and a 25% contribution from the component with the vector perpendicular to this axis.

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Molecular and Crystal Structure of the Octahedral Nickel(II) Complex with N-γ-Dimethylaminopropylsalicylaldimine

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The crystal structure of bis(N-γ-dimethylaminopropylsalicylaldiminato)nickel(II) has been determined by three-dimensional X-ray analysis. Cell dimensions are: $a = 10.226 \pm 0.008$ A, $b = 15.254 \pm 0.012$ A, $c = 15.333 \pm 0.008$ A, $\beta = 107° 12' \pm 4'$, $Z = 4$, space group $P2_1/c$. The structure consists of discrete molecules in which nickel(II) exhibits a distorted octahedral coordination. Although the nickel atom does not lie on a crystallographic center of symmetry, the molecules are almost centrosymmetrical, the average deviations of the atomic positions from exact centrosymmetry being of the order of magnitude of the standard deviations.

Introduction

N-Substituted salicylaldimines form, with first-row transition metals, complexes with a large variety of stereochemistries. The structures of planar, tetrahedral, and square-pyramidal nickel(II) salicylaldimine complexes have been determined by X-ray diffraction.[1]

However, no structure of an octahedral nickel(II) complex with this type of ligand has been so far described, although it would seem interesting to compare the results with those of the four- and five-coordinated complexes.

Complexes of nickel(II) with Schiff bases formed from ring-substituted salicylaldehydes and N,N-substituted derivatives of 1,3-diaminopropane have been recently studied.[2] Diamagnetic planar or paramagnetic octahedral complexes are obtained depending on the nature of the N substituent.

N-γ-Dimethylaminopropylsalicylaldimine forms with nickel(II) a complex of the formula $[OC_6H_4CHN(CH_2)_3N(CH_3)_2]_2Ni$, in which the ligand is tridentate. Spectral and magnetic measurements suggest for this complex an octahedral configuration, although somewhat distorted.[3]

A further point of interest for the determination of this structure was to establish whether the salicylaldimine residues would assume a *cis* configuration as in the complex bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II)[1d] or a *trans*-planar configuration.

We report here the results of the three-dimensional X-ray analysis on this compound.

Experimental Section

Collection of the X-Ray Data.—The complex was prepared by the reaction between nickel salicylaldehydate and N,N-dimethyltrimethylenediamine in ethanol solution. Crystals suitable for X-ray analysis were grown from ethanol solutions.

Cell dimensions were determined from two equatorial Weissenberg photographs taken around the a and b axes, using Cu Kα radiation (λ 1.5418). An NaCl rotation pattern ($a = 5.6273$ A) was superimposed on each film for calibration. 2θ values were measured for about 20 reflections and the data were treated by a least-squares technique. The results are: $a = 10.226 \pm 0.008$ A, $b = 15.254 \pm 0.012$ A, $c = 15.333 \pm 0.008$ A, $\beta = 107° 12' \pm 4'$, $d_c = 1.37$ g cm^{-3}, $Z = 4$.

Systematic absences of $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ indicated the space group to be $P2_1/c$. A few weak reflections violated the space group conditions: 103, 105, $10\bar{3}$, 205, $30\bar{9}$, $50\bar{7}$, $70\bar{9}$. These reflections were clearly Renninger spots, since their occurrence depended on the wavelength and on the technique used in taking the photographs. The successful determination of the structure in $P2_1/c$ confirmed this assumption.

The crystal chosen for the collection of the data had the shape of a truncated six-sided bipyramid, with dimensions 0.25 × 0.25 × 0.15 mm. $0kl$ through $8kl$ double integrated Weissenberg photographs were taken on a Nonius integrating camera, using

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[1] (a) E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959); (b) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, **21**, 546 (1966); (c) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *ibid.*, **17**, 1159 (1964); (d) P. L. Orioli, M. Di Vaira, and L. Sacconi, *J. Am. Chem. Soc.*, **88**, 4383 (1966).

[2] L. Sacconi, N. Nardi, and F. Zanobini, *Inorg. Chem.*, **5**, 1872 (1966).

[3] A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965).

