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The Crystal and Molecular Structure of Dimeric 2-Carboxyethyl-π-allylnickel Bromide

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Dimeric 2-carboxyethyl-π-allylnickel bromide, $[\pi\text{-}CH_2C(CO_2C_2H_5)CH_2NiBr]_2$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.17 \pm 0.01$ A, $b = 12.73 \pm 0.02$ A, $c = 4.83 \pm 0.01$ A, $\alpha = 77.4 \pm 0.2°$, $\beta = 97.6 \pm 0.2°$, $\gamma = 105.0 \pm 0.2°$, $Z = 1$. Despite the abnormally large mosaic spread of the crystal diffraction data, an X-ray structural analysis of the complex has been completed. The final discrepancy index is 14.2% for complete three-dimensional counter data collected with Mo Kα radiation ($\sin \theta_{max} = 0.41$). The molecule possesses a crystallographic center of symmetry, the over-all metal coordination scheme being similar to that established for π-allylpalladium chloride. The π-allyl and carboxylate groups are coplanar, the dihedral angle between this plane and the nickel coordination plane being 106.2°—a value in the range predicted from orbital overlap considerations.

Introduction

Many π-allyl–transition metal complexes are known,[1] and the crystal structures of a number of palladium[2-5] and nickel[6-7] derivatives have been determined. Crystallographic studies have also confirmed the existence of π-allyl–metal bonding in molecules containing such organic ligands as: azulene [in $C_{10}H_8Fe_2(CO)_5$],[8] cyclooctatetraene $[C_8H_8Fe_2(CO)_5]$,[9] bicyclo[3.2.1]octadienyl $[C_8H_9Fe(CO)_3{}^+BF_4{}^-]$,[10] perfluorocyclopentadiene $[C_5F_6Co_2(CO)_7]$,[11] and cycloocta-2,4-dienyl $[C_8H_{11}Pd(acac)]$.[12] The π-allyl system often occurs in organo-transition metal species formed as intermediates in the oligomerization (or cyclooligomerization) of unsaturated organic molecules—the complexes $RuCl_2(C_4H_6)_3$,[13] $Co_2(CO)_4(HC_2(t\text{-}C_4H_9))_2(HC_2H)$,[14] and $(isoprene)_2RuCl_3$[15] have been shown to contain α,ω-diallyls. Finally, the complexes $(C_6H_5C_2H)_3COFe_2(CO)_5$[16] and *trans*-(cyclododeca-1,5-dienyl)Rh(en)Cl_2[17] have also been found to contain π-allyl–metal linkages.

Although the delocalized π-allyl ligands are parallel in such species as $[CH_2C(CH_3)CH_2]_2Ni$,[6] the dihedral angle between the metal coordination plane and the π-allyl ligand in palladium complexes of the type $[\pi\text{-}C_3H_5PdX]_2$ does not have the expected value of 90°, but is typically about 110–120°.[18,19] This last result has been explained[19] in terms of the various π-allyl–metal overlap integrals, which also indicate that the corresponding π-allyl–nickel complexes (which have distinctly different chemical properties) should have the π-allyl group inclined at a similar angle to the metal coordination plane.

In order to determine the dihedral angle between the π-allyl ligand and the nickel coordination plane, a crystallographic determination of the structure of dimeric 2-carboxyethyl-π-allylnickel bromide was undertaken.

Experimental Section

Dimeric 2-carboxyethyl-π-allylnickel bromide, $[CH_2C(CO_2C_2H_5)CH_2NiBr]_2$, was prepared[20] from the reaction of 2-carboxyethylallyl bromide and nickel tetracarbonyl. The complex was isolated as extremely air-sensitive red plates and needles which decompose by an apparently autocatalytic route. For the crystallographic analysis, crystals were inserted into 0.2-mm thin-walled capillary tubes, under an argon atmosphere. Of some 30 specimens examined, only one (an irregular needle of dimension 0.10 × 0.12 × 0.72 mm) was found to give an acceptable pattern, and even this showed an abnormally large mosaic spread. The compound appeared to crystallize in the triclinic habit; since a survey of the reciprocal lattice failed to indicate any diffraction symmetry other than that imposed by the Friedel condition ($\bar{1}$), the crystals were assumed to be truly triclinic. Unit-cell parameters, obtained from zero-layer Weissenberg (*hk*0) and precession (0*kl* and *h*0*l*) photographs taken with Mo Kα radiation (λ 0.7107 A) and calibrated with sodium chloride ($a_{NaCl} = 5.640$ A) are: $a = 7.17 \pm 0.01$ A, $b = 12.73 \pm 0.02$ A, $c = 4.83 \pm 0.01$ A, $\alpha = 77.4 \pm 0.2°$, $\beta = 97.6 \pm 0.2°$, $\gamma = 105.0 \pm 0.2°$. There are no systematic absences, and the unit-cell volume is 414.5 A^3. The calculated density[21] is 2.016 g cm^{-3} for $M = 503.3$ and $Z = 1$. Of the possible space groups P1 (No. 1) and $P\bar{1}$ (No. 2), the latter was considered the more likely due to its greater frequency of occurrence and to the likelihood that the molecule might contain a center of symmetry. The linear absorption coefficient (μ) is 73.7 cm^{-1}. To a first approximation the specimen may be treated

