Crystal and Molecular Structure of the Five-Coordinated Nickel(II) Complex with N-β-Diethylaminoethyl-5-chlorosalicylaldimine

P. L. Orioli, M. Di Vaira, and L. Sacconi

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Firenze, Florence, Italy. *Received April 26, 1966*

Abstract: The crystal structure of bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II) has been determined by X-ray analysis. The cell dimensions are: $a = 12.68, b = 21.77, c = 12.05$ A, $\beta = 122° 48'$, $Z = 4$, space group $P2_1/c$. The structure consists of discrete molecules, in which the nickel atom shows the coordination number of five. The coordination polyhedron can be described as a distorted square pyramid formed by the two oxygen atoms, the two azomethine nitrogen atoms, and the β-nitrogen atom of one ethylenediamine group. Sixfold coordination appears to be essentially prevented by steric hindrance of the two ethyl groups. The steric requirements of the ligand molecule are the main factors determining the distribution of the ligands about the metal atom. This is the first complete structure of a high-spin five-coordinated nickel(II) complex.

Schiff bases formed by the reaction between ring-substituted salicylaldehydes and N,N-diethylethylenediamine give complexes with nickel(II) of the general formula $[\text{X-SALen-N}(C_2H_5)_2]_2\text{Ni}$. Paramagnetic octahedral or diamagnetic planar complexes are formed depending on the nature of the X substituent in the benzene ring. When X = 3-Cl, 5-Cl, or 3,4-benzo, paramagnetic complexes are formed whose reflectance spectra are not readily assigned on the basis of either octahedral or tetrahedral forms.[1]

In a previous communication[2] we reported preliminary results on the structure of the 5-Cl derivative and have shown the cobalt(II) analog to be isomorphous with the nickel complex. We wish now to report the complete results of the three-dimensional X-ray investigation on this compound.

Experimental Section

The preparation of the compound has been described elsewhere.[1] Monoclinic needles were grown from chloroform and petroleum ether (bp 40–70°) solutions, the axis of elongation being [001]. Cell dimensions, determined from rotation and Weissenberg photographs, are: $a = 12.68, b = 21.77, c = 12.05$ A, $\beta = 122° 48'$, $Z = 4$, calculated density 1.32 g cm^{-3}. The NaCl rotation pattern was superimposed on each film for calibration. Systematic absences of ($h0l$) for l odd and ($0k0$) for k odd indicated the space group to be $P2_1/c$.

The crystals, perfectly stable in the air, slowly transform under exposure to X-rays into a brown diamagnetic powder. Analysis of the powder shows that decomposition takes place. Owing to the decomposition, four different crystals, of about the same size, were employed for the collection of the intensities. Data were collected around the needle axis on a Nonius integrating Weissenberg camera with nickel-filtered Cu Kα radiation (1.5418 A). $hk0$ through $hk9$ reciprocal lattice levels were collected using the multiple-film equiinclination technique. The various levels were scaled by means of two special integrated Weissenberg photographs, containing 30° samples from each layer.

The appearance of the photographs was very poor. The intensities of the reflections fell off rapidly with sin θ and no reflection could be observed beyond sin $\theta/\lambda = 0.45$, even with high-exposure times. All the photographs showed a fairly intense background.

Nevertheless, 1968 reflections were examined, but 478 were found too weak to be measured. The intensities of the integrated diffraction spots were measured on a Nonius microdensitometer, the density being assumed proportional to the intensity of the reflections. Intensities were corrected for Lorentz and polarization factors.

No correction was applied for absorption and for anomalous dispersion. The reflection $\bar{3}02$ was later considered to be affected by secondary extinction and omitted from the least-squares refinement and from the calculation of the final R factor.

The atomic scattering factors used were those of Viervoll and Øgrim[3] for nickel, those of Berghuis, *et al.*,[4] for chlorine, oxygen, nitrogen, and carbon, and those of McWeeny[5] for hydrogen.

