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The Crystal and Molecular Structure of Bis(*o*-phenylenediamino)nickel, Ni$[C_6H_4(NH)_2]_2$[1]

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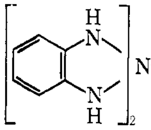
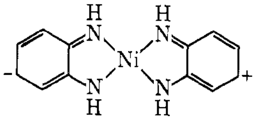
The crystal and molecular structure of bis(*o*-phenylenediamino)nickel, Ni$[C_6H_4(NH)_2]_2$, has been determined by single-crystal X-ray diffraction techniques. The crystals are monoclinic ($P2_1/c$) with $a = 5.845 \pm 0.020$ Å, $b = 7.485 \pm 0.026$ Å, $c = 25.27 \pm 0.09$ Å, $\beta = 90° 10' \pm 10'$, and $Z = 4$. The observed and calculated densities are, respectively, 1.62 ± 0.02 and 1.64 ± 0.01 g/cm^3. The structure was refined by least-squares methods to a conventional R factor of 11.1% for 792 nonzero independent reflections collected at room temperature by film techniques. The nickel atom is four-coordinate in the monomeric, planar Ni$[C_6H_4(NH)_2]_2$ molecule. The average Ni–N bond length of 1.832 ± 0.011 Å is one of the shortest yet observed, and the bond lengths in the chelate rings (N–C, 1.38 ± 0.02; C–C, 1.41 ± 0.02 Å) indicate substantial delocalization of the π bonds. The observed structure seems inconsistent with a formulation based on nickel(IV), but it supports the assignment of this compound as the neutral central member of a family of complexes which are interrelated by electron-transfer reactions.

Introduction

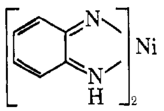
In 1927 Feigl and Fürth[2] reported the preparation of the dark purple complex $NiC_{12}H_{12}N_4$ by air oxidation of a solution of Ni^{2+} and *o*-phenylenediamine in aqueous ammonia. They formulated it as **1**, the Ni(IV) complex of the dianion of *o*-phenylenediamine. Nyholm[3] later suggested the bond arrangement **2**, which seems unlikely to make a large contribution because of charge separation but does avoid Ni(IV); however Bardoděj[4] questioned the correctness of the empirical formula and favored **3**. Analytical studies in our laboratory[5] supported the composition reported by Feigl and Fürth, and convincing evidence from mass and infrared spectra has confirmed their assignment of the number and arrangement of the hydrogen atoms. These studies[6,7] also demonstrated that Ni$[C_6H_4(NH)_2]_2$ is the central member of a five-membered series of complexes interrelated by reversible one-electron-transfer reactions. We had noticed earlier that there are appreciable differences between the 500–1000-mμ absorption spectra of the solid and solutions,[8] and we began this structural study in order to establish firmly the geometry of the complex and to discover whether the altered absorption spectrum of the solid is indicative of any unusual intermolecular interaction.



1



2



3

Experimental Section

Preparation.—The compound was prepared by the method of Feigl and Fürth[2] and was purified by Soxhlet extraction into acetone. The dark-purple material which crystallized from the boiling acetone consisted of thin platelets, which were both multiply twinned [on (102)] and lamellar. Thicker pseudo-hexagonal tablets were prepared by slow evaporation of a carefully filtered, nearly saturated solution of the complex in dry dimethyl sulfoxide. These were nearly always simple twins (*vide infra*), although single individuals could occasionally be found. Traces of moisture in the solution caused more or less pronounced streaking along reciprocal-lattice rows parallel to c^*, and larger amounts resulted once again in very thin, multiply twinned platelets.

Crystal Data.—Ni$[C_6H_4(NH)_2]_2$, mol wt 270.93, crystallizes in the monoclinic system. Unit cell constants, measured at room temperature on quartz-calibrated ($a = 4.913$ Å) precession photographs taken with Mo Kα radiation (λ 0.7107 Å), are $a = 5.845 \pm 0.020$ Å, $b = 7.485 \pm 0.026$ Å, $c = 25.27 \pm 0.09$ Å, $\beta = 90° 10' \pm 10'$, and $V = 1106$ Å^3. The standard deviations reported are the sums of the standard deviations in the measurements of the cell dimensions of quartz and Ni$[C_6H_4(NH)_2]_2$. The density, measured by flotation in carbon tetrachloride–bromoform, is 1.62 ± 0.02 g/cm^3; and the X-ray density, using $Z = 4$, is 1.64 ± 0.01 g/cm^3. The conditions for reflection, observed on precession films taken with Mo Kα radiation, are $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$). The probable space group is $P2_1/c$. Twinned crystals, which may be either contact or interpenetration twins, have a common b axis and a reentrant angle of $130° 20' \pm 10'$. The twin and composition plane is therefore (102). The crystals are dichroic in plane-polarized light transmitted normal to the ab plane. Very thin individuals are light green when the electric vector ϵ is parallel to b but are deep purple when ϵ is parallel to a.