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as a cylinder of radius 0.055 mm; hence $\mu R = 0.405$. Since the variation of transmission factor with θ is small,[22] no correction for absorption was applied.

Data were collected with a 0.01° incrementing Buerger automated diffractometer in conjunction with a fully-stabilized Phillips X-ray generator (operated at 45 kv/17 ma), a Phillips transistorized scintillation counter, and a Phillips electronics panel. Within a given zone, the over-all stability of the entire system was monitored by remeasuring a carefully-selected check reflection after every 20 reflections had been collected. No variation greater than $3\sqrt{\text{count}}$ was detected. The scintillation count was adjusted to receive Mo Kα radiation (λ 0.7107 A), the Mo Kβ radiation being virtually eliminated by the use of a 0.003-in. Zirconium filter at the X-ray source. The base line of the pulse-height analyzer, the window voltage, and the counter voltage were maintained at constant values throughout the analysis. The diffractometer was programmed[23] to collect all data in a given Weissenberg zone, using a stationary background, ω scan, stationary background counting sequence. Owing to the unusually large mosaic spread of the diffraction peaks, the angle scanned (ω) was greater than usual [$\omega = (3.0 + 1/L)°$], where $1/L$ is the Lorentz factor. (The inclusion of the term involving the Lorentz factor allows for the divergence of the X-ray beam which is usually associated with distorted low-order reflections on upper-level data.[24]) $I(hkl)$, the intensity of a reflection hkl (having the Weissenberg coordinates $\Upsilon_0(hkl)$ and $\Phi_0(hkl)$[25]), was recorded in the following way: (i) The counter was positioned to $\Upsilon_0(hkl)$, where it remained during the subsequent steps. (ii) The crystal was rotated to Φ_1 [$=\Phi_0(hkl) - \omega(hkl)/2$] and the first background (B_1) counted for t seconds. (iii) The crystal was slowly rotated by $\omega(hkl)$ degrees at a constant rate of 2°/min to ϕ_2 [$=\Phi_0(hkl) + \omega(hkl)/2$]. The entire scan took $2t$ seconds, the integrated count being C. (iv) The second background (B_2) was measured for t seconds at ϕ_2.

Reflections for which $I(hkl)$ [$= C - (B_1 + B_2)$] were negative or zero were removed from the analysis. Observed reflections were weighted according to the scheme

$$\sigma[I(hkl)] = 0.1(C + B_1 + B_2) + 2|B_1 - B_2|]$$

(The large mosaic spread of the diffraction peaks resulted in an overlap problem; the weighting scheme adopted is sensitive to any asymmetry between the background counts B_1 and B_2 and gives a low weight to any reflection showing a significant asymmetry. While this is not a very satisfactory state of affairs, the quality of the crystals which could be obtained was such as to preclude a more accurate analysis.) The zones $hk0$ through $hk5$, representing complete three-dimensional data to $\sin\theta = 0.41$, were collected, corrected for Lorentz and polarization effects, and placed on an absolute scale by means of a Wilson plot.

The Solution of the Structure

The positions of the nickel ($X = 0.143$, $Y = 0.097$, $Z = 0.148$) and bromine ($X = 0.190$, $Y = -0.060$, $Z = 0.019$) atoms were quickly and unambiguously determined from a three-dimensional Patterson[26] synthesis, which had been sharpened so that the average intensity was independent of $\sin\theta$, and which had the origin peak reduced to the size of a single Ni···Ni interaction. A structure-factor calculation[27] based only on the contributions from nickel and bromine atoms ($R_F = \Sigma||F_o| - F_c||/\Sigma F_o = 0.374$) was used to phase a three-dimensional Fourier synthesis, from which it was possible to locate each of the carbon and oxygen atoms in the molecule. Structure-factor calculations, phased by one nickel, one bromine, two oxygen, and six carbon atoms, had an initial discrepancy index (R_F) of 0.35, which converted to a value of 0.179 after four cycles of positional and isotropic thermal parameter refinement. A survey of a difference Fourier at this stage showed signs of anisotropic motion associated with the heavy atoms, and refinement was continued using anisotropic thermal parameters, which were of the form