Determination of the Structure

From a three-dimensional Patterson synthesis the nickel atoms were easily located. A Fourier synthesis, calculated with the contribution of the nickel atoms only, showed more or less clearly all the atoms of the salicylaldimine residues. Interpretation of the Fourier synthesis was made with the aid of a model. Two successive Fourier and one ΔF synthesis gave the positions of all 35 nonhydrogen atoms. The location of the carbon atoms of the ethyl groups attached to N_3 (Figure 1) presented some difficulties, owing to the poor resolution of the electron density peaks. Geometrical considerations were also employed for the location of these atoms.

At this point the conventional R factor was 30.0%. This rather high value was due mainly to the difficulty of guessing proper temperature factors for the atoms, in a structure where thermal motion seems to be quite important. R is throughout defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, where the sums are over the independent, observed reflections.

Refinement was continued by means of block diagonal least squares, with individual isotropic temperature factors. Only the observed reflections were introduced in the least-squares calculations.

The function minimized was $\Sigma w||F_o| - |F_c||^2$. Weights were assigned according to the function: $w = 1/(a + F_o + cF_o^2)$ with $a \simeq 2F_{\min}$ and $c \simeq 2/F_{\max}$.[6] Convergence proceeded slowly and after several cycles it was decided to try full-matrix least-squares

---

[1] L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, 4, 943 (1965).

[2] L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, 87, 2059 (1965).

[3] H. Viervoll and O. Øgrim, *Acta Cryst.*, 2, 277 (1949).

[4] J. Berghuis, I. M. Haanappel, M. Potters, B. O. Loopstra, C. H. Mac Gillavry, and A. L. Veenendaal, *ibid.*, 8, 478 (1955).

[5] R. McWeeny, *ibid.*, 4, 513 (1951).

[6] D. W. Cruickshank, *et al.*, "Computing Methods and the Phase Problem in X-ray Crystal Analysis," Pergamon Press, Oxford, 1961.

Table I. Positional Parameters, Temperature Factors, and Their Estimated Standard Deviations

Atom	x/a	$\sigma_x \times 10^5$	y/b	$\sigma_y \times 10^5$	z/c	$\sigma_z \times 10^5$	B, A^2	σ_B, A^2
Ni	0.0566	31	0.1785	16	−0.1288	31	4.03	0.07
Cl-1	−0.0217	72	0.0451	35	0.3698	74	8.58	0.18
Cl-2	−0.4099	71	0.3776	35	−0.6402	72	8.31	0.18
O-1	0.1256	129	0.1777	67	0.0585	134	6.46	0.32
O-2	−0.0634	118	0.2436	59	−0.1625	122	4.96	0.29
N-1	−0.0461	148	0.1051	72	−0.1544	155	5.26	0.36
N-2	0.0293	154	0.1943	73	−0.3058	157	4.76	0.37
N-3	−0.3331	218	0.0896	117	−0.4990	226	11.49	0.59
N-4	0.2363	173	0.1424	90	−0.0879	181	6.54	0.45
C-1	−0.0623	186	0.0803	93	−0.0667	197	5.14	0.46
C-2	0.0013	181	0.0991	89	0.0682	182	4.56	0.42
C-3	−0.0366	189	0.0670	91	0.1418	195	5.28	0.45
C-4	0.0258	191	0.0810	94	0.2744	193	5.67	0.46
C-5	0.1201	199	0.1242	97	0.3367	200	6.19	0.48
C-6	0.1585	188	0.1534	92	0.2618	196	5.46	0.45
C-7	0.0948	194	0.1448	97	0.1271	200	5.22	0.45
C-8	−0.1259	207	0.0771	103	−0.2938	210	6.21	0.53
C-9	−0.2519	228	0.1108	109	−0.3599	232	7.33	0.58
C-10	−0.3618	305	0.0294	168	−0.5079	319	16.65	0.91
C-11	−0.3657	314	0.0128	164	−0.6644	333	17.68	0.96
C-12	−0.4807	306	0.1201	160	−0.5599	312	15.80	0.88
C-13	−0.4606	302	0.1829	159	−0.5779	316	14.86	0.84
C-14	−0.0511	196	0.2312	93	−0.3985	191	5.06	0.44
C-15	−0.1367	169	0.2655	84	−0.3854	170	3.94	0.38
C-16	−0.2188	193	0.2993	91	−0.5014	193	4.51	0.45
C-17	−0.3023	211	0.3371	100	−0.4954	216	6.14	0.53
C-18	−0.3084	216	0.3461	105	−0.3903	233	6.25	0.54
C-19	−0.2276	229	0.3128	112	−0.2716	234	6.44	0.57
C-20	−0.1407	199	0.2723	98	−0.2727	204	5.11	0.48
C-21	0.1158	238	0.1572	116	−0.3258	245	7.63	0.63
C-22	0.2503	274	0.1626	134	−0.1936	291	11.59	0.76
C-23	0.3548	272	0.1691	142	0.0370	288	11.73	0.73
C-24	0.3477	253	0.2332	137	0.0526	264	9.98	0.69
C-25	0.2374	237	0.0767	123	−0.0567	240	8.32	0.62
C-26	0.3562	263	0.0404	125	−0.0289	267	10.20	0.71