Intensity Data.—The crystal used to collect intensity data was tabular (001) with a hexagonal outline, elongated a. It had approximate dimensions $0.15 \times 0.11 \times 0.06$ mm. The crystal was first mounted with the b axis as the rotation axis, and multiple-film equiinclination Weissenberg photographs were taken at room temperature using nickel-filtered copper radiation for layers with $k = 0$–4. The crystal was then remounted for rotation about the a axis, and equiinclination Weissenberg photographs were taken for $h = 0$–3. Additional $h0l$, $0kl$, and $hk0$ data were collected with a precession camera using zirconium-filtered molybdenum radiation. The relative intensities were estimated by visual comparison with a series of timed exposures

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[1] Taken in part from G. L. Swartz, Master's Thesis, Dartmouth College, Hanover, N. H., 1967.

[2] F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927).

[3] R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

[4] Z. Bardoděj, *Collection Czech. Chem. Commun.*, **20**, 176 (1955).

[5] R. Roll, Master's Thesis, Dartmouth College, Hanover, N. H., 1964.

[6] E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965).

[7] A. L. Balch and R. H. Holm, *ibid.*, **88**, 5201 (1966).

[8] The visible–near-infrared absorption spectrum of Ni$[C_6H_4(NH)_2]_2$ in dimethyl sulfoxide solution is described in ref 7. We have observed essentially the same spectrum for solutions in N,N-dimethylformamide and acetone. The spectrum of the solid (mineral oil mull) shows a broad band with maxima at 618 and 685 mμ with shoulders at 865 and 915 mμ. There is also an absorption maximum at 325 mμ.

of a selected reflection. A total of 792 independent reflections of measurable intensity were collected. The usual Lorentz and polarization corrections were applied,[9] and the Weissenberg data were scaled to a common scale by comparison with the precession data. The linear-absorption coefficient for Cu Kα radiation is 22.8 cm^{-1}, and an approximate test calculation indicates that the absorption correction factor (A^*) varies from 1.15 to 1.33. No correction was made for absorption.

Determination of the Structure

The positions of the nickel atoms were easily established from two- and three-dimensional Patterson functions. An electron-density map was calculated in the region of a nickel atom using three-dimensional data with phases obtained from the contributions from the nickel atoms alone. This revealed the positions of the four nitrogen atoms in a planar arrangement around the nickel atom. We then determined the coefficients of a plane passing approximately through these five atoms and calculated an electron density map in this plane and in several parallel to it using phases determined by the nickel and nitrogen atoms.[10] The positions of all of the 17 nonhydrogen atoms in the asymmetric unit were determined from this calculation. At this point a structure factor calculation using tabulated values[11] of the atomic scattering factors of the neutral nickel, nitrogen, and carbon atoms, including a correction[12] for the real part of the anomalous scattering of nickel, yielded a value of R_1[13] of 0.36.

The structure was refined by least-squares techniques by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ using isotropic temperature factors.[14] The hydrogen atoms were not included in the structure factor calculations. Four cycles of refinement during which the temperature factors were not changed lowered R_1 to 0.14. Four more cycles in which both thermal and positional parameters were refined lowered R_1 to 0.111 and gave a value of R_2[13] of 0.133. The corrections in the last cycle were less than 30% of the estimated standard deviations. Structure factors were calculated for all of the unobserved reflections, and none was found to be significantly above the minimum value observed on our films. The standard deviation of an observation of unit weight is 4.72.[15] Observed and calculated structure factors are listed in Table I, and atomic positional and thermal parameters are given in Table II.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×10)