$$T = \exp[-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl]$$

Three cycles of refinement of the 90 positional and anisotropic thermal parameters led to a final residual $R_F = 0.142$ for the 1140 independent reflections, at which stage refinement was judged to be complete, since the maximum suggested coordinate shifts were less than 10% of the standard deviation for the parameter considered. [The rather high value of R_F is attributable to the overlap of adjacent reflections (*vide supra*).] Contributions from the nine hydrogen atoms were not included in the analysis, nor were their positions detected from a final difference Fourier.

During the analysis the scattering factors for neutral nickel, bromine, oxygen, and carbon were used.[28] No corrections were made for dispersion. The residual minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$. Final observed and calculated structure factors are shown in Table I; atomic coordinates are given in Table II, and thermal parameters in Table III.

Molecular Structure

The successful determination of the crystal structure confirmed that the true space group is P$\bar{1}$ (No. 2), with the dimeric molecule possessing a crystallographic center of symmetry. As such, the situation is analogous to that of $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$ which has two molecules in space group P2_1/n.[2d]

The stereochemistry of dimeric 2-carboxyethyl-π-allylnickel bromide is shown in Figure 1; the packing of molecules in the unit cell is illustrated by Figure 2. Interatomic distances[29] are collected in Table IV; bond angles[29] are shown in Table V.

Each of the (equivalent) d^8 Ni(II) cations in the molecule is in a formally square-planar environment; the donation of two electrons from each bromine and four electrons from the substituted π-allyl anion results in the stable 16-electron configuration for each of the nickel ions, in keeping with the observed diamagnetism of such d^8 square-planar complexes. The NiBr$_2$Ni bridge is accurately planar and approximately sym-

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(22) "International Tables for X-Ray Crystallography," Vol. 2, The Kynoch Press, Birmingham, England, 1959, p 295.

(23) Using the program PREPAR by G. N. Reeke.

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(27) Structure-factor calculations and full-matrix least-squares refinement of positional and thermal parameters were performed using ORFLS, a Fortran crystallographic least-squares program by W. R. Busing, K. O. Martin, and H. A. Levy.

(28) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England. Values for nickel and bromine are taken from p 211; those for oxygen and carbon from p 202.

(29) Interatomic distances and angles were calculated using ORFFE, a crystallographic function and error program by W. B. Busing and H. A. Levy.

TABLE I

$[\pi\text{-}CH_2C(CO_2C_2H_5)CH_2NiBr]_2$: FINAL OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

