U, 336, 368, 177, 304, 166, 393, 89/ H84 (0-14) 263, 181, 221, 181, 94, 334, U, 298, 315, 75, 90, 183, U, 78, 271/
H94 (0-13) 330, 243, 172, U, 151, 205, 182, 301, 119, 220, 306, 207, 435, 363/ H, 10, 4 (0-12) U, 75, 110, U, 384, 225, U, U, 99, 148,
100, U, U/ H, 11, 4 (0-10) 123, 426, U, 312, U, 186, 109, U, 190, 224, 93/ H, 12, 4 (3-7) U, 222, 80, 80, 70/ H05 (0-16) 81, 287, U,
357, 318, U, 249, 362/ H15 (0-16) U, 761, U, 484, 259, U, U, U, 387, 151, U, 301, 114, 97, 117, 161, 288/ H25 (-16) U, 62, U, 318, U,
U, 103, 316, 617, 208, 474, 286, 174, 256, 83, 252, 73/ H35 (0-16) 335, 849, 254, 547, 143, 406, 151, 327, 66, 65, 283, 265, U, 198,
207, 132, U/ H45 (0-15) 138, 211, U, 208, 125, 681, 167, 611, 353, 710, 341, 405, 134, 192, U, U/ H55 (0-15) 488, 88, 480, 187, 620,
183, 126, 110, 279, 225, 522, 182, 349, U, 284, U/ H65 (0-14) U, 90, 130, U, U, 478, 99, 694, 82, 353, 71, 378, 62, 73, 76/ H75 (0-13)
138, 127, 284, 152, 113, U, 171, 68, U, 231, 195, 235, 388, 170/ H85 (0-12) U, U, U, 159, U, 223, 416, 228, 225, 120, 206, U, U/ H95
(2-10) 149, U, 149, U, 223, 86, 179, U, 85/ H, 10, 5 (5-7) 159, 223, 327/ H06 (2-14) 177, U, 434, 71, 160, 286, 162/ H16 (1-14)
194, 87, 638, U, 280, U, 110, 86, 125, U, U, 156, 115, 270/ H26 (1-13) 66, U, 76, U, 82, 208, 155, 222, 164, 265, 155, U, 223/ H36
(1-13) U, 186, 266, 88, 97, 191, 245, U, U, 105, 76, 280, 271/ H46 (2-12) 99, 183, U, 242, U, 272, 172, 134, 171, 331, U/ H56 (3-11)
66, 363, 97, 204, 65, 63, 178, U, U/ H66 (5-9) U, 67, 182, U, 146/ H0$\bar{1}$ (0-14) 1121, 1884, U, 467, 974, 422, 431, U/ H1$\bar{1}$ (1-15) 264,
669, 2818, 344, 1640, 291, 1196, 191, 153, 245, 212, 125, U, 135, U/ H2$\bar{1}$ (0-15) 1561, 78, 241, 87, 1087, U, 758, 475, 404, 266, 401,
379, 301, 167, 283, 166/ H3$\bar{1}$ (1-14) 1177, 1416, 180, 326, 1308, 780, 698, 530, 104, 74, 140, 233, 420, 429/ H4$\bar{1}$ (1-14) 669, 141, 573,
543, 347, U, 641, 249, 581, 484, 436, 245, 237, 322/ H5$\bar{1}$ (1-14) 1327, 671, 145, 1239, 889, 1010, 209, 172, 189, 78, U, U, 164/ H6$\bar{1}$
(1-13) 348, 733, 615, U, U, 548, 680, 105, 616, 94, 100, 343/ H7$\bar{1}$ (1-13) 1043, 598, 361, 831, 594, 268, 363, 344, 97, 67, 251, 71/
H8$\bar{1}$ (1-12) 358, 960, 101, U, 165, 431, 354, 151, 507, 67, 359, 163/ H9$\bar{1}$ (1-11) 265, 1047, 367, 655, 571, 637, 407, 245, 125, U, U/
H, 10, $\bar{1}$ (1-11) 99, 87, 353, 75, 166, 163, 444, U, U, 140, 191/ H, 11, $\bar{1}$ (0-10) U, 353, 76, 435, 84, 812, 119, 70, 359, 215, 73/
H, 12, $\bar{1}$ (1-8) 143, 449, 90, 212, 63, 105, 321, 230/ H, 13, $\bar{1}$ (0-7) U, 129, 86, 488, 379, 382, U, U/ H, 14, $\bar{1}$ (1-5) 161, 339, U, U,