H	L	OBS	CAL
****		K= 0	****
1	0	389	390
2	0	599	-638
3	0	432	-475
4	0	263	283
5	0	318	319
-5	2	60	-52
-4	2	160	-151
-3	2	619	500
-2	2	473	544
0	2	1425	-1261
1	2	127	154
2	2	127	144
3	2	303	250
4	2	285	-338
5	2	279	-257
-5	4	162	151
-3	4	992	-874
-2	4	184	-173
-1	4	561	658
1	4	226	-209
2	4	79	66
4	4	431	416
5	4	192	185
-5	6	282	-327
-4	6	199	184
-3	6	925	1098
-2	6	103	105
-1	6	183	-208
0	6	614	-538
1	6	444	447
2	6	670	612
4	6	233	-326
5	6	109	-127
-5	8	141	142
-4	8	268	-243
-3	8	525	-529
-2	8	179	182
-1	8	315	321
0	8	48	58
1	8	427	-409
2	8	570	-534
3	8	319	267
4	8	401	408
-5	10	64	-69
-4	10	228	255
-3	10	226	224
-2	10	143	-149
-1	10	324	-414
1	10	785	694
2	10	334	284
3	10	346	-350
4	10	262	-311
5	10	101	88
-4	12	183	-245
-3	12	241	-223
-2	12	317	317
-1	12	283	252
0	12	138	-157
1	12	1372	-1244
2	12	201	-204
3	12	504	520
4	12	220	220
-4	14	92	75
-3	14	81	73
-2	14	445	-392
-1	14	287	-379
0	14	163	163
1	14	693	626
3	14	343	-295
4	14	139	-123
-4	16	136	-129
-2	16	477	511
-1	16	139	166
0	16	312	-372
1	16	265	-256
2	16	206	206
3	16	118	145
-3	18	87	-108
-2	18	750	-722
-1	18	68	-62
0	18	369	358
1	18	199	212
2	18	229	-242
3	18	390	-340
-3	20	95	121
-2	20	233	291
-1	20	144	-135
0	20	249	-295
1	20	79	-78
2	20	205	229
3	20	224	213
-2	22	97	-88
-1	22	114	117
0	22	231	283
2	22	173	-207
0	24	217	-204
****		K= 1	****
1	0	1517	-1355
2	0	273	-335
3	0	394	485
4	0	359	427
5	0	114	-107
-3	1	54	-56
-2	1	69	-111
-1	1	82	71
0	1	51	62
-4	2	476	527
-3	2	280	263
-2	2	448	-545
-1	2	76	-98
0	2	322	369
1	2	1780	2042
3	2	571	-516
4	2	313	-273
5	2	190	180
-5	3	97	79
-3	3	127	125
-1	3	106	-135
0	3	104	82
1	3	169	197
2	3	430	528
-4	4	409	-405
-3	4	156	-151
-2	4	433	393
-1	4	557	530
1	4	556	-522
4	4	159	178
5	4	223	-240
-1	5	43	-31
0	5	72	-83
1	5	107	115
4	5	95	-96
-5	6	250	214
-4	6	437	441
-3	6	135	-121
-2	6	544	-790
-1	6	99	-96
0	6	588	647
1	6	512	571
2	6	231	-271
3	6	192	-168
4	6	55	-60
5	6	313	322
-4	7	47	52
-2	7	76	-76
-1	7	110	-111
2	7	48	-62
4	7	103	113
-5	8	179	-208
-4	8	332	-301
-3	8	219	235
-2	8	751	905
0	8	244	-208
1	8	258	-295
2	8	479	456
3	8	469	477
4	8	76	-70
5	8	350	-304
-2	9	102	92
-1	9	148	103
0	9	92	-77
1	9	96	70
-5	10	197	206
-4	10	142	172
-3	10	201	-206
-2	10	301	-297
-1	10	118	182
0	10	847	736
1	10	251	217
2	10	581	-475
3	10	256	-316
4	10	163	183
5	10	328	301
1	11	131	-177
2	11	75	-74
-4	12	74	-72
-3	12	282	355
-2	12	313	318
-1	12	163	-145
0	12	476	-548
2	12	671	737
3	12	238	249
4	12	189	-253
1	13	55	89
-3	14	250	-300
-2	14	193	-202
-1	14	432	392
0	14	269	253
1	14	235	-201
2	14	693	-628
3	14	50	-51
4	14	329	283
1	15	59	-83
2	15	50	-54
3	15	131	-196
-4	16	45	51
-3	16	360	311
-2	16	67	84
-1	16	389	-361
0	16	284	-281
1	16	156	198
2	16	484	435
4	16	52	-63
-2	17	88	-94
-3	18	277	-265
-2	18	95	90
-1	18	614	562
0	18	146	128
1	18	341	-306
2	18	317	-281
3	18	164	164
-2	19	57	90
0	19	75	63
-3	20	149	142
-2	20	131	-132
-1	20	635	-562
1	20	276	256
2	20	160	157
3	20	200	-194
0	21	114	-139
2	22	64	86
-1	22	170	207
0	22	65	-72
1	22	92	-99
2	22	48	-61
0	24	131	127
****		K= 2	****
0	0	2371	-2503
1	0	159	-173
2	0	552	475
3	0	406	375
4	0	217	-226
5	0	276	-272
-4	1	60	-68
-2	1	224	221
-1	1	108	64
0	1	317	-303
1	1	1705	-1346
2	1	64	41
3	1	62	-60
-5	2	120	139
-4	2	94	124
-3	2	547	-483
-2	2	522	-450
-1	2	227	222
0	2	835	837
1	2	361	-302
2	2	434	-462
3	2	268	-234
4	2	262	313
5	2	194	219
-4	3	205	-210
-2	3	73	-53
-1	3	81	-100
1	3	892	741
3	3	58	69
4	3	75	67
-5	4	169	-187
-3	4	555	620
-2	4	185	193
-1	4	540	-542