H	K	5FO	5FC
••• L =			0 ••
0	0	----	1240
2	0	-272	-282
3	0	-298	-307
4	0	-163	-157
5	0	96	99
6	0	78	80
7	0	38	32
2	-1	-154	-169
2	1	-188	-185
3	-1	-231	-242
3	1	-383	-392
4	1	-102	-130
5	-1	34	30
5	1	122	129
6	-1	31	6
6	1	97	109
7	-1	-19	-10
7	1	45	42
1	2	108	126
2	-2	-98	-105
2	2	-246	-228
3	-2	14	10
3	2	-324	-310
4	-2	-12	-11
4	2	-15	-6
5	2	95	109
6	-2	-36	-27
6	2	102	117
7	-2	-35	-40
7	2	10	11
8	-2	28	10
0	3	173	176
1	-3	-179	-178
1	3	68	51
2	-3	-84	-87
2	3	-63	-50
3	-3	97	101
3	3	-163	-162
4	-3	115	118
4	3	-29	-31
5	-3	34	37
5	3	74	77
6	-3	-78	-90
6	3	90	94
7	-3	-47	-64
7	3	34	10
8	-3	10	6
0	4	-250	-235
1	-4	-201	-207
1	4	136	133
2	4	59	70
3	-4	181	173
3	4	-26	-33
4	-4	218	219
4	4	-47	-17
5	-4	-34	-29
5	4	22	29
6	-4	-77	-89
6	4	31	33
7	-4	-67	-85
7	4	28	6
8	-4	13	11
0	5	-218	-201
1	-5	-261	-261
1	5	57	61
2	-5	-85	-78
2	5	73	60
3	-5	273	270
3	5	120	120
4	-5	215	211
4	5	-34	-17
5	-5	-48	-33
5	5	-43	-28
6	-5	-78	-80
6	5	20	22
7	-5	-54	-61
0	6	-270	-255
1	-6	-339	-340
2	-6	-16	-18
-2	-6	278	262
3	-6	175	168
3	6	118	111
4	-6	220	215
4	6	-45	-37
5	-6	60	45
5	6	-59	-47
6	-6	-122	-118
6	6	-14	-28
7	-6	-36	-31
8	-6	-24	-5
0	7	-219	-215
1	-7	-307	-318
1	7	69	62
2	-7	-11	-5
2	7	259	249
3	-7	158	151
3	7	130	129
4	-7	96	104
4	7	-60	-39
5	-7	35	4
5	7	-86	-73
6	-7	-52	-35
6	7	-58	-59
7	-7	-32	-18
1	-8	-149	-140
1	8	90	90
2	-8	-61	-49
2	8	120	142
3	-8	76	69
3	8	98	102
4	-8	39	23
4	8	-46	-44
5	8	-106	-94
6	-8	11	3
7	-8	26	22
0	9	-74	-42
1	-9	-44	-20
1	9	28	24
2	-9	20	24
2	9	115	116
3	-9	27	11
4	-9	-64	-59
4	9	-43	-43
5	-9	-28	-25
6	-9	-22	-5
7	-9	51	43
0	10	41	17
1	10	-38	-41
1	-10	52	55
2	10	24	10
2	-10	65	70
3	-10	35	9
3	10	31	12
4	-10	-104	-100
4	10	-20	-18
5	-10	-91	-75
6	-10	39	29
7	-10	68	42
0	11	-40	-19
1	-11	117	127
1	11	-39	-35
2	11	-53	-51
2	-11	77	88
3	-11	-48	-42
3	11	-29	-6
4	-11	-86	-74
5	-11	-82	-67
6	-11	17	19
0	12	26	9
1	12	-52	-66
1	-12	77	92
2	12	-61	-57
-2	12	82	93
3	-12	-25	-13
4	-12	-96	-89
5	-12	-51	-39
0	13	12	21
1	13	-65	-74
1	-13	64	73
2	-13	56	67
4	-13	-54	-57
5	-13	-39	-31
1	-14	53	59
2	-14	31	38
3	-14	-30	-19
••• L =			1 ••
1	0	-204	-190
-1	0	368	363
2	0	-289	-293
-2	0	-18	-26
3	0	-250	-276
-3	0	-135	-134
4	0	25	35
-4	0	-149	-147
5	0	108	125
6	0	57	75
-6	0	34	29
-7	0	10	13
0	-1	366	414
1	-1	171	161
-1	-1	474	456
1	1	-15	-25
2	-1	-316	-321
-2	-1	-70	-74
2	1	-276	-274
-2	1	-69	-73
3	-1	-271	-291
-3	-1	-327	-302
3	1	-196	-213
-3	1	-165	-153
4	-1	-23	-1
-4	-1	-214	-204
-4	1	54	51
5	-1	69	67
-5	-1	42	45
5	1	126	150
-5	1	11	18
6	-1	56	72
-6	-1	79	76
6	1	62	87
-6	1	35	4
-7	-1	15	34
7	1	-26	-18
-7	1	-46	-54