U/ H0$\bar{2}$ (0-12) 2753, 97, 487, 876, 659, 560 U/ H1$\bar{2}$ (1-13) 836, 81, 475, 68, 1575, 598, 651, 253, 392, U, 245, 100, U/ H2$\bar{2}$ (1-13)
1283, 186, 664, U, 85, 756, 212, 794, 111, 214, U, 272, 253/ H3$\bar{2}$ (1-13) 260, 577, 83, 797, 984, 527, 174, 353, 125, U, 138, 200, 197/
H4$\bar{2}$ (1-12) 602, 477, 69, 348, 616, 262, 664, 1027, 668, 131, 549, 151/ H5$\bar{2}$ (1-12) 474, 903, 195, 830, U, 1018, 155, 724, 204, U, 70,
308/ H6$\bar{2}$ (1-12) 381, 487, U, 420, 385, 124, 948, 223, 754, U, 482, U/ H7$\bar{2}$ (1-11) 213, 441, 552, 306, 247, 385, 385, 208, U, U, 124/
H8$\bar{2}$ (1-10) 233, 534, 73, 64, 239, 102, 188, 331, 197, 443/ H9$\bar{2}$ (1-10) 556, 348, 374, 462, 194, 183, U, U, 106, U/ H, 10, $\bar{2}$ (1-9)
119, 133, U, 138, 74, 280, 206, 125, 216/ H, 11, $\bar{2}$ (1-8) 704, 66, 701, 192, 125, 187, 78, 133/ H, 12, $\bar{2}$ (1-6) 187, 193, U, U, U, U/
H, 13, $\bar{2}$ (1-4) 462, 384, 571, U/ H, 14, $\bar{2}$ (1-2) 182, U/ H0$\bar{3}$ (2-10) 761, 469, U, 294, 355/ H1$\bar{3}$ (1-11) 469, 566, 82, 448, U, U, 86,
U, 63, 182, 88/ H2$\bar{3}$ (1-11) 149, 243, 596, 298, 122, 307, 180, 497, 463, 211/ H3$\bar{3}$ (1-10) 831, 679, 623, 168, 114, 250, 324, U, U, U/
H4$\bar{3}$ (1-10) 619, 227, U, 84, 609, 371, 424, 280, 547, 146/ H5$\bar{3}$ (1-10) 214, 795, 260, 513, 111, 301, 358, 142, U, 204/ H6$\bar{3}$ (1-9) 158,
328, 206, 85, 392, 63, 272, U, 409/ H7$\bar{3}$ (1-8) 170, 651, U, 358, 733, 221, 454, U/ H8$\bar{3}$ (1-8) 275, 211, U, U, 125, 65, 201, 227/ H9$\bar{3}$
(1-7) 458, U, 258, 110, U, 273, U/ H, 10, $\bar{3}$ (1-6) 139, 103, 131, 86, 72, 270/ H, 11, $\bar{3}$ (1-5) 549, U, 64, 86, 49/ H, 12, $\bar{3}$ (1-3)
191, 82, 176/ H0$\bar{4}$ (2-8) 291, U, 152, U/ H1$\bar{4}$ (0-7) U, 930, 420, 253, 87, U, 260, U/ H2$\bar{4}$ (1-8) 335, 582, U, 296, 365, U, U, U/ H3$\bar{4}$
(1-8) 722, 486, 468, 530, 198, 104, 157, 81/ H4$\bar{4}$ (1-7) 324, 220, 166, 345, 346, 244, 264/ H5$\bar{4}$ (1-7) 139, 740, 265, 380, U, 122,
196/ H6$\bar{4}$ (1-6) 88, 192, 545, 99, 233, 130/ H7$\bar{4}$ (1-6) 199, 562, U, 265, U, U/ H8$\bar{4}$ (1-5) 69, 174, 165, U, 258/ H9$\bar{4}$ (1-4) 287,
205, 114, 97/ H, 10, $\bar{4}$ (0-2) U, U, 110/ H, 11, $\bar{4}$ (1) 291/ H0$\bar{5}$ (2-4) 700, 457/ H1$\bar{5}$ (0-4) U, 501, 334, 126, 295/ H2$\bar{5}$ (0-4) U,
130, 364, 202, 429/ H3$\bar{5}$ (1-4) 289, 233, U, 231/ H4$\bar{5}$ (1-4) 366, 83, 244, 162/ H5$\bar{5}$ (1-3) 76, 151, 112/ H6$\bar{6}$ (0-2) U, 80, 159/ H7$\bar{6}$
(1) 98