refinement. This new series of cycles was executed at the University of Washington, with the least-squares program of Busing and Levy, adapted for the 7094 by Stewart.[7]

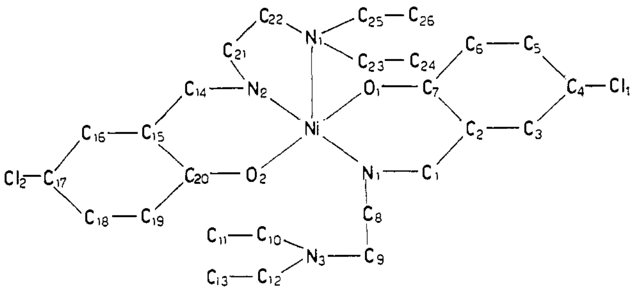


Figure 1. Schematic drawing of the molecule showing the labeling of the atoms.

The weighting scheme used in this series of cycles was: $\sqrt{w} = 1$ for reflections with $F_o \leqslant 40$; $\sqrt{w} = 40/F_o$ for $F_o > 40$. After two cycles all the shifts in the coordinates were less than the standard deviations, but the temperature factors still showed large shifts. The R factor at this point was 15.7%. Convergence for the temperature factors was attained after four more cycles, but R improved only slightly, the standard deviations of the coordinates increased by *ca.* 1.5 times, and a few C–C bond lengths showed oscillations up to 2–3σ. This behavior is certainly to be attributed to the abnormally high values reached by the temperature factors of the atoms, in the attempt to allow for the decomposition of the crystals.

The atomic coordinates and temperature factors with their estimated standard deviations, reported in Table I, are from the second full-matrix cycle.[8] Standard deviations were estimated by the least-squares program, using the formula

$$\sigma_j = \sqrt{\frac{a^{jj}\ \Sigma w \Delta F^2}{m - n}}$$

where m is the number of reflections, n is the number of parameters, and a^{jj} is the jj element of the inverse matrix. The behavior of C_{10}, C_{11}, C_{12}, and C_{13} during the least-squares cycles was strongly indicative of disorder. The shifts in the coordinates were inconsistent, the temperature factors much higher than those of the other ethyl carbon atoms, and the bond lengths and angles in which these atoms were involved, almost meaningless. A final ΔF synthesis, calculated without the contribution of these four atoms, showed at their positions only diffuse regions of low electron density. Anyhow, it should be noted that the R factor increases to 18.0% without the contribution of these atoms. No detailed study of the disorder has been made in

---

(7) J. M. Stewart, Technical Report TR-64-6, University of Maryland Computer Science Center, 1964.