0	-2	545	522
0	2	-119	-121
1	-2	17	10
-1	-2	378	351
1	2	324	298
-1	2	-44	-39
2	-2	-229	-226
-2	-2	-174	-160
2	2	-212	-201
-2	2	-40	-30
3	-2	-119	-119
-3	-2	-343	-313
3	2	-132	-139
-3	2	-13	-7
4	-2	-22	-20
-4	-2	-206	-200
4	2	30	45
-4	2	142	146
5	-2	38	45
-5	-2	9	27
5	2	73	77
-5	2	69	54
-6	-2	143	148
6	2	62	67
-6	2	-52	-56
-7	-2	52	55
7	2	-30	-21
-7	2	-83	-87
-8	2	-22	-16
0	-3	198	196
0	3	174	164
1	-3	28	5
-1	-3	45	39
1	3	-49	-53
-1	3	-277	-275
2	-3	-13	-2
-2	-3	20	31
2	3	-9	-20
-2	3	-131	-140
3	-3	-45	-31
-3	-3	-290	-256
3	3	22	6
-3	3	207	188
4	-3	42	44
-4	-3	-165	-153
4	3	-21	-12
-4	3	171	178
-5	-3	82	85
5	3	38	52
-5	3	76	62
6	-3	-55	-82
-6	-3	99	93
6	3	40	32
-6	3	-79	-88
-7	-3	57	62
-7	3	-73	-75
-8	3	-15	-33
0	-4	-25	-35
0	4	-98	-95
1	-4	-69	-64
-1	-4	88	81
1	4	80	92
-1	4	-359	-355
2	-4	50	34
-2	-4	-55	-44
2	4	166	147
-2	4	-125	-127
3	-4	139	134
-3	-4	-139	-128
3	4	25	21
-3	4	96	99
4	-4	49	34
-4	-4	-57	-48
4	4	-49	-48
-4	4	301	305
5	-4	-12	-32
-5	-4	59	64
-5	4	107	105
6	-4	-50	-54
-6	-4	68	70
6	4	-10	-0
-6	4	-95	-98
7	-4	-55	-46
-7	4	-88	-97
0	-5	-173	-158
0	5	-259	-253
1	-5	-123	-137
-1	-5	29	38
1	5	210	203
-1	5	-393	-388
2	5	247	234
-2	5	-223	-214
3	-5	253	233
-3	-5	18	13
3	5	68	79
-3	5	192	188
4	-5	113	104
-4	-5	22	2
4	5	-51	-55
-4	5	283	278
5	-5	-38	-56
-5	-5	-42	-21
5	5	-58	-52
-5	5	75	71
6	-5	-100	-83
-6	-5	63	56
-6	5	-69	-67
7	-5	-54	-39
-7	5	-74	-74
0	-6	-241	-237
0	6	-78	-78
1	-6	-162	-156
-1	-6	-117	-108
1	6	148	140
-1	6	-337	-342
2	-6	97	90
-2	-6	164	161
2	6	294	278
-2	6	-198	-197
3	-6	207	198
-3	-6	96	87
3	6	66	60
-3	6	122	121
4	-6	130	111
4	6	-83	-76
-4	6	139	128
5	-6	-55	-46
-5	-6	-35	-10
5	6	-89	-81
-5	6	92	91
6	-6	-98	-91
-6	6	-59	-59
7	-6	-18	-25
-7	6	-10	-20
-8	6	108	5
0	-7	-236	-228
0	7	-49	-59
1	-7	-190	-190
-1	-7	-39	-33
1	7	195	189
-1	7	-221	-221
2	-7	78	66
-2	-7	110	102
2	7	216	204
-2	7	-94	-81
3	-7	187	176
-3	-7	157	152
-3	7	33	34
4	-7	109	92
4	7	-82	-78
-4	7	64	47
5	-7	-39	-44
-5	-7	-10	-41
5	7	-81	-86
-5	7	12	9
6	-7	-42	-36
-6	7	-47	-12
7	-7	-34	-28
-8	7	16	28
0	-8	-233	-240
0	8	-49	-37
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0	2	104	72
1	-2	-44	-29
-1	-2	-79	-21
1	2	78	60
-2	2	-76	-46
-3	2	-186	-105
0	-3	-72	-47
0	3	53	75
1	-3	-98	-52
-1	-3	47	11
1	3	53	44
2	3	-54	-31
-2	3	-68	-34
-3	3	-89	-59
-4	3	-44	-36
1	4	-75	-5
-1	4	41	34
-2	4	-43	-28
-3	4	25	4
-4	4	-108	-27
-1	5	60	34
2	5	-71	-14
-3	5	-18	-5
-4	5	49	25
0	6	-19	-30
-1	6	-41	-8
-2	6	56	39
-3	6	67	46
-4	6	74	31
0	7	-47	-39
-1	7	-27	-42
-2	7	69	26
-3	7	154	90
-4	7	74	36
0	8	-33	-46
-1	8	-68	-57
-2	8	52	7
-3	8	114	65
-1	9	-124	-52