*10 F_{obs} given for each HKL.

H is the running index and each KL set is given.

Space Group Requires that HOL, H = 2n and OKO, K = 2n.

U means unobserved.

Busch[3] have now concluded that the TRI ligand is a closed ring structure and the coordination around the nickel ion is octahedral. These conclusions have been confirmed by our work.

Experimental

The crystals of Ni(TRI)$(H_2O)_2(NO_3)_2$ were kindly supplied by Busch. They were dissolved in weak HNO_3 and recrystallized. The solvent was allowed to evaporate, and the resulting crystals were used without any further treatment. Our method of preparation of the crystals differed from that of Busch in that he iso-

---

(3) G. A. Melson and D. H. Busch, private communication, to be published.

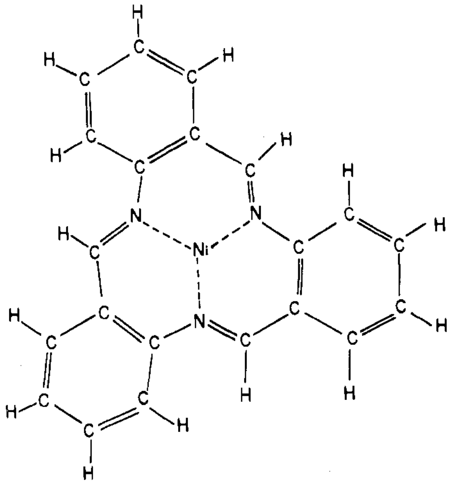

Figure 1.—The TRI ligand.

lated the crystals by suction filtration and dried them *in vacuo* at room temperature over anhydrous $Mg(ClO_4)_2$. This may account for the difference in water content of our material and Busch's. We found two waters per nickel ion while his analysis clearly showed only one water per nickel.

Precession photographs of a single crystal showed the crystal to be monoclinic. The unit cell dimensions are $a = 20.0 \pm 0.1$ Å., $b = 16.70 \pm 0.08$ Å., $c = 7.24 \pm 0.04$ Å., $\beta = 64° 35' \pm 30'$. The unit cell volume is 2185 Å.^{3}. The density as determined by the flotation method is 1.59 ± 0.02 g./cm.^{3}. The calculated density is 1.60 g./cm.^{3} with four molecules per unit cell. Systematic extinctions of reflections for ($h0l$) when h is odd and for ($0k0$) when k is odd determined the space group uniquely as $P2_1/a$. Three-dimensional intensity data were collected using the G.E. XRD-5 with a Eulerian cradle and Cu Kα radiation. The intensities of 1750 independent reflections with $0 < 2\theta < 90°$ were measured using a scintillation counter.[4] Of these 85% or 1487 had intensities that were measurable. The intensities were determined by taking a 10-sec. reading on the peak and subtracting from this a background reading taken at a 2θ value 3° from the peak. For low 2θ values where the background readings differed significantly on either side of the peak, the average of the two background readings was used. An unground crystal averaging about 0.25 mm. in diameter was used and no absorption correction was required. The set of intensities was corrected for Lorentz and polarization factors.

Determination of Structure

A Patterson synthesis, $P(uvw)$, using all the measured reflections led immediately to the nickel positions. The value of R ($R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$) was 0.535 for the nickel contributions alone. A series of three-dimensional Fourier syntheses using an over-all thermal parameter B and the carbon form factor for all light atoms was then used to arrive at the final structure by successive approximations. Atom contributions were included as the atoms appeared as peaks in the Fourier maps. In the early stages of the determination no molecular model was assumed since at that time we did not know whether the trimer was open or closed, how many water molecules were present, or where the nitrates and waters were located around the nickel. The structural analysis proceeded by the usual Fourier techniques until all the atoms were found and assigned.