TABLE I

POSITIONAL PARAMETERS, TEMPERATURE FACTORS, AND THEIR ESTIMATED STANDARD DEVIATIONS[a]

	Positional parameter × 10^4			Thermal parameter × 10^5					
Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	2560 (1)	1220 (1)	2446 (1)	887 (22)	306 (4)	395 (5)	−16 (5)	133 (5)	43 (3)
O(1)	3973 (4)	613 (2)	3466 (3)	556 (55)	284 (16)	334 (19)	23 (21)	75 (24)	40 (14)
O(2)	1171 (4)	1839 (3)	1442 (3)	397 (63)	347 (18)	390 (20)	10 (22)	57 (25)	80 (15)
N(1)	4088 (5)	2030 (3)	2320 (3)	725 (66)	234 (19)	328 (22)	4 (26)	112 (30)	39 (16)
N(2)	1025 (6)	404 (3)	2580 (3)	890 (81)	198 (18)	329 (23)	26 (26)	102 (34)	53 (16)
N(3)	2290 (6)	2329 (4)	3412 (4)	813 (92)	214 (23)	318 (31)	4 (33)	111 (41)	−13 (20)
N(4)	2810 (5)	128 (3)	1487 (3)	788 (72)	272 (21)	322 (25)	28 (28)	118 (33)	−52 (18)
C(1)	6035 (8)	1211 (5)	3257 (4)	461 (116)	363 (33)	245 (31)	−7 (40)	45 (44)	−60 (25)
C(2)	5290 (8)	600 (4)	3644 (4)	541 (113)	274 (31)	248 (31)	51 (38)	63 (43)	−39 (23)
C(3)	6091 (8)	−21 (5)	4250 (5)	923 (113)	358 (35)	332 (33)	128 (42)	197 (44)	21 (26)
C(4)	7471 (10)	−61 (6)	4460 (6)	865 (146)	460 (45)	416 (42)	264 (56)	71 (59)	39 (34)
C(5)	8191 (8)	541 (6)	4079 (6)	630 (108)	568 (47)	439 (42)	36 (52)	19 (52)	−90 (35)
C(6)	7483 (8)	1154 (6)	3508 (5)	818 (107)	421 (42)	371 (38)	−64 (44)	204 (47)	−79 (32)
C(7)	5375 (9)	1924 (4)	2684 (5)	1048 (121)	253 (27)	298 (33)	−96 (40)	182 (50)	−23 (24)
C(8)	−895 (7)	1208 (4)	1611 (4)	513 (89)	362 (29)	289 (26)	118 (34)	85 (37)	−28 (23)
C(9)	−152 (7)	1837 (4)	1248 (4)	814 (95)	306 (27)	254 (27)	62 (34)	49 (37)	−2 (21)
C(10)	−952 (7)	2483 (5)	654 (4)	774 (103)	463 (34)	342 (32)	101 (39)	82 (42)	114 (25)
C(11)	−2333 (8)	2498 (6)	431 (5)	838 (113)	676 (49)	428 (38)	311 (52)	104 (47)	128 (33)
C(12)	−3088 (7)	1865 (6)	762 (5)	562 (89)	755 (52)	410 (36)	123 (49)	−13 (42)	22 (34)
C(13)	−2333 (8)	1236 (5)	1334 (5)	1020 (107)	495 (39)	308 (32)	−63 (45)	160 (45)	−62 (28)
C(14)	−254 (7)	504 (3)	2191 (4)	612 (88)	272 (24)	292 (30)	−56 (33)	6 (41)	−39 (21)
C(15)	3651 (8)	2890 (4)	1913 (5)	845 (107)	188 (24)	426 (41)	−60 (36)	172 (53)	97 (24)
C(16)	3336 (8)	3479 (4)	2610 (6)	878 (107)	239 (28)	533 (48)	−45 (39)	218 (54)	71 (27)
C(17)	2116 (9)	3176 (4)	2938 (5)	1319 (120)	165 (23)	474 (44)	64 (39)	265 (59)	70 (25)
C(18)	3455 (8)	2346 (5)	4254 (5)	982 (106)	384 (39)	359 (36)	−28 (47)	46 (47)	−60 (29)
C(19)	1059 (9)	2172 (5)	3685 (6)	861 (114)	370 (36)	435 (42)	−19 (45)	252 (55)	−48 (31)
C(20)	1481 (7)	−445 (4)	3002 (5)	947 (90)	187 (21)	455 (33)	−8 (32)	186 (44)	101 (21)
C(21)	1817 (7)	−1038 (4)	2319 (5)	921 (98)	188 (25)	583 (39)	−25 (34)	194 (47)	−25 (24)
C(22)	3000 (8)	−730 (4)	1964 (5)	1153 (100)	220 (26)	536 (40)	36 (38)	254 (50)	−16 (25)
C(23)	1625 (7)	84 (5)	659 (5)	904 (101)	521 (40)	363 (34)	23 (45)	−35 (43)	−81 (28)
C(24)	4029 (8)	281 (5)	1194 (5)	998 (110)	431 (34)	378 (36)	−9 (44)	240 (51)	−43 (27)