0	4	376	-298
1	4	193	201
2	4	375	349
3	4	66	55
4	4	421	-367
5	4	184	-175
-4	5	299	268
-3	5	111	95
-2	5	276	292
-1	5	81	-106
1	5	368	363
2	5	106	106
3	5	153	-147
4	5	71	-84
-5	6	270	256
-4	6	144	-132
-3	6	561	-681
-1	6	242	297
0	6	363	402
1	6	329	-349
2	6	570	-508
4	6	229	255
5	6	115	101
-5	7	61	59
-3	7	71	-90
-2	7	453	-409
0	7	52	56
1	7	72	-74
3	7	95	118
-5	8	153	-144
-4	8	248	235
-3	8	456	431
-2	8	185	-196
-1	8	746	-613
0	8	152	-139
1	8	491	449
2	8	402	427
3	8	262	-233
4	8	294	-341
-3	9	74	103
-2	9	185	199
-1	9	118	-127
0	9	306	332
1	9	134	137
-4	10	276	-240
-3	10	209	-258
-2	10	198	174
-1	10	692	592
0	10	93	63
1	10	462	-562
2	10	282	-288
3	10	390	306
4	10	258	301
-2	11	69	54
-1	11	57	62
0	11	477	-377
1	11	148	-152
2	11	99	89
3	11	81	80
-4	12	206	239
-3	12	225	191
-2	12	311	-271
-1	12	293	-246
0	12	99	121
1	12	850	797
2	12	134	136
3	12	434	-410
4	12	183	-183
-2	13	40	-62
0	13	129	116
1	13	62	74
2	13	252	254
-4	14	156	-164
-3	14	64	-77
-2	14	307	399
-1	14	333	304
0	14	203	-180
1	14	570	-499
2	14	64	67
3	14	304	284
4	14	75	102
-3	15	134	166
2	15	117	-125
-2	16	350	-396
-1	16	162	-158
0	16	339	332
1	16	230	294
2	16	118	-162
3	16	189	-184
-3	17	228	-199
-2	17	73	-64
2	17	99	-122
3	17	61	-62
-3	18	74	89
-2	18	575	502
0	18	231	-317
1	18	214	-189
2	18	241	209
3	18	310	274
-1	19	142	160
-2	20	237	-249
-1	20	118	114
0	20	343	298
1	20	62	77
2	20	202	-213
-1	21	69	-62
0	21	67	69
-1	22	107	-109
0	22	212	-233
****		K= 3	****
1	0	749	694
2	0	264	257
3	0	325	-319
4	0	326	-289
5	0	92	54
-5	1	47	66
-4	1	60	57
-3	1	102	99
-2	1	67	98
-1	1	155	-130
0	1	66	-69
1	1	96	105
2	1	96	121
3	1	111	-105
4	1	74	-67
-4	2	357	-332
-3	2	207	-208
-2	2	445	406
-1	2	329	375
0	2	179	-208
1	2	755	-904
3	2	306	401
4	2	209	225
5	2	141	-140
-5	3	95	-124
-4	3	57	-85
-3	3	154	-193
-2	3	97	93
-1	3	205	209
0	3	131	-120
1	3	319	-291
2	3	659	-703
3	3	144	126
-4	4	249	255
-3	4	76	67
-2	4	543	-461
-1	4	437	-394
0	4	304	271
1	4	531	463
2	4	163	-169
3	4	336	-359
4	4	131	-157
5	4	177	204
-3	5	76	-62
-1	5	65	-43
0	5	104	137
1	5	75	-65
2	5	90	94
3	5	90	-94
4	5	115	122
-4	6	270	-288
-2	6	441	541
-1	6	149	131
0	6	353	-429
1	6	468	-422
2	6	190	172
3	6	418	366
4	6	62	65
-4	7	92	-100
-2	7	155	144
-1	7	165	160
0	7	108	-92
1	7	75	-69
2	7	102	122
3	7	72	66
4	7	176	-158
-4	8	241	241
-3	8	172	-183
-2	8	621	-582
0	8	418	381
1	8	297	294
2	8	264	-313
3	8	348	-386
-4	9	83	88
-2	9	141	-174
-1	9	95	-100
0	9	221	197
1	9	102	-113
2	9	99	-109
3	9	74	-84
4	9	95	92
-4	10	169	-152
-3	10	192	236
-2	10	297	305
-1	10	166	-169
0	10	797	-722
1	10	151	-203
2	10	463	404
3	10	243	255
4	10	152	-157
-3	11	55	68
-2	11	55	54
0	11	129	-129
1	11	196	188
2	11	149	135
-4	12	74	64
-3	12	222	-238
-2	12	185	-252
-1	12	153	142
0	12	412	513
2	12	341	-383
3	12	184	-169
4	12	164	189
-3	13	65	-62
1	13	85	-88
2	13	54	-56
3	13	74	-87
-3	14	192	261
-2	14	137	159
-1	14	264	-279
0	14	326	-279
1	14	129	110
2	14	324	283
-3	15	87	79
-1	15	78	-67
0	15	72	-75
1	15	159	198
2	15	89	93
3	15	214	230
-3	16	304	-291
-2	16	66	-70
-1	16	361	316
0	16	226	281
1	16	160	-205
2	16	313	-307
3	16	69	59
-2	17	106	134
-1	17	61	56
1	17	73	-68
3	17	55	-63
-1	18	261	-312
0	18	93	-102
1	18	257	239
2	18	238	230
-2	19	59	-81
-1	19	73	-77
0	19	120	-103
-2	20	92	97
-1	20	232	292
1	20	273	-239
2	20	115	-121
-1	21	82	73
0	21	163	207
1	21	64	-57
0	22	88	88
****		K= 4	****
0	0	245	333
2	0	293	-309
3	0	207	-232
4	0	150	136
-3	1	59	-76
-2	1	180	-170
0	1	106	109
1	1	602	653
2	1	125	-130
4	1	45	51
-4	2	90	-71