(8) Calculated and observed structure factors are deposited as Document No. 8976 with the ADI Auxiliary Publications Project Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

view of the poor quality of the data. For the same reason, no attempt has been made to locate the hydrogen atoms or to introduce anisotropic temperature factors in the refinement. All the calculations, with the exception of the full-matrix least-squares cycles, have been performed on an IBM 1620 computer with a set of programs written by Albano, Bellon, Pompa, and Scatturin.[9]

Discussion

The structure consists of discrete molecules (Figure 2) in which nickel(II) is five-coordinated by the two oxygen atoms, the two azomethine nitrogen atoms, and the β-nitrogen atom of one (en) group. The arrangement of the ligands about the metal atom can be described as a distorted square pyramid, with N-2, O-2, O-1, and N-4 forming the base and N-1 at the apex.

The best least-squares plane through the four basal atoms has the equation: $1.558x + 4.469y - 0.204z = 1$ (monoclinic coordinates). The base is not strictly planar, as shown by the deviations of the atoms from the mean plane: O-1, −0.089; O-2, +0.093, N-2, −0.096; N-4, +0.092 A. The nickel atom is 0.36 A above the plane. The position of the metal atom above the basal plane seems to be a general feature of square-pyramidal complexes of transition metals.[10]

It has been pointed out[11] that as far as ligand–ligand repulsions are concerned, this configuration is more stable than that with the metal atom lying in the basal plane and only slightly less stable than the trigonal-bipyramidal configuration. The value of the L_{base}–M–L_{ap} angle (L_{base} = any of the basal ligands, M = metal, L_{ap} = apical ligand) which minimizes the repulsions has been shown to be $\simeq 100°$. Bond lengths and angles in the coordination polyhedron with their estimated standard deviations are given in Table II.

Table II. Bond Lengths and Angles about the Nickel Atom with Their Estimated Standard Deviations

Bond	Length, A	σ, A
Ni-O-1	1.929	0.016
Ni-O-2	1.954	0.014
Ni-N-1	1.977	0.017
Ni-N-2	1.997	0.021
Ni-N-4	2.199	0.023

Angle	Angle, deg	σ, deg
N-1-Ni-O-1	91.0	0.7
N-1-Ni-O-2	100.4	0.7
N-1-Ni-N-2	104.7	0.7
N-1-Ni-N-4	105.1	0.8
O-1-Ni-O-2	93.3	0.7
O-2-Ni-N-2	89.3	0.7
N-2-Ni-N-4	81.9	0.8
N-4-Ni-O-1	88.6	0.7
O-1-Ni-N-2	163.3	0.7
O-2-Ni-N-4	154.3	0.7

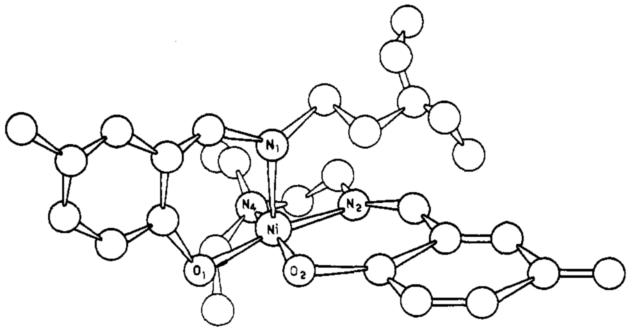


Figure 2. A perspective drawing of the bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II) molecule.

As evident from the values of the angles, distortions in the pyramid are mainly caused by the geometry of the ligand, which imposes the angles N-1–Ni–O-1 to be 91° and N-2–Ni–N-4 to be 82°.