[a] Anisotropic thermal factors are of the form: $\exp(-\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij})$.

the multiple-film, equiinclination technique. The intensities of the reflections were measured on a Nonius microdensitometer, the intensity being assumed proportional to the density of the spots. The various levels were scaled by means of two Weissenberg photographs, containing 30° samples from each level; 3891 independent reflections were examined, but 1305 were too weak to be measured. Intensities were corrected for Lorentz and polarization effects and for spot elongation on upper levels according to Phillips.[4]

The reflections 021, 122, $11\bar{3}$, $12\bar{4}$, and $15\bar{5}$ were later considered affected by extinction and omitted from the least-squares calculations. No correction was made for absorption nor for anomalous dispersion.

The atomic scattering factors were taken from the Dirac–Slater calculations of Cromer and Waber.[5]

Structure Determination.—The structure has been solved by the heavy-atom technique. The positions of the nickel atoms were determined from a three-dimensional Patterson function. The three-dimensional Fourier synthesis, calculated with phases from the nickel atoms, clearly showed all the atoms of the salicylaldimine residues. Two additional Fourier syntheses gave the positions of all the nonhydrogen atoms. The electron density syntheses were interpreted with the aid of a model.

At this point the R factor was 20.7%. R is throughout defined as $\Sigma||F_o| - |F_o||/\Sigma|F_o|$ where the sums are over the independent, observed reflections. The temperature factors assumed in the calculation of the structure factors were (in A^2): $B_{Ni} = 2.5$, $B_{O,N} = 3.0$, $B_C = 3.5$.

Refinement was continued by means of the least-squares technique, using the block diagonal approximation and individual isotropic temperature factors. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Only the observed reflections were included in this series of calculations. Reflections were weighted according to the function[6] $w = 1/(a + F_o + cF^2)$, with $a = 10.0$ and $c = 0.04$. A series of six cycles reduced the R factor to 11.3%.

Further refinement was continued with the full-matrix, least-squares program of Busing and Levy, adapted for the IBM 7090 by Stewart.[7] Unobserved reflections were also introduced in this series of calculations with an intensity equal to the minimum observable intensity. The weighting scheme used was $w = 0$ for unobserved reflections for which $F_o \leqslant F_{min}$, $w = 1$ for unobserved reflections for which $F_c > F_{mim}$ and for observed reflections with $F_o \leqslant 25$, and $\sqrt{w} = 25/F_o$ for observed reflections with $F_o > 25$.

One cycle with isotropic temperature factors for each atom and one cycle with anisotropic temperature factors reduced the R factor to 8.6%.

At this point the hydrogen atoms were introduced in calculated positions (assuming a C–H distance of 1.07 A) with a temperature factor $B = 4.0$ A^2 and their coordinates were not refined. One more cycle varying the level scale factors and the thermal and positional parameters of the nonhydrogen atoms gave a final R of 7.6%.

The final values of the parameters and their estimated standard deviations are reported in Table I. Standard deviations of the parameters were calculated by the least-squares program, according to the expression

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

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[4] D. C. Phillips, *Acta Cryst.*, **9**, 819 (1956).