-3	2	310	352
-2	2	216	291
-1	2	266	-286
0	2	359	-372
1	2	231	229
2	2	587	603
3	2	170	189
4	2	207	-230
-4	3	110	132
-3	3	43	59
-2	3	114	119
-1	3	60	-41
0	3	130	-113
1	3	383	-354
2	3	239	207
4	3	104	-106
-3	4	269	-273
-2	4	181	-159
-1	4	402	368
0	4	434	450
1	4	169	-160
2	4	676	-607
3	4	80	-70
4	4	264	254
-4	5	157	-186
-3	5	69	-59
-2	5	236	-225
-1	5	86	99
0	5	118	100
1	5	195	-206
2	5	208	-181
4	5	82	86
-4	6	92	64
-3	6	185	185
-1	6	327	-377
0	6	201	-262
1	6	272	236
2	6	395	361
4	6	174	-167
-3	7	71	60
-2	7	115	135
-1	7	170	-148
1	7	103	113
3	7	129	-118
-4	8	186	-183
-3	8	300	-258
-2	8	127	112
-1	8	750	692
0	8	151	189
1	8	405	-377
2	8	265	-270
3	8	149	146
4	8	174	219
-3	9	102	-140
-2	9	59	-76
-1	9	265	247
0	9	148	-138
1	9	164	-184
3	9	75	65
4	9	52	58
-4	10	181	190
-3	10	244	236
-2	10	146	-177
-1	10	665	-605
0	10	58	-69
1	10	307	338
2	10	209	221
3	10	216	-210
4	10	259	-234
-3	11	51	53
-1	11	152	-133
0	11	122	149
1	11	125	113
3	11	83	-82
-3	12	150	-134
-2	12	198	198
-1	12	208	236
0	12	75	-96
1	12	284	-257
3	12	251	229
-2	13	85	79
-1	13	48	53
0	13	106	-150
1	13	81	-76
2	13	156	-177
3	13	57	51
-3	14	68	63
-2	14	296	-255
-1	14	226	-193
0	14	143	157
1	14	295	284
2	14	69	-60
3	14	185	-235
-3	15	125	-110
-2	15	79	-75
-1	15	58	-51
0	15	58	63
2	15	80	81
3	15	53	-65
-2	16	245	211
-1	16	118	117
0	16	269	-236
1	16	280	-276
2	16	82	87
-2	17	59	56
0	17	92	-66
2	17	118	101
-2	18	167	-182
0	18	248	232
1	18	110	140
2	18	125	-146
-1	19	113	-104
0	19	54	61
0	20	201	-255
****		K= 5	****
1	0	293	-308
2	0	199	-176
3	0	156	179
4	0	138	161
-4	1	72	-67
-3	1	87	-77
-1	1	108	134
1	1	75	-100
2	1	62	-62
3	1	125	119
4	1	65	63
-4	2	148	170
-3	2	115	130
-2	2	295	-245
-1	2	301	-340
0	2	86	92
1	2	280	319
3	2	298	-259
4	2	122	-155
-3	3	106	96
-2	3	108	-97
-1	3	123	-147
0	3	74	79
1	3	169	174
2	3	241	262
3	3	127	-148
-2	4	395	340
-1	4	243	240
0	4	243	-233
1	4	369	-375
2	4	141	117
3	4	435	390
-3	5	55	57
-2	5	108	93
-1	5	129	107
0	5	110	-112
1	5	66	-75
3	5	128	161
-2	6	322	-306
-1	6	144	-124
0	6	299	277
1	6	242	266
2	6	102	-100
3	6	262	-344
-2	7	124	-126
-1	7	60	-79
0	7	164	141
1	7	69	71
2	7	127	-112
3	7	95	-103
-3	8	111	103
-2	8	324	305
0	8	404	-393
1	8	254	-220
2	8	150	173
3	8	231	254
-2	9	122	131
0	9	223	-197
2	9	105	105
3	9	76	68
-3	10	217	-190
-2	10	224	-236
-1	10	130	113
0	10	398	450
1	10	102	109
2	10	255	-250
3	10	151	-166
-3	11	73	-60
-2	11	121	-107
0	11	192	175
2	11	83	-100
-2	12	176	164
-1	12	120	-127
0	12	349	-344
2	12	157	156
-1	13	47	-59
0	13	55	-79
-2	14	101	-106
-1	14	181	167
0	14	258	237
1	14	50	-63
2	14	110	-105
-1	15	68	75
0	15	51	55
1	15	125	-114
2	15	59	-66
-1	16	219	-209
0	16	149	-147
1	16	156	145
****		K= 6	****
1	0	58	-62
2	0	220	204
3	0	157	140
-3	1	72	77
-2	1	90	105
1	1	58	-64
2	1	134	144
-3	2	194	-182
-2	2	142	-169
-1	2	193	165
0	2	195	185
2	2	304	-354
3	2	127	-120
-3	3	67	-73
-2	3	74	-102
-1	3	94	93
0	3	124	127
2	3	173	-196
-2	4	100	92
-1	4	217	-219
0	4	291	-270
1	4	80	84
2	4	383	376
-2	5	76	75
-1	5	108	-98
0	5	109	-106
1	5	93	81
2	5	166	155
-2	6	54	-53
-1	6	296	284
0	6	139	169
1	6	144	-159
2	6	229	-257
-2	7	90	81
-1	7	177	168
1	7	108	-101
2	7	66	-62
-1	8	420	-382
0	8	94	-117
1	8	235	216
2	8	163	162
-1	9	198	-192
1	9	150	135
2	9	46	57
-2	10	117	116
-1	10	371	334
1	10	220	-192
2	10	106	-114
-1	11	149	129
1	11	67	-70
-1	12	202	-190
0	12	69	87
1	12	90	105
0	13	75	78
****		K= 7	****
1	0	162	151
-1	1	104	-113
1	1	90	94
-1	2	176	154
1	2	119	-147
-1	3	90	99
1	3	76	-132
0	4	141	134
0	5	95	79