Considering the salicylaldimine donor atoms, the Ni–O (av 1.94 A) and the Ni–N (av 1.99 A) distances are in good agreement with the corresponding Ni–O (av 1.95 A) and Ni–N (av 2.00 A) distances found in the five-coordinated complex of nickel(II) with bis(salicylidene-γ-iminopropyl)methylamine.[12]

It is interesting to note that these distances are intermediate between those found in the tetrahedral bis(N-isopropylsalicylaldiminato)nickel(II)[13] (Ni–O = 1.90 and Ni–N = 1.97 A) and those found in the octahedral bis(N-γ-dimethylaminopropylsalicylaldiminato)nickel(II)[14] (Ni–O = 2.00 and Ni–N = 2.05 A). The Ni–N-4 distance of 2.20 A is in good agreement with the analogous nickel–tertiary nitrogen distance of 2.22 A found in the octahedral complex dinitrobis(N,N-dimethylethylenediamine)nickel(II).[15] These distances are about 0.1 A longer than the nickel–primary nitrogen distances found in octahedral nickel(II) complexes.[16] This lengthening, in the present structure, is attributed mainly to short intramolecular contacts between the two ethyl groups attached to N-4 and the other ligands (see Table III). Bond lengths and angles in the rest of the molecule (Tables III and IV) appear to be normal, except, of course, in the ethyl groups attached to N-3.

In spite of the poor quality of the experimental data, the values reported show a good internal consistency in the two halves of the molecule, and are in good agreement with the values from analogous structures. However, the high values of the standard deviations preclude any detailed discussion of the results.

The equations for the mean planes passing through the salicylaldimine residues, the chlorine atoms, and C-8 or C-21 are: salicylaldimine 1, $-5.103x + 9.378y + 1.303z = 1$; salicylaldimine 2, $2.018x + 4.505y - 0.187z = 1$ (monoclinic coordinates). Deviations of the various atoms from these planes are reported in Table V.

As found in many salicylaldiminato complexes, the metal atom lies out of both planes, the distance from the plane being 0.21 A in one case and 0.36 A in the other. O-1 is also significantly out of the plane in

---

(9) V. Albano, P. L. Bellon, and F. Pompa, *Ric. Sci.*, **33**, 285 (1963); V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, **33**, 1067 (1963).

(10) J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 375 (1965).

(11) R. J. Gillespie, *J. Chem. Soc.*, 4679 (1963).

(12) P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Commun.*, 300 (1966).

(13) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *Acta Cryst.*, **17**, 1159 (1964).

(14) M. Di Vaira and P. L. Orioli, to be published.

(15) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(16) L. N. Swink and M. Atoji, *Acta Cryst.*, **13**, 639 (1960); B. W. Brown and E. C. Lingafelter, *ibid.*, **16**, 753 (1963).

Table III. Intramolecular Distances in the Salicylaldimine Groups and Their Estimated Standard Deviations

Bond	Length, A	σ, A	Bond	Length, A	σ, A
C-1–C-2	1.428	0.028	C-14–C-15	1.395	0.035
C-2–C-3	1.403	0.037	C-15–C-16	1.415	0.024
C-3–C-4	1.379	0.029	C-16–C-17	1.373	0.038
C-4–C-5	1.380	0.028	C-17–C-18	1.324	0.044
C-5–C-6	1.390	0.040	C-18–C-19	1.426	0.031
C-6–C-7	1.379	0.029	C-19–C-20	1.417	0.040
C-7–C-2	1.410	0.028	C-20–C-15	1.394	0.037
O-1–C-7	1.303	0.033	O-2–C-20	1.305	0.022
N-1–C-1	1.298	0.034	N-2–C-14	1.303	0.023
N-1–C-8	1.541	0.026	N-2–C-21	1.483	0.039
C-8–C-9	1.532	0.034	C-21–C-22	1.586	0.031
N-3–C-9	1.487	0.031	N-4–C-22	1.446	0.047
N-3–C-10	1.349	0.045	N-4–C-23	1.552	0.029
N-3–C-12	1.730	0.045	N-4–C-25	1.477	0.034
C-10–C-11	1.894	0.062	C-23–C-24	1.417	0.043
C-12–C-13	1.428	0.051	C-25–C-26	1.568	0.045
C-4–Cl-1	1.745	0.029	C-17–Cl-2	1.762	0.021
C-23–O-1	3.060	0.044	C-25–0-1	3.302	0.037
C-24–Ni	3.328	0.027	C-25–N-1	3.179	0.034
C-24–O-1	3.100	0.040			