TABLE II

PARAMETER DATA: COORDINATES AND STANDARD DEVIATIONS ($\times 10^4$)

Atom	X	σX	Y	σY	Z	σZ
Ni	2897	1	5439	1	−0598	3
O_1	3102	5	6563	5	−2072	13
O_2	3939	5	5061	5	−2735	14
O_3	2504	5	5040	5	−2677	13
O_4	1953	6	6131	6	−2893	16
O_5	1773	6	5052	6	−4201	15
O_6	4462	7	7146	7	−4241	22
O_7	4840	7	6062	7	−5735	18
O_8	5587	7	6989	11	−6374	19
N_1	1905	7	5824	8	1545	19
N_2	2657	5	4387	6	0945	14
N_3	3290	5	5768	6	1457	15
N_4	2060	6	5409	7	−3253	16
N_5	4997	7	6744	8	−5509	18
C_1	1818	7	6428	7	2719	20
C_2	2009	8	4089	8	1813	20
C_3	3617	7	5320	8	2190	20
C_4	1262	7	5330	8	1849	20
C_5	0611	8	5697	9	2008	22
C_6	−0009	9	5191	9	2357	23
C_7	0064	9	4375	10	2414	24
C_8	0724	8	4013	9	2222	22
C_9	1343	7	4496	8	1879	20
C_{10}	3236	7	3986	8	1205	19
C_{11}	3336	8	3155	8	0917	21
C_{12}	3928	9	2787	10	1200	24
C_{13}	4404	8	3221	9	1707	22
C_{14}	4300	8	4071	9	2037	21
C_{15}	3718	7	4443	8	1735	20
C_{16}	3146	7	6590	8	2121	19
C_{17}	3714	8	7070	9	2263	21
C_{18}	3560	9	7866	10	2873	25
C_{19}	2868	9	8155	10	3442	24
C_{20}	2290	8	7702	9	3346	22
C_{21}	2437	7	6898	8	2648	18

Structurally distinct classes of atoms were then assigned their proper form factors and individual isotropic thermal parameters were introduced. Final refinements of coordinates and thermal parameters were calculated by a number of cycles of least squares. Anisotropic thermal parameters were then introduced for the eleven atoms lying outside the ligand (Ni, 8 oxygens, N_4, N_5). A final cycle of least squares on coordinates produced the final R value of 0.088 for observed intensities and 0.111 for all 1750 intensities. Table I gives the observed structure amplitudes. The final difference map showed the positions of sixteen of the nineteen hydrogen atoms. No refinement was made on the hydrogen coordinates and their contributions are not included in the final value of R.

Tables II and III list the atomic coordinates with associated standard deviations and the individual thermal parameters.

Discussion of Results

The bond distances and bond angles for the complex are shown in Figures 2–4 and given in Tables IV–VII. The nickel ion is 1.27 ± 0.02 Å. above the plane

---

[4] The calculated structure factors for each of 57 pairs of ($0kl$) and ($0k\bar{l}$) reflections were averaged and the mean structure factor assigned the Miller indices ($0kl$). The average standard deviations of the pairs is under 10%, indicating minimal absorption errors.