The unweighted least-squares plane for the nickel, nitrogen, and carbon atoms was then determined; and a final electron density map was calculated in this plane and in a region of the unit cell containing all points less than 4 Å from the nickel atom. A difference Fourier map calculated for the same region failed to give a clear indication of the positions of the hydrogen atoms and did not show evidence of anisotropic thermal motion of the nickel atom. It showed no peaks higher than 1.2 e$^-$/Å^3, about 13% of the height of a carbon peak. We therefore feel that the structure has been refined to a degree appropriate to the number and quality of the intensity data.

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(9) This and all other calculations reported in this paper were carried out with programs written locally in the Basic language on the GE 625 computer, operating in time-sharing mode, at the Kiewit Computation Center at Dartmouth College.

(10) The lack of an efficient Fourier summation program limited our three-dimensional electron-density calculations to regions where atoms might be expected.

(11) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202–205.

(12) D. T. Cromer, *Acta Cryst.*, **18**, 17 (1965).

(13) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. The weighting scheme used was $w = 1/(a + |F_o| + b|F_c|^2)$, where $a = 2F_{\min}$ and $b = 2/F_{\max}$.

(14) The structure was refined with a modified diagonal approximation to least squares modeled after that described by D. W. J. Cruickshank and D. E. Pilling in "Computing Methods and the Phase Problem in X-Ray Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press Inc., New York, N. Y., 1961, Paper 6. In the initial refinement the eight strongest reflections were omitted from the least-squares process as a precaution against extinction. This procedure was questioned by two referees and in retrospect seems foolish. An additional cycle of refinement was run with the eight reflections included. The largest parameter shifts were still less than 30% of the estimated standard deviations, so the effect of this omission on the refined structure is negligible.

(15) The standard deviation for an observation of unit weight is defined by $[\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - m)]^{1/2}$, where n is the number of observations (792) and m is the number of variables (68).

TABLE II

POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	B, Å^2
Ni_1	0.2097 (9)[a]	0.2377 (7)	0.2748 (2)	2.51 (10)
N_2	0.3036 (24)	0.3197 (19)	0.3393 (6)	5.1 (9)
C_3	0.1573 (26)	0.2865 (20)	0.3807 (7)	8.0 (14)
C_4	0.1832 (30)	0.3324 (24)	0.4341 (8)	6.8 (12)
C_5	0.0160 (36)	0.2864 (28)	0.4697 (8)	8.7 (15)
N_6	−0.0450 (25)	0.1534 (17)	0.3096 (4)	5.4 (9)
C_7	−0.0375 (27)	0.1938 (23)	0.3642 (5)	7.5 (11)
C_8	−0.2085 (29)	0.1467 (26)	0.4012 (7)	6.9 (12)
C_9	−0.1790 (34)	0.1928 (28)	0.4528 (8)	9.0 (15)
N_{10}	0.4633 (24)	0.3210 (20)	0.2397 (6)	4.8 (8)
C_{11}	0.4643 (26)	0.2872 (19)	0.1872 (5)	7.3 (12)
C_{12}	0.6318 (31)	0.3317 (25)	0.1494 (7)	8.3 (11)
C_{13}	0.6031 (34)	0.2861 (26)	0.0979 (7)	9.2 (15)
N_{14}	0.1162 (22)	0.1559 (17)	0.2104 (4)	5.7 (10)
C_{15}	0.2661 (21)	0.1922 (18)	0.1700 (6)	7.2 (12)
C_{16}	0.2362 (28)	0.1428 (25)	0.1156 (7)	7.1 (12)
C_{17}	0.4034 (31)	0.1889 (27)	0.0800 (7)	8.4 (12)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits.

Description of the Structure

The structure consists of planar molecules packed together in such a way (Figure 1) that their long axes are essentially parallel but their molecular planes are not. The shortest Ni–Ni distances, 4.65 Å, are between a molecule at [x, y, z] and those at [$-x$, $y \pm 0.5$, $-z + 0.5$]. The closest intermolecular approaches to the nickel atom in the molecule at [x, y, z] are made by C_{15} (3.67 Å) and N_{10} (3.68 Å) of molecules at [$-x$, $y + 0.5$, $-z + 0.5$] and [$-x + 1$, $y - 0.5$, $-z + 0.5$], respectively. Other intermolecular contacts seem reasonable; those less than 3.6 Å are listed in Table III.

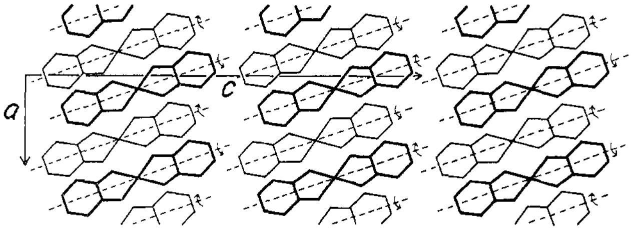

Figure 1.—The projection of the structure on the *ac* plane. The long molecular axes (– – – –) are very nearly parallel to the *ac* plane, but the molecular planes are rotated ±29° 50′ from the *ac* plane about these axes. The y coordinates of the nickel atoms of molecules which are adjacent in the *a* direction and are drawn with light and heavy lines, respectively, differ by $b/2$ because they are related by twofold screw axes normal to the *ac* plane.

The long axes of the molecules are very nearly parallel to the *ac* plane and deviate about 20° from the *c* direction. The only contact between successive layers of molecules in this direction occurs at the ends of the phenyl groups. It is probably this minimal overlap between layers of molecules that leads to both the one-dimensional disorder[16] observed in that direction and the lamination parallel to the *ab* plane in grossly imperfect crystals. The *c* direction is also the direction of slowest growth.