Table IV. Bond Angles in the Salicylaldimine Groups and Their Estimated Standard Deviations

Angle	Angle, deg	σ, deg	Angle	Angle, deg	σ, deg
C-2–C-3–C-4	116.4	1.9	C-15–C-16–C-17	115.8	2.4
C-3–C-4–C-5	124.4	2.5	C-16–C-17–C-18	125.8	2.0
C-4–C-5–C-6	117.6	2.0	C-17–C-18–C-19	120.1	2.6
C-5–C-6–C-7	121.0	1.9	C-18–C-19–C-20	116.5	2.8
C-6–C-7–C-2	119.0	2.4	C-19–C-20–C-15	120.9	1.9
C-7–C-2–C-3	121.0	1.9	C-20–C-15–C-16	120.8	2.1
C-7–C-2–C-1	125.3	2.4	C-20–C-15–C-14	127.4	1.6
C-2–C-1–N-1	124.5	1.9	C-15–C-14–N-2	121.9	2.4
C-1–N-1–Ni	126.2	1.3	C-14–N-2–Ni	128.6	1.9
Ni–O-1–C-7	130.2	1.2	Ni–O-2–C-20	129.0	1.7
O-1–C-7–C-2	121.8	1.9	O-2–C-20–C-15	122.4	2.2
O-1–C-7–C-6	119.1	1.9	O-2–C-20–C-19	116.6	2.4
C-1–C-2–C-3	113.6	1.8	C-14–C-15–C-16	111.6	2.1
Ni–N-1–C-8	118.5	1.6	Ni–N-2–C-21	111.3	1.3
C-1–N-1–C-8	115.0	1.7	C-14–N-2–C-21	120.0	2.2
N-1–C-8–C-9	105.1	2.0	N-2–C-21–C-22	106.5	2.3
C-8–C-9–N-3	109.1	2.3	C-21–C-22–N-4	106.5	2.7
C-9–N-3–C-10	112.5	2.4	C-22–N-4–C-23	102.9	2.3
C-9–N-3–C-12	106.7	2.4	C-22–N-4–C-25	122.0	2.4
C-10–N-3–C-12	99.0	2.5	C-23–N-4–C-25	104.2	1.7
N-3–C-12–C-13	101.0	2.8	N-4–C-23–C-24	113.5	2.0
N-3–C-10–C-11	97.2	3.0	N-4–C-25–C-26	114.7	2.6
Cl-1–C-4–C-3	118.6	1.7	Cl-2–C-17–C-18	117.2	1.9
Cl-1–C-4–C-5	116.9	1.8	Cl-2–C-17–C-16	116.9	2.1
C-22–N-4–Ni	107.5	1.5	C-23–N-4–Ni	115.1	1.9
C-25–N-4–Ni	105.6	1.8			

Table V. Distances from Least-Squares Planes of Salicylaldimine Residues

	d, A		d, A
C-1	0.026	C-14	0.047
C-2	−0.019	C-15	−0.028
C-3	0.001	C-16	0.002
C-4	0.024	C-17	0.005
C-5	0.016	C-18	0.036
C-6	0.048	C-19	0.003
C-7	−0.066	C-20	−0.022
C-8	0.029	C-21	0.010
Cl-1	−0.026	Cl-2	−0.023
O-1[a]	−0.168	O-2	−0.001
N-1	−0.033	N-2	−0.030
Ni[a]	−0.360	Ni[a]	−0.210

[a] Atoms not included in the calculation of the least-squares plane.

salicylaldimine 1. It is interesting to note that O-1 has short molecular contacts with the carbon atoms of the ethyl groups attached to N-4 (Table III).