[5] D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

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

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

Table II: Observed and Calculated Structure Factors[a]

0,0,L		
4	131	62
6	789	-897
8	510	625
10	1066	-1120
12	465	406
16	189	184
18	102	-141
0,1,L		
3	329	-323
4	467	-449
5	199	192
6	141	-137
7	91	-112
9	359	351
10	188	-182
11	257	-260
12	116	107
17	84	79
18	66	-71
0,2,L		
1	1208	-2103
3	314	-185
4	148	-133
5	191	87
7	701	786
9	1032	-965
11	677	661
13	225	-208
17	95	-105
0,3,L		
1	491	-431
2	355	299
3	189	157
4	129	65
5	88	81
6	71	47
7	249	233
8	208	198
9	174	-168
10	157	-146
11	220	224
13	143	-147
0,4,L		
0	374	227
1	102	-96
2	1619	1696
3	141	137
4	792	-849
5	110	98
6	110	145
8	810	-850
10	282	292
12	313	-310
14	316	322
0,5,L		
1	77	93
2	414	421
3	179	-157
5	367	-349
6	627	-616
7	453	426
8	151	133
9	100	-109
12	168	-159
14	161	155
15	99	96
17	85	-98
0,6,L		
0	65	-3
1	65	40
2	117	116
3	690	-757
5	267	362
6	226	-209
7	128	93
11	133	-125
13	286	274
15	246	-225
17	104	108
0,7,L		
1	388	391
2	508	-480
3	612	-604
4	231	183
5	83	-91
6	263	271
7	354	334
8	159	-151
10	107	99
11	155	-148
13	156	141
14	101	97
16	120	-114
0,8,L		
0	452	424
1	108	70
3	82	-64
4	322	365
6	434	-456
8	118	100
10	502	-542
11	135	-125
12	418	418
14	190	-200
16	128	141
0,9,L		
1	86	-75
2	94	-103
6	147	-133
9	168	167
10	123	-120
11	191	-171
13	170	157
14	91	80
15	136	-138
0,10,L		
0	166	173
1	796	-814
2	115	-121
3	579	584
5	371	-358
7	306	296
9	312	-322
11	301	301
13	223	-197
15	108	123
0,11,L		
1	322	301
2	400	-387
3	462	-433
4	248	232
7	141	121
12	119	105
15	59	87
0,12,L		
0	566	-596
1	140	-139
2	702	760
3	106	123
4	389	-410
6	202	216
7	119	127
8	408	-424
9	120	-115
10	191	175
12	179	-161
14	152	180
0,13,L		
1	200	-185
2	264	-248
3	109	116
4	157	-164
5	110	108
6	258	262
8	220	-213
11	139	136
12	79	68
13	100	-119
0,14,L		
0	186	-175
1	545	530
2	131	150
3	417	-392
5	306	288
6	107	115
7	329	-331
8	116	-123
9	291	291
11	204	-206
13	99	141
0,15,L		
10	120	108
0,16,L		
0	486	485
1	136	141
2	182	-189
6	91	-101
8	80	83
10	167	-181
0,17,L		
2	92	-86
4	91	-122
5	83	91
6	82	119
8	63	-76
9	50	82
0,18,L		
0	141	155
1	272	-295
0,19,L		
1	61	-92
3	55	91
1,0,L		
4	85	100
6	98	-79
8	257	252
10	121	-119
-4	234	-256
-6	127	120
-8	174	-176
-10	180	170
-12	288	-277
-14	196	-173
-16	143	-126
-18	110	118
1,1,L		
2	555	680
3	601	690
4	487	-545
5	306	-360
6	432	482
7	545	609
8	648	-703
9	643	-669
10	327	327
11	148	150
12	112	-119
-3	1337	-1552
-4	511	-585
-5	452	525
-6	268	314
-7	300	-340
-8	330	-352
-9	310	320
-10	344	326
-11	399	-394
-12	440	-414
-13	344	329
-14	153	139
-15	119	-104
-17	92	82
-18	105	107
-19	71	-75
1,2,L		
1	94	65
2	1731	-1867
3	53	13
4	190	196
5	67	-75
6	630	-647
7	194	191