TABLE III

THERMAL PARAMETERS (ANISOTROPIC THERMAL PARAMETER AND STANDARD DEVIATION) × 10^5

	β_{11}	σ_{11}	β_{22}	σ_{22}	β_{33}	σ_{33}	β_{12}	σ_{12}	β_{13}	σ_{13}	β_{23}	σ_{23}
Ni	281	8	300	9	2340	60	−17	7	−296	17	−19	20
O_1	296	35	195	43	1752	27	6	31	−207	80	−86	85
O_2	237	38	268	44	1854	284	−112	32	−2	85	+44	89
O_3	306	36	214	42	2123	272	−93	31	−524	82	−39	83
O_4	439	44	239	54	3631	335	−134	41	−685	99	81	110
O_5	389	42	386	50	2918	324	−34	36	−733	95	−37	100
O_6	510	65	477	78	5944	489	−74	56	−672	150	443	152
O_7	550	52	266	62	4425	387	52	48	−581	116	−117	131
O_8	354	86	1758	102	3057	653	−631	77	−53	201	639	203
N_1	2.20	0.27[a]										
N_2	2.04	0.24[a]										
N_3	2.23	0.25[a]										
N_4	264	52	267	61	1117	382	12	47	23	113	−86	130
N_5	232	67	425	78	2319	509	−20	61	−398	153	−183	162
C_1	2.77	0.32[a]										
C_2	3.01	0.34[a]										
C_3	2.64	0.32[a]										
C_4	2.74	0.33[a]										
C_5	3.91	0.39[a]										
C_6	4.29	0.41[a]										
C_7	4.54	0.42[a]										
C_8	3.96	0.39[a]										
C_9	2.85	0.33[a]										
C_{10}	2.57	0.33[a]										
C_{11}	3.24	0.35[a]										
C_{12}	4.42	0.42[a]										
C_{13}	3.88	0.38[a]										
C_{14}	3.38	0.36[a]										
C_{15}	2.98	0.34[a]										
C_{16}	2.80	0.32[a]										
C_{17}	3.44	0.36[a]										
C_{18}	4.69	0.42[a]										
C_{19}	4.56	0.41[a]										
C_{20}	3.86	0.39[a]										
C_{21}	2.11	0.29[a]										

[a] Isotropic thermal parameter *B* and standard deviation.

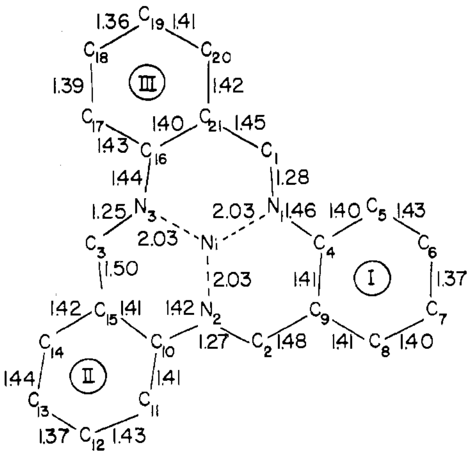

Figure 2.—Bond distances in the TRI ligand.

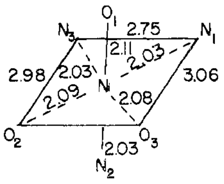

Figure 3.—Octahedral configuration around the nickel ion.

TABLE IV

BOND LENGTHS WITH STANDARD DEVIATIONS IN Å.

	d	σd		d	σd
Ring I			Twelve-Membered Ring		
C_4–C_5	1.40	0.02	C_1–N_1	1.28	0.02
C_5–C_6	1.43	0.02	N_1–C_4	1.46	0.02
C_6–C_7	1.37	0.02	C_9–C_2	1.48	0.02
C_7–C_8	1.40	0.02	C_2–N_2	1.27	0.02
C_8–C_9	1.41	0.02	N_2–C_{10}	1.42	0.02
C_9–C_4	1.40	0.02	C_{15}–C_3	1.50	0.02
			C_3–N_3	1.25	0.02
Ring II			N_3–C_{16}	1.44	0.02
C_{10}–C_{11}	1.41	0.02	C_{21}–C_1	1.45	0.02
C_{11}–C_{12}	1.43	0.02			
C_{12}–C_{13}	1.37	0.02	Coordinating Nitrate		
C_{13}–C_{14}	1.44	0.02	O_3–N_4	1.28	0.02
C_{14}–C_{15}	1.42	0.02	O_4–N_4	1.23	0.02
C_{15}–C_{10}	1.41	0.02	O_5–N_4	1.22	0.02
Ring III			Unbound Nitrate		
C_{16}–C_{17}	1.43	0.02	O_6–N_5	1.26	0.02
C_{17}–C_{18}	1.39	0.02	O_7–N_5	1.21	0.02
C_{18}–C_{19}	1.36	0.02	O_8–N_5	1.15	0.02
C_{19}–C_{20}	1.41	0.02			
C_{20}–C_{21}	1.42	0.02			
C_{21}–C_{16}	1.40	0.02			

formed by the three coordinating nitrogens (N_1, N_2, N_3) and located equidistant (2.03 Å.) from them. The TRI ligand itself is slightly propeller-shaped. The

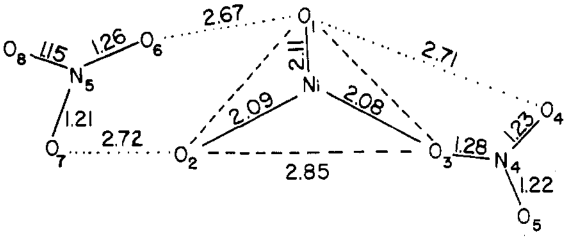

Figure 4.—The nickel, water, and nitrate configuration.