[a] The table gives h, k, $5F_o$, and $5F_c$ in blocks of constant l.

metrical, the mean Ni–Br distance being 2.356 A. The Ni–Br–Ni angle is 87°, and the Br–Ni–Br angle 93°. The increase in the Br–Ni–Br angle from the expected square-planar value of 90° is perhaps best rationalized as a result of the minimization of intermolecular van der Waals repulsive forces, since the Br · · · Br distance of 3.147 A is less than the van der Waals contact distance of ~3.9 A.[30] The nickel–nickel distance of 3.245 A in the present complex is sufficiently great to preclude the possibility of any significant metal–metal interaction in the system. The distances of the carbon atoms of the π-allyl group from the nickel show a symmetrical pattern, the terminal carbon atoms being more distant (Ni–C_1 = 2.05 A, Ni–C_3 = 2.06 A) than the central carbon atom (Ni–C_2 = 1.90 A). Although this difference appears to be significant, it should be remembered that the report of Oberhansli and Dahl[2c] that a similar variation occurred in $[\pi\text{-}C_3H_5PdCl]_2$ was not substantiated by a low-temperature study[2d] of that compound. The mean C–C bond length of 1.455 A in

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(30) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

TABLE II

$[\pi\text{-CH}_2\text{C(CO}_2\text{C}_2\text{H}_5\text{)CH}_2\text{NiBr}]_2$: FINAL ATOMIC POSITIONS, WITH ESTIMATED STANDARD DEVIATIONS[a]

Atom	X	$10^4\sigma$ (X)	Y	$10^4\sigma$ (Y)	Z	$10^4\sigma$ (Z)
Ni	0.14291	3.4	0.09719	1.9	0.14844	5.5
Br	0.19040	2.9	−0.05955	1.5	0.01848	4.9
C_1	0.4132	22	0.1373	15	0.3558	45
C_2	0.3170	28	0.2277	16	0.2375	38
C_3	0.1337	27	0.2253	14	0.3382	46
C_4	0.3985	27	0.3233	14	−0.0180	39
C_5	0.6489	28	0.3991	13	−0.3163	45
C_6	0.8142	26	0.3634	16	−0.3991	46
O_1	0.3116	18	0.3894	10	−0.1152	28
O_2	0.5608	17	0.3116	9	−0.0849	26

[a] Estimated standard deviations (esd's) are derived from the appropriate diagonal elements (a_{jj}) of the matrix inverse to the normal matrix; the esd of the jth parameter is given by $\sigma(j) = [a_{jj}\Sigma\omega\Delta^2/(m - n)]^{1/2}$, where m is the number of observed structure factors, n the number of parameters being varied, and $\Sigma\omega\Delta^2$ the customary summed, weighted discrepancy between observed and calculated structure factors.

TABLE III

$[\pi\text{-CH}_2\text{C(CO}_2\text{C}_2\text{H}_5\text{)CH}_2\text{NiBr}]_2$: FINAL ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$), WITH ESTIMATED STANDARD DEVIATIONS[a]

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B_{equ}[b]
Ni	241.2 (7.5)	66.4 (2.0)	357.6 (15.4)	3.2 (3.0)	126.1 (9.5)	−5.7 (4.9)	3.87
Br	272.8 (6.1)	71.8 (1.6)	714.2 (16.6)	31.7 (2.5)	151.0 (8.9)	−30.1 (4.6)	5.23
C_1	117 (38)	114 (18)	806 (155)	14 (21)	−82 (67)	−102 (47)	5.3
C_2	346 (58)	127 (19)	302 (114)	44 (28)	−38 (71)	−145 (41)	5.6
C_3	316 (55)	96 (17)	820 (158)	−3 (25)	131 (83)	−184 (46)	6.3
C_4	234 (46)	71 (14)	372 (115)	29 (22)	37 (64)	−43 (34)	4.0
C_5	358 (56)	68 (14)	705 (139)	−3 (23)	251 (80)	25 (38)	5.7
C_6	231 (49)	124 (20)	774 (151)	19 (25)	136 (78)	23 (46)	6.2
O_1	351 (39)	91 (11)	665 (95)	74 (18)	108 (53)	38 (28)	6.0
O_2	307 (36)	91 (10)	466 (76)	29 (16)	127 (46)	−18 (24)	5.1

[a] Estimated standard deviations are derived from diagonal elements of the matrix (see note a, Table II). [b] B_{equ} is an approximate "equivalent isotropic thermal parameter."

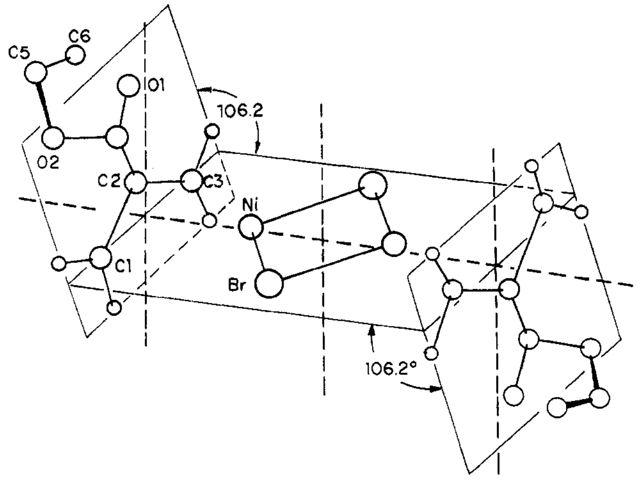

Figure 1.—Stereochemistry and numbering of atoms in $[\pi\text{-CH}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{NiBr}]_2$.

the π-allyl group is rather longer than those previously determined, but, since $\sigma(\text{C–C}) \geqslant 0.03$ A, the difference is not statistically significant. The angle of 119.6° at the apex of the π-allyl group is in good agreement with the previously observed values of 119.8° for $[\pi\text{-C}_3\text{H}_5\text{PdCl}]_2$[2d] and 119.0° for $\text{C}_8\text{H}_{11}\text{Pd(acac)}$[12] and is indistinguishable from the expected sp² value of 120°. Other bond distances and angles within the organic framework are within the expected range.