8	191	-168
9	230	-222
10	332	318
12	288	270
-2	679	693
-3	320	299
-4	2024	2251
-5	339	-343
-6	358	-347
-7	106	113
-8	95	-73
-9	168	-179
-11	205	200
-13	192	-169
-14	152	-122
-15	145	144
-17	90	-68
1,3,L		
0	487	382
1	428	-314
2	586	-468
3	282	179
4	212	-230
5	625	633
6	763	808
7	700	-749
8	603	-636
9	271	277
10	352	376
11	212	-222
12	172	-165
13	244	261
14	212	200
-1	241	115
-2	237	305
-3	816	916
-4	1809	-1961
-5	883	-910
-6	825	844
-7	226	249
-8	220	-249
-9	344	-369
-10	455	454
-11	243	239
-12	229	-217
-14	281	244
-15	160	146
-16	137	-114
1,4,L		
1	120	-69
2	58	-47
3	467	492
4	96	-78
5	618	-572
6	205	193
7	258	191
8	137	-129
9	317	284
14	117	127
-1	498	-454
-2	71	-67
-3	755	-767
-4	571	573
-5	1605	1670
-6	372	-345
-7	242	-192
-9	150	-134
-10	157	-148
-11	227	-212
-12	111	94
-13	249	187
-14	243	-212
-16	169	166
1,5,L		
0	268	312
1	421	468
2	496	-512
3	648	-734
4	784	829
5	994	1044
6	819	-821
7	538	-545
8	215	203
12	113	105
13	165	154
14	132	-122
15	105	-88
-1	291	-362
-2	459	-495
-3	1021	1116
-4	897	1030
-5	1214	-1367
-6	429	-440
-7	205	203
-8	120	139
-9	109	56
-11	125	106
-13	238	-225
-14	233	-220
-15	292	286
-16	200	209
-17	120	-111
-18	111	-134
1,6,L		
0	67	-8
1	68	44
2	519	-525
4	660	-626
5	133	124
6	436	369
7	102	-102
8	265	-267
10	110	102
12	165	132
15	119	103
-1	75	63
-2	523	520
-3	122	-125
-5	254	251
-6	138	167
-7	89	-89
-8	506	505
-9	120	-146
-10	226	-207
-12	206	-249
-13	191	167
-15	139	-184
-17	124	119
-18	69	-78
1,7,L		
0	214	-102
1	132	23
2	212	-254
3	429	460
4	647	703
5	413	-434
6	403	-420
7	187	204
8	145	145
9	167	-162
10	214	-213
11	166	162
12	319	317
13	157	-141
14	108	-103
15	88	68
-2	232	-214
-3	121	-152
-4	202	242
-5	323	341
-6	596	-653
-7	533	-533
-8	147	201
-9	128	103
-10	240	221
-12	193	204
-13	162	160
-14	194	-193
-15	129	-122
-16	132	119
-17	99	103
1,8,L		
1	465	-408
2	102	-91
3	594	594
4	151	134
5	438	-416
6	135	-138
7	171	149
8	107	87
10	163	-160
11	113	94
12	189	184
15	98	-99
-1	163	-125
-2	82	58
-3	244	182
-5	345	332
-6	231	244
-7	226	-235
-8	157	-145
-9	145	134
-10	111	-106
-11	177	-177
-12	117	-116
-13	110	94
-14	125	122
-16	107	-74
1,9,L		
0	333	-353
1	442	-467
2	364	384
3	570	599
4	338	-347
5	465	-482
6	180	153
7	228	227
8	175	-170
9	332	-344
10	318	325
11	399	427
12	227	-229
13	154	-152
14	88	84
-1	438	460
-2	284	275
-3	326	-315
-4	297	-295
-5	587	610
-6	646	688
-7	736	-830
-8	400	-376
-9	166	139
-12	221	-216
-13	159	162
-14	125	116
-15	108	-101
-16	99	-86
-17	83	99
1,10,L		
2	286	-240
4	179	-177
5	124	-98
10	112	-102
11	108	102
12	172	180
-1	95	66
-2	538	547
-4	464	-479
-6	469	473
-7	162	149
-8	111	118
-12	286	-281
-14	121	88
-15	109	120
1,11,L		
0	437	-446
1	387	406
2	476	507
3	279	-285
4	431	-428
5	251	246
6	360	377
7	171	-165
8	212	-221
9	160	163
10	220	208