TABLE V
OCTAHEDRAL COORDINATION

	d, Å.	σd		Angle, deg.	σ∠
N_1–Ni	2.03	0.01	N_1NiN_2	86.0	0.1
N_2–Ni	2.03	0.01	N_1NiN_3	85.0	0.1
N_3–Ni	2.03	0.01	N_2NiN_3	84.6	0.1
O_1–Ni	2.11	0.01	O_1NiO_2	88.8	0.1
O_2–Ni	2.09	0.01	O_1NiO_3	88.4	0.1
O_3–Ni	2.08	0.01	O_2NiO_3	86.3	0.1
O_1–O_2	2.94	0.01	O_1NiN_2	177.0	0.3
O_1–O_3	2.92	0.01	O_2NiN_1	177.7	0.3
O_2–O_3	2.85	0.01	O_3NiN_3	177.0	0.3
N_1–N_2	2.77	0.01	$N_1N_2N_3$	59.9	0.3
N_1–N_3	2.75	0.01	$N_2N_3N_1$	60.7	0.3
N_2–N_3	2.73	0.01	$N_3N_1N_2$	59.4	0.3
O_1–N_1	2.96	0.01	$O_1O_2O_3$	60.6	0.3
O_1–N_2	4.14	0.01	$O_2O_3O_1$	61.2	0.3
O_1–N_3	3.04	0.01	$O_3O_1O_2$	58.3	0.3
O_2–N_1	4.12	0.01			
O_2–N_2	3.01	0.01			
O_2–N_3	2.98	0.01			
O_3–N_1	3.06	0.01			
O_3–N_2	2.97	0.01			
O_3–N_3	4.12	0.01			

TABLE VI
Hydrogen Bond Parameters

	d, Å.	σd		Angle, deg.	σ∠
$O_6\cdots O_1(H_2O)$	2.67	0.02	$O_6O_1O_4$	135.6	1.1
$O_4\cdots O_1(H_2O)$	2.71	0.02	$O_7O_2O_3$	109.7	1.1
$O_7\cdots O_2(H_2O)$	2.72	0.02			

Averaged Parameters

Bond type	d, Å.
C(benzene)—C(benzene)	
Ring I	1.40
Ring II	1.41
Ring III	1.40
All rings	1.40
C—C(benzene)	1.48
C=N	1.27
C(benzene)—N	1.44

TABLE VII
BOND ANGLES

	Angle, deg.	σ∠		Angle, deg.	σ∠
Ring I			Twelve-Membered Ring		
$C_4C_5C_6$	117.5	1.3	$C_{21}C_1N_1$	122.1	1.2
$C_5C_6C_7$	119.7	1.3	$C_1N_1C_4$	118.9	1.2
$C_6C_7C_8$	122.1	1.3	$N_1C_4C_9$	117.5	1.2
$C_7C_8C_9$	119.3	1.3	$C_4C_9C_2$	124.4	1.2
$C_8C_9C_4$	118.2	1.3	$C_9C_2N_2$	123.3	1.2
$C_9C_4C_5$	122.9	1.3	$C_2N_2C_{10}$	117.8	1.2
Ring II			$N_2C_{10}C_{15}$	118.3	1.2
$C_{10}C_{11}C_{12}$	118.6	1.3	$C_{10}C_{15}C_3$	123.2	1.2
$C_{11}C_{12}C_{13}$	121.9	1.3	$C_{15}C_3N_3$	122.5	1.2
$C_{12}C_{13}C_{14}$	120.0	1.3	$C_3N_3C_{16}$	119.6	1.2
$C_{13}C_{14}C_{15}$	118.5	1.3	$N_3C_{16}C_{21}$	118.4	1.2
$C_{14}C_{15}C_{10}$	120.6	1.3	$C_{16}C_{21}C_1$	124.2	1.2
$C_{15}C_{10}C_{11}$	120.4	1.3	$N_1C_4C_5$	119.5	1.2
Ring III			$C_2C_9C_8$	117.0	1.2
$C_{16}C_{17}C_{18}$	118.9	1.3	$N_2C_{10}C_{11}$	121.3	1.2
$C_{17}C_{18}C_{19}$	119.6	1.3	$C_{14}C_{15}C_3$	116.0	1.2
$C_{18}C_{19}C_{20}$	123.2	1.3	$N_3C_{16}C_{17}$	120.4	1.2
$C_{19}C_{20}C_{21}$	118.5	1.3	$C_{20}C_{21}C_1$	117.1	1.2
$C_{20}C_{21}C_{16}$	118.4	1.3	Coordinating Nitrate		
$C_{21}C_{16}C_{17}$	121.2	1.3	$O_3N_4O_4$	118.7	0.7
Unbound Nitrate			$O_4N_4O_5$	121.0	0.7
$O_6N_5O_7$	114.2	1.3	$O_3N_4O_5$	120.2	0.7
$O_7N_5O_8$	121.8	1.3			
$O_6N_5O_8$	124.0	1.3			