The coordination plane of the nickel atoms (*i.e.*, the NiBr_2Ni plane, which has the equation[31] $-0.3101X - 0.3010Y + 0.9017Z = 0$) cuts the π-allyl skeleton at a line about two-thirds the way along from the central (C_2) to the terminal (C_1 and C_3) carbon atoms. The terminal carbon atoms are 0.24 A (C_1) and 0.27 A (C_3) below this plane, whereas the central carbon atom (C_2) is 0.44 A above this plane.

Within the limits of experimental error, the six atoms constituting the π-allyl group and the carboxylate group form a plane, the root-mean square deviation from this plane being 0.02 A (see Table VI), indicating that the π-allyl and carbonyl groups form a single conjugated system.

The carboxylatoallyl plane is inclined at an angle of 106.2 ± 1.7° to the nickel coordination plane. This result is not greatly different from the value of 111.5°

TABLE IV

$[\pi\text{-CH}_2\text{C(CO.C}_2\text{H}_5\text{)CH}_2\text{NiBr}]_2$: INTERATOMIC DISTANCES[a,b]

Atoms	Distance, A	Atoms	Distance, A
Bond Distances			
Ni—Br	2.334 ± 0.005	C_1—C_2	1.46 ± 0.026
Ni—Br*	2.378 ± 0.005	C_2—C_3	1.45 ± 0.028
		C_2—C_4	1.59 ± 0.021
Ni—C_1	2.05 ± 0.017	C_4—O_1	1.16 ± 0.023
Ni—C_2	1.90 ± 0.021	C_4—O_2	1.30 ± 0.022
Ni—C_3	2.06 ± 0.025	O_2—C_5	1.47 ± 0.020
		C_5—C_6	1.50 ± 0.029
Other Distances			
Ni···Ni*	3.245 ± 0.009	C_3···O_1	2.85 ± 0.021
Br···Br*	3.147 ± 0.006	C_3···O_2	3.70 ± 0.025
Br···C_1	3.24 ± 0.024	C_1···O_1	3.69 ± 0.021
Br*···C_1	4.41 ± 0.018	C_1···O_2	2.81 ± 0.020
Br···C_2	3.88 ± 0.024	C_1···C_5	4.28 ± 0.025
Br*···C_2	3.91 ± 0.021	C_1···C_6	4.87 ± 0.028
Br···C_3	4.37 ± 0.025		
Br*···C_3	3.29 ± 0.024		

[a] Atoms related to the basic asymmetric unit by inversion through the center of symmetry at 0, 0, 0 are indicated by an asterisk. [b] Estimated standard deviations have been calculated from the full correlation matrix using ORFFE (ref 25). They are probably underestimates, because of known systematic errors (see text).

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[31] Planes are expressed in Cartesian coordinates, related to triclinic coordinates by the following transformations

$$X = xa \sin\gamma + zc(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma$$

$$Y = yb + xa\cos\gamma + zc\cos\alpha$$

$$Z = zc[(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)/\sin^2\gamma]^{1/2}$$