The molecular configuration of the complex appears to be determined mainly by the steric requirements of the ligand. Since C-21, attached to the sp^2-hybridized N-2, must lie in the salicylaldimine plane, N-4 must coordinate *trans* to O-2. The other salicylaldimine group must therefore coordinate in the *cis* position, the angle between the two mean planes through the salicylaldimine groups being 85.1°. Coordination in the sixth position appears to be prevented by steric hindrance of the bulky ethyl groups attached to N-4.

It should be pointed out that assuming a C–H distance of 1.05 A, a hydrogen atom from the methyl group of C-24 fills almost exactly the octahedral position at a distance of 2.59 A from the nickel atom. (The distance is calculated assuming the hydrogen atom in the closest position to the metal, on the cone having the C-23–C-24 bond as axis). The presence of a hydrogen atom filling the vacant octahedral site in square-pyramidal complexes has been also mentioned by other authors.[17]

Whether in these complexes the metal atom has to be considered truly five-coordinated with steric hindrance in the sixth position or six-coordinated with a weak metal–hydrogen interaction cannot be decided on purely geometrical basis. In the absence of any other evidence, we are inclined to speak of five-coordination at least in the reported cases, where the metal–hydrogen distance is about what is expected from van der Waals radii. In this connection it is interesting to point out that in the series of (X-SALen-NR$_2$)$_2$Ni(II) complexes, only those having R = C_2H_5 are five-coordinated in the solid state. Intermolecular distances less than 3.6 A are reported in Table VI. The Ni–N-3 distance is 4.92 A.

Table VI. Intermolecular Distances Less Than 3.6 A

Atom 1[a]	Atom 2	Distance, A	Molecule position
O-1	C-14	3.237	$x, 1/2 - y, 1/2 + z$
O-2	C-14	3.148	$x, 1/2 - y, 1/2 + z$
O-2	C-16	3.559	$x, 1/2 - y, 1/2 + z$
C-2	C-16	3.294	$x, 1/2 - y, 1/2 + z$
C-3	C-16	3.531	$x, 1/2 - y, 1/2 + z$
C-3	C-17	3.522	$x, 1/2 - y, 1/2 + z$
C-6	N-2	3.591	$x, 1/2 - y, 1/2 + z$
C-6	C-14	3.398	$x, 1/2 - y, 1/2 + z$
C-7	C-14	3.192	$x, 1/2 - y, 1/2 + z$
C-7	C-15	3.460	$x, 1/2 - y, 1/2 + z$
Cl–1	Cl-1	3.484	$-x, -y, 1 - z$

[a] In x, y, z.

The single example of a five-coordinated nickel(II) complex so far described by X-ray analysis is NiBr$_2$·triarsine (triarsine = $(CH_3)_2As(CH_2)_3As(CH_3)(CH_2)_3As(CH_3)_2$), which is a low-spin type complex.[18] The nickel atom is in a distorted square-pyramidal environment, with the three As and one Br forming the base

---

[17] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965); N. A. Bailey, J. M. Jenkins, R. Mason, and B. L. Shaw, *Chem. Commun.*, 237 (1965); M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19**, 886 (1965).

[18] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

and the other Br the apex. The set of basal ligands are not coplanar. Bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II) is the first example of a high-spin, five-coordinated nickel(II) complex, whose structure has been described by X-ray analysis.

Five-coordinated complexes of transition metals have been found to have square-pyramidal or trigonal-bipyramidal structures. Among the factors determining the stability of square-pyramidal or trigonal-bipyramidal configurations are: ligand–ligand repulsions, the type of metal–ligand bond, crystal-field stabilization energy (CFSE), crystal packing forces, steric effects.