TABLE III

INTERMOLECULAR CONTACTS LESS THAN 3.6 A

Atom in molecule at x, y, z	Distance, Å	Atom	Neighboring molecule
N_2	3.50	C_8	$1 + x, y, z$
C_3	3.52	C_{16}	$-x, 0.5 + y, 0.5 - z$
C_5	3.55	C_5	$-x, 1 - y, 1 - z$
N_6	3.56	C_{12}	$1 - x, -0.5 + y, 0.5 - z$
C_8	3.55	C_{13}	$-x, -0.5 + y, 0.5 - z$
C_8	3.50	N_2	$-1 + x, y, z$
C_{12}	3.48	N_{14}	$1 + x, y, z$
C_{12}	3.56	N_6	$1 - x, 0.5 + y, 0.5 - z$
C_{13}	3.55	C_8	$-x, 0.5 + y, 0.5 - z$
C_{14}	3.48	C_{12}	$-1 + x, y, z$
C_{16}	3.52	C_3	$-x, -0.5 + y, 0.5 - z$

The $Ni[C_6H_4(NH)_2]_2$ molecule is rigorously planar. The nickel atom deviates 0.002 ± 0.006 Å and the light atoms deviate 0.001–0.007 ± 0.016 Å from the unweighted least-squares plane $-12.57x + 29.90y - 19.95z + 1 = 0$ (monoclinic coordinate system). The principal intramolecular distances and angles are given in Table IV and Figure 2. The molecule has no crystallographically required symmetry, but it is described by point group D_{2h} within the limit of accuracy of the determination.[17]

TABLE IV

PRINCIPAL INTRAMOLECULAR DISTANCES AND ANGLES

Atoms	Distance, Å	Atoms	Angle, deg
Ni_1–N_2	1.826 (11)	N_2–Ni_1–N_6	86.0 (7)
Ni_1–N_6	1.841 (12)	N_{10}–Ni_1–N_{14}	85.7 (7)
Ni_1–N_{10}	1.836 (11)	Ni_1–N_2–C_3	116 (1)
Ni_1–N_{14}	1.823 (11)	Ni_1–N_6–C_7	112 (1)
N_2–C_3	1.37 (2)	N_2–C_3–C_7	112 (1)
C_3–C_4	1.40 (2)	N_6–C_7–C_3	115 (1)
C_3–C_7	1.40 (2)	C_4–C_3–C_7	120 (1)
C_4–C_5	1.37 (2)	C_3–C_7–C_8	120 (1)
C_5–C_9	1.40 (3)	C_3–C_4–C_5	120 (1)
N_6–C_7	1.41 (2)	C_7–C_8–C_9	119 (1)
C_7–C_8	1.41 (2)	C_4–C_5–C_9	120 (2)
C_8–C_9	1.36 (2)	C_5–C_9–C_8	121 (2)
N_{10}–C_{11}	1.35 (2)	Ni_1–N_{10}–C_{11}	115 (1)
C_{11}–C_{12}	1.41 (2)	Ni_1–N_{14}–C_{15}	114 (1)
C_{11}–C_{15}	1.43 (2)	N_{10}–C_{11}–C_{15}	113 (1)
C_{12}–C_{13}	1.35 (2)	N_{14}–C_{15}–C_{11}	113 (1)
C_{13}–C_{17}	1.45 (3)	C_{12}–C_{11}–C_{15}	118 (1)
N_{14}–C_{15}	1.37 (2)	C_{11}–C_{15}–C_{16}	121 (1)
C_{15}–C_{16}	1.43 (2)	C_{11}–C_{12}–C_{13}	120 (1)
C_{16}–C_{17}	1.37 (2)	C_{15}–C_{16}–C_{17}	118 (1)
		C_{12}–C_{13}–C_{17}	122 (2)
		C_{13}–C_{17}–C_{16}	120 (2)

The average Ni–N bond length of 1.83 Å is among the shortest now known, and it may be compared with values of 1.85 Å in bis(dimethylglyoximato)nickel(II)[18]

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(16) Early in our work a crystal of this compound was grown by evaporation of a DMSO solution in an open beaker in dry weather. X-Ray examination (precession camera) showed that it was monoclinic with $a = 5.92 \pm 0.03$ Å, $b = 7.45 \pm 0.04$ Å, $c = 12.58 \pm 0.06$ Å, $\beta = 91° 50' \pm 10'$, $V = 554$ Å^3, and $d_c \approx d_o = 1.63$ g/cm^3. The condition for reflection ($0k0$, $k = 2n$) indicates that the space group is either $P2_1/m$ or $P2_1$. The $h0l$ photographs for this crystal and those with $c = 25.27$ Å are similar, indicating that the projections of the two structures on (010) are nearly the same. The $hk0$ photographs, however, show significant differences. This crystal was lost, and we have been unable to grow another like it. It appears that the layers of molecules can be stacked in the *c* direction in either of two distinct patterns of nearly equal energy: AAAA. . . ($c = 12.58$ Å) or ABAB. . . ($c = 25.27$ Å). Most crystals have the latter pattern with more or less one-dimensional disorder.

(17) Because the complex in the solid shows no substantial departure from planarity, the alteration of the 500–1000-mμ absorption spectrum probably results from several close intermolecular contacts (see Table III).