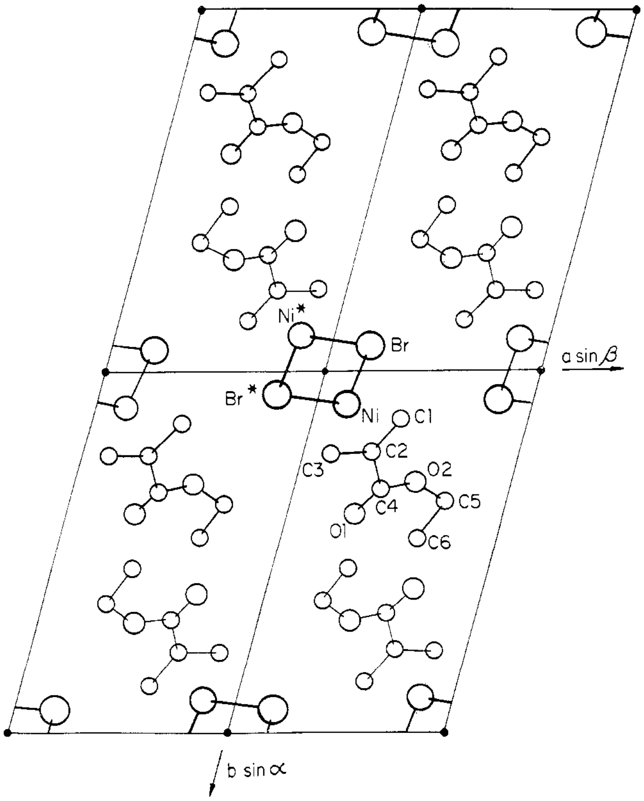

Figure 2.—The packing of molecules in the [π-$CH_2C(CO_2C_2H_5)$-$CH_2NiBr]_2$ crystal, viewed along *c*.

observed for [π-$C_3H_5PdCl]_2$[2d] and is in the range predicted by the overlap calculations of Kettle and Mason.[19]

Table V

[π-$CH_2C(CO_2C_2H_5)CH_2NiBr]_2$:

Bond Angles with Estimated Standard Deviations[a]

Atoms	Angle, deg	Atoms	Angle, deg
Ni–Br–Ni*	87.05 ± 0.19	C_1–C_2–C_3	119.6 ± 1.3
Br–Ni–Br*	92.95 ± 0.19	C_1–C_2–C_4	121.6 ± 1.8
Br–Ni–C_1	95.09 ± 0.67	C_3–C_2–C_4	118.6 ± 1.4
Br*–Ni–C_3	95.45 ± 0.57	C_2–C_4–O_1	119.1 ± 1.7
C_1–Ni–C_2	43.3 ± 0.80	C_2–C_4–O_2	110.6 ± 1.4
C_2–Ni–C_3	42.9 ± 0.81	O_1–C_4–O_2	130.3 ± 1.4
C_1–Ni–C_3	75.6 ± 0.88	C_4–O_2–C_5	114.0 ± 1.3
		O_2–C_5–C_6	107.1 ± 1.4

[a] Estimated standard deviations are obtained from the full correlation matrix, using ORFFE

Table VI

[π-$CH_2C(CO_2C_2H_5)CH_2NiBr]_2$: Least-Squares Plane through the π-Allyl and Carboxylate Groups (Atoms Weighted Equally)

Plane:[a] $0 4535X + 0.5919Y + 0.6622Z = 3.1818$

Atom	Deviation from plane	Atom	Deviation from Plane
C_1	−0.027	C_4	+0.006
C_2	+0.033	O_1	−0.023
C_3	+0.001	O_2	+0.010

[a] Orthogonal coordinates; see ref 31.

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Contribution from the Chemistry Department,
Queen's University, Belfast, Northern Ireland

High-Spin Five-Coordinate Complexes of Nickel(II) with Di(2-pyridyl-β-ethyl)amine and Di(2-pyridyl-β-ethyl) Sulfide

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The tridentate ligands di(2-pyridyl-β-ethyl)amine (DPEA) and di(2-pyridyl-β-ethyl) sulfide (DPES) form stable, crystalline complexes with nickel(II) of general formula $NiLX_2$, where L = DPEA or DPES and $X^- = Cl^-, Br^-, I^-$, or NCS^-. Magnetic, electronic spectral, conductivity, and molecular weight data indicate that the halide complexes have high-spin five-coordinate configurations both in the solid state and in solution in solvents of low polarity. The stereochemistries of the thiocyanato complexes are not certain. In the case of $Ni(DPEA)(NCS)_2$ the available evidence supports a binuclear, six-coordinate structure containing both bridging and terminal NCS groups. The results are discussed in relation to steric and possible π-bonding effects.

Five-coordination in nickel(II) complexes is now well known.[1] Almost all such complexes are, however, low-spin and usually contain ligand atoms such as P, As, S, or Se capable of forming strong covalent bonds with the metal ion. They also possess vacant d orbitals so there is also the possibility that π bonding may play a part in promoting spin pairing in these compounds. Recently, however, a few high-spin five-coordinate complexes of nickel(II) have been reported. These have contained N-substituted salicylaldimines,[2] ali-

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[1] See, for example: G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965); G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398, (1965); D. W. Meek, G. Dyer, M. Workman, and G. S. Benner, Abstracts, 9th International Conference on Coordination Chemistry, St. Moritz, Switzerland, 1966.

[2] L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965); L. Sacconi, P. Nannelli, N. Nardi, and V. Campigli, *Inorg. Chem.*, **4**, 943 (1965).