shape of the ligand can be visualized by first considering the entire ligand as planar. Then raise N_1 about 0.35 Å. out of the plane pulling C_4 up slightly, and lower C_2 about 0.25 Å. below the plane pulling C_9 down slightly. The plane of benzene I then makes an angle of 15 ± 3° with the plane formed by N_1, N_2, and N_3. Now if N_2 and N_3 are raised out of the plane and C_3 and C_1 lowered below the plane by similar amounts, benzenes II and III will be twisted so they make angles of 13 ± 3° and 10 ± 3°, respectively, with the plane of the three nitrogens. The average bond distances for benzene rings I, II, and III are 1.40 ± 0.02 Å., 1.41 ± 0.02 Å., and 1.40 ± 0.02 Å., respectively, as compared with the accepted value of 1.395 Å. The average value for an interior angle for each benzene ring as well as for the main twelve-membered ring is 120 ± 2°.

Figures 3 and 4 represent the positions around the nickel of the atoms in the complex excluding the TRI ligand. The two nitrate groups are planar. If the three coordinating oxygens (O_1, O_2, O_3) are considered to be in the plane of Figure 4, then the plane of the coordinating nitrate (O_3, O_4, O_5, N_4) makes a clockwise angle of 28 ± 2° and that of the noncoordinating nitrate (O_6, O_7, O_8, N_5) makes a counterclockwise angle of 38 ± 2° with the plane of the figure and the coordinating oxygens. The nickel ion is behind the plane of the figure 1.25 Å. The TRI ligand is behind the plane of the figure with the plane of (N_1, N_2, N_3) being parallel to that of (O_1, O_2, O_3) and 2.53 ± 0.03 Å. away from it. There appears to be a hydrogen bond between the water molecule of O_1 and the oxygens O_4 and O_6 in the coordinating and noncoordinating nitrates, respectively. Similarly, a hydrogen bond appears to exist between the water molecule of O_2 and the oxygen O_7 of the unbound nitrate. This hydrogen bonding is probably responsible for the orientation of the two nitrates.

If the coordination around the nickel postulated by Melson and Busch was present in the crystals they worked with, one of the waters we found present must have come off when the crystals were vacuum dried. The noncoordinating nitrate would then have popped into the position formerly occupied by the water to complete the octahedral coordination around the nickel.

Figure 3 represents the octahedral coordination around the nickel. The configuration of atoms can be thought of as two parallel equilateral triangles with the nickel ion between them. One triangle has the three coordinating nitrogens (N_1, N_2, N_3) at its vertices and has an average side of 2.75 ± 0.004 Å. The other triangle has the three coordinating oxygens (O_1, O_2, O_3) at its vertices with an average side of 2.90 ± 0.006 Å. The average distance between a nitrogen and the two nearest oxygens on the parallel triangle is 3.00 ± 0.006 Å. The angle taken with the nickel as the vertex between a nitrogen and the oxygen farthest from its averages 177 ± 2°, which is very close to the angle of 180° expected for octahedral coordination. The angle made between the planes of the two triangles infinitely extended is 179.5 ± 2°, so that they can be considered parallel.