(18) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81**, 755 (1959).

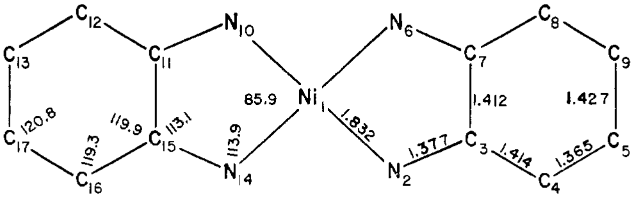

Figure 2.—The planar $Ni[C_6H_4(NH)_2]_2$ molecule showing the numbering scheme and average lengths and angles for bonds assumed to be chemically equivalent.

and 1.84 Å in bis(salicylaldiminato)nickel(II).[19] The average N–N chelate "bite" distance is 2.49 Å, and the average interligand N–N distance is 2.68 Å. The average C–N bond length of 1.38 Å is significantly longer than the 1.30 Å bond found in bis(dimethylglyoximato)nickel(II)[18] and the average length of 1.29 Å determined from various salicylaldimine complexes.[20] It is, however, much shorter than the sum (1.47 Å) of the single-bond covalent radii.[21] We note that the C–S distances in a number of sulfur-donor complexes characterized by similar electron-transfer reactions fall in the range 1.69–1.75 Å,[22] intermediate between the single- and double-bond lengths[21] of 1.81 and 1.61 Å, respectively. Thus it appears that the π bonding is delocalized throughout the ligand system. Although the differences in bond lengths within the benzene rings are of only marginal significance, the slightly shorter C_4–C_5, C_8–C_9, C_{12}–C_{13}, and C_{16}–C_{17} bonds suggest a bit of α-diimine character.

The bond lengths in the chelate rings, especially the 1.38-Å C–N distance, seem inconsistent with the early formulation[2] based on nickel(IV), but the electronic delocalization of which both they and the fact of planarity itself are indicative is consistent with the convincing evidence of Balch and Holm[7] that this is the neutral central member of a family of complexes interrelated by electron-transfer reactions. The similarity of the molecular structures of $Ni[C_6H_4(NH)_2]_2$ and $Ni[S_2C_2(C_6H_5)_2]_2$[22] should be noted because the latter compound plays the same role in a family of sulfur-bonded complexes. Others[6,7,22] have recognized that the electronic structures of highly delocalized complexes such as these cannot be adequately described by simply assigning oxidation states to the metal ions but must instead be approached through rather complete molecular orbital treatments.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-5656.

[19] J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, **12**, 842 (1959).

[20] E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).

[21] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 224–230.

[22] D. Sartain and M. R. Truter, *J. Chem. Soc., A*, 1264 (1967); R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967), and references therein.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720,
AND FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

The Crystal and Molecular Structure of Tetra-n-butylammonium Tribromo(quinoline)nickelate(II), $[(n\text{-}C_4H_9)_4N][Ni(C_9H_7N)Br_3]$[1a]

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The structure of tetra-n-butylammonium tribromo(quinoline)nickelate(II), $[(n\text{-}C_4H_9)_4N][Ni(C_9H_7N)Br_3]$, has been determined by single-crystal X-ray diffraction methods. The crystals are triclinic, space group $P\bar{1}$, with $a = 12.282$ Å, $b = 10.291$ Å, $c = 12.726$ Å, all ± 0.002 Å; $\alpha = 101.02°$, $\beta = 99.51°$, $\gamma = 106.55°$, all $\pm 0.01°$. For $Z = 2$ the measured and calculated densities are 1.51 ± 0.01 and 1.512 g/cm³, respectively. Counter data were collected for 5830 independent reflections by the θ–2θ scan technique. The structure was refined, including hydrogens, by least-squares methods to a conventional R value of 0.061. The anion has roughly tetrahedral coordination about the nickel by three bromine atoms and the quinoline nitrogen, with an average Ni–Br distance of 2.375 Å and an Ni–N distance of 2.029 Å. The average N–Ni–Br angle is 105.1° while the Br–Ni–Br angles average 113.3°. The coordinated quinoline is accurately planar; however, the Ni–N–Q bond makes an angle of 4.5° with the quinoline plane. The bond distances internal to the quinoline correlate well with variations predicted by π-MO theory. The cations approach the anions such that there are four distances between ion centers (Ni–N-CAT) in the range 5.98–6.89 Å. Three of the four cation butyl chains adopt the *trans* conformation while the fourth has the *gauche* conformation with a dihedral angle of 66.5°.

Introduction

Reliable evidence concerning the existence of nickel(II) complexes with tetrahedral or pseudo-tetrahedral coordination has been available only within the past decade.[2] These complexes fall into several stoichiometric classes: NiX_4^{2-}, $NiLX_3^-$, NiL_2X_2, and $Ni(L\text{–}L)_2$, where X is a halogen, L a neutral ligand such as an amine, phosphine, or phosphine oxide, and L–L repre-

[1] (a) This work was done at the Lawrence Radiation Laboratory and the University of California under the auspices of the U. S. Atomic Energy Commission and was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Contract AF 49(638)-1492; (b) Princeton University; (c) University of California; (d) Lawrence Radiation Laboratory.

[2] For a discussion see F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 883 ff.