We have already mentioned that, as far as ligand–ligand repulsions are concerned, a square-pyramidal configuration with L_{base}–M–$L_{ap} \simeq 100°$ is only slightly less stable than the trigonal-bipyramidal configuration. On the other hand, it has been shown[19] that for nickel(II) complexes, with this type of ligands, CFSE favors the square-pyramidal arrangement by 10 kcal/mole. CFSE effects should predominate in high-spin complexes, thus stabilizing the square-pyramidal configuration. Anyhow, the present structure does not constitute any definite proof in favor of this hypothesis, since the steric requirements of the ligand molecule determine essentially the distribution of the donor atoms about the metal.

Acknowledgment. We wish to thank the Research Computer Laboratory of the University of Washington for free time on the 7090. P. L. O. wishes to thank Professor E. C. Lingafelter for his kind hospitality. Financial support of the Italian Consiglio Nazionale delle Ricerche is gratefully acknowledged.

---

[19] M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

Intermediates in the Conversion of π- to σ-Allylic Complexes of Palladium(II)[1]

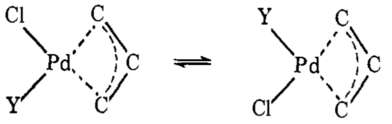
Kermit C. Ramey and Gary L. Statton

Contribution from the Atlantic Refining Company, Research and Development Division, Glenolden, Pennsylvania. *Received May 12, 1966*

Abstract: The temperature dependence of the nmr spectra of a number of allylic complexes of palladium yielded information on the intermediates in the conversion of π to σ complexes. The results are interpreted in terms of a number of processes including ligand exchange (as shown in eq 1) and π to σ equilibration (eq 2), which may be followed by a head-over-tail equilibration (eq 3).

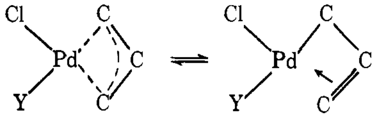
The allylic complexes of transition metals have been studied by a variety of techniques, including X-ray,[2] infrared,[3,4] and nmr.[1,4–8] Nevertheless, the structure of the intermediates in the conversion of π- to σ-allylic complexes and the mechanism by which the conversion takes place are not well understood. Most of the results have been based on nmr spectra as obtained at room temperature.

In a recent communication[1] we reported on the temperature dependence of the nmr spectra of some allylic complexes of palladium. The results for the triphenylphosphine adduct of methallylpalladium(II) chloride indicated that the system was involved in a number of equilibrations and the spectra were interpreted in terms of two equilibrating π structures which were followed by a π to σ equilibration. In this report the temperature dependence of the nmr spectra of a number of allylic complexes of palladium was studied in detail and the results are interpreted in terms of a number of processes including: ligand exchange



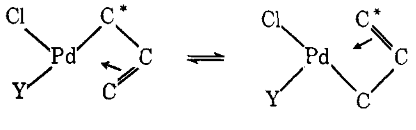
(1)

and π to σ equilibration



(2)

which may be followed by a head-over-tail equilibration



(3)

where Y = DMSO-d_6, $(Ph)_3As$, and $(Ph)_3P$.

Experimental Section

The nmr spectra were obtained with solutions containing approximately 10% of complex in solution in either $CDCl_3$ or o-$C_6H_4Cl_2$. A Varian HA-100 spectrometer equipped with a variable-temperature probe and accessories was used. The chemical shifts are reported in τ units.

---

[1] For part I see G. L. Statton and K. C. Ramey, *J. Am. Chem. Soc.*, **88**, 1327 (1966).

[2] J. M. Rowe, *Proc. Chem. Soc.*, **66** (1962).

[3] H. P. Fritz, *Chem. Ber.*, **94**, 1217 (1961).

[4] H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960).

[5] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963).

[6] B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961).

[7] D. W. Moore, H. B. Jonassen, T. B. Joyner, and A. J. Bertrand, *ibid.*, 1304 (1960).

[8] J. Powell, S. D. Robinson, and B. L. Shaw, *Chem. Commun.*, 78 (1965).