The NiTRI complex is very inert with respect to hydrolysis by strong acids.[3] This could be accounted for by the positioning of the nitrogen atoms in the TRI ligand. The nitrogen atoms are all "turned up" toward the nickel. In this position they are effectively shielded from attack by protons from the rear by the large benzene rings and the nonbenzene carbons that are "turned down" below each of the turned up nitrogens. The nitrogens are similarly shielded on the other side by the nickel, two waters, and two nitrates that effectively block any possibility of attack from the front. Some idea of the shielding available can be had by constructing a model of the molecule using the Stuart and Briegleb models.

CONTRIBUTION NO. 3198 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,
CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

Acetylacetone Complexes of Vanadium(II)

BY WILLIAM P. SCHAEFER

Received December 14, 1964

Vanadium(II) forms mono, bis, and tris acetylacetone complexes; the formation constants in 1.00 *F* KCl are $\log \beta_1 = 5.383$, $\log \beta_2 = 10.189$, $\log \beta_3 = 14.704$. These formation constants are compared with those for the acetylacetone complexes of all the other divalent ions of the first transition series. The vanadium(II) complex is an intense blue color, with $\epsilon_{\max}$ 2700 at 700 mμ. The standard potential for the oxidation of the tris complex to the vanadium(III) complex is +1.0 v. *vs.* n.h.e., indicating the vanadium(II) complex is a powerful reducing agent.

In the course of a survey of the properties of various complexes of vanadium(II), the acetylacetone (2,4-pentanedione) complex was prepared. Aqueous solutions of this complex were so intensely colored that a further study of the system seemed useful. This paper reports the results of spectrophotometric, potentiometric, and pH studies of the vanadium(II)–acetylacetone complexes. A least-squares method of computing complex ion stability constants is also described. A paper has appeared[1] reporting $\log \beta_1$ and $\log \beta_2$ values for these complexes in aqueous dioxane, but no other information was given. The present work was done in water solutions of ionic strength 1.00; in this medium a tris complex is formed, and values for all three stability constants have been obtained.

Experimental

Chemicals. Preparation of Vanadium(II) Solutions.—Reagent grade vanadium pentoxide was heated with excess concentrated hydrochloric acid until it appeared that all the vanadium was reduced to the +4 state. As much as possible of the excess acid was then evaporated off, and the solution was diluted with distilled water to give an acid solution of $VOCl_2$ of the desired concentration. This was placed in a cell and electrolyzed at a mercury cathode under a positive pressure of nitrogen until it appeared that all the vanadium was in the +2 state, and then for 30 min. longer; then it was transferred directly to a storage buret.[2] This method of preparation resulted in a solution containing only V^{2+}, H^+, and Cl^- ions. The V^{2+} content was determined by coulometric titration with bromine and the H^+ content by titration with ethylenediamine solution. The total vanadium content was determined by titration with potassium permanganate solution; the V^{2+} always accounted for at least 99.7% of the vanadium and any other species were ignored.

Other Chemicals.—Acetylacetone, Eastman White Label, was distilled within 24 hr. of its use. Ethylenediamine, practical grade, was used without further purification. The standard hydrochloric acid and sodium hydroxide were prepared from p-H Tamm ampoules (Chem-Tam, Sweden) and were checked by standard procedures; all other chemicals were reagent grade.

Instrumental.—Polarograms were recorded on a Sargent Model XV polarograph; the cell used was a conventional H-cell with a saturated calomel reference electrode. No special care was taken in measuring half-wave potentials; they are considered accurate to ±0.02 v.

The pH measurements were made with a Radiometer Model pHM 4c pH meter, a Beckman Type E-2 glass electrode, and a pressurized, carborundum-frit type saturated calomel electrode (Beckman). The electrode pair was used to measure hydrogen ion concentration as described previously, with an estimated precision of ±0.005 log $[H^+]$ unit.[3] All equilibrium constants

---

[1] J. M. Crabtree, D. W. Marsh, J. C. Tomkinson, R. J. P. Williams, and W. C. Fernelius, *Proc. Chem. Soc.*, 336 (1961).

[2] R. L. Pecsok and W. P. Schaefer, *J. Am. Chem. Soc.*, **83**, 62 (1961).

[3] W. P. Schaefer and M. E. Mathisen, *Inorg. Chem.*, **4**, 431 (1965).