11	188	-185
12	139	-104
14	70	64
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-2	143	113
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-4	362	-357
-5	395	-399
-6	387	380
-7	151	137
-8	113	-107
-14	134	147
-15	97	89
1,12,L		
1	141	-120
5	140	103
6	140	117
7	180	-169
11	117	124
-1	247	-243
-3	504	534
-5	284	-311
-9	131	125
-13	123	-122
-14	112	-127
1,13,L		
0	121	120
1	217	222
2	169	-159
3	283	-273
4	173	177
5	377	380
6	192	-199
7	409	-426
8	194	178
9	210	204
10	126	-112
13	103	119
-1	234	-223
-2	255	-236
-3	554	557
-4	418	406
-5	563	-570
-6	191	-188
-7	247	259
-8	110	102
-9	259	-252
-10	165	-150
-11	140	146
-12	107	121
-13	128	-138
-14	138	-130
1,14,L		
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6	155	-157
7	122	-123
10	178	180
12	60	-77
-1	139	124
-2	220	233
-3	144	-127
-5	117	121
-6	177	181
-7	117	-122
-12	73	73
-13	73	76
1,15,L		
4	141	145
5	105	-82
6	216	-220
7	132	124
8	201	195
9	106	-114
-2	432	-447
-3	273	-265
-4	384	390
-6	140	-125
-8	113	108
-10	94	-86
-12	117	123
1,16,L		
5	96	81
7	155	-145
9	124	133
1,17,L		
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5	141	-141
6	105	95
7	132	137
8	93	-88
-1	277	285
-2	187	180
-3	288	-306
-4	90	-86
-5	118	101
-7	76	-71
-9	111	117
1,18,L		
6	99	-95
-4	115	124
1,19,L		
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1	61	64
-1	62	-65
-2	91	107
-4	84	-94
2,0,L		
2	1054	1211
4	1275	-1404
6	652	756
8	319	-333
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12	278	-264
-4	260	100
-6	147	189
-10	447	441
-12	462	-452
-14	307	285
-18	76	64
2,1,L		
0	470	474
1	343	-291
2	370	-328
3	543	520
4	652	655
5	640	-625
6	229	-203
7	79	-47
8	231	-204
10	107	109
11	231	224
13	105	-122
-2	186	180
-3	168	177
-4	74	88
-5	493	434
-6	471	-465
-8	88	-64
-9	213	-201
-10	150	-152
-11	98	89
-12	139	145
-13	193	-175
-16	106	97
-17	89	75
-19	102	132
2,2,L		
0	39	-49
1	45	83
3	231	-293
4	60	48
5	579	640
7	449	-483
8	122	-113
9	538	533
11	491	-497
13	306	307
-1	263	-391
-2	82	-53
-3	75	94
-4	49	-43
-5	334	-394
-6	277	250
-7	530	553
-9	270	-295
-11	371	365
-13	272	-239
-16	105	-133
-19	58	78
2,3,L		
0	373	329
1	395	327
2	105	-79
3	326	305
4	546	-507
5	378	-315
7	500	-470
8	366	333
9	364	346
12	170	-170
14	98	87
-1	370	-328
-2	518	-477
-3	52	51
-4	365	-298
-5	887	879
-6	566	486
-7	690	-631
-8	196	194
-9	115	120
-10	169	-158
-11	142	-141
-12	175	175
-15	107	-101
-16	104	-110
-17	102	122
-18	78	-87
2,4,L		
0	783	804
1	93	78
2	1011	-1042
4	751	795
6	692	-744
7	147	-144
8	540	584
12	129	130
14	130	-187
-2	1494	-1512
-3	192	166
-4	902	965
-5	261	-237
-6	956	-1008
-7	332	294
-8	985	1027
-9	164	-145
-10	490	-532
-12	383	354
-14	161	-132
-15	138	114
-16	191	189
-18	157	-187
2,5,L		
0	536	505
1	196	-199
2	417	344
3	543	-472
4	427	-381
5	211	188
7	125	-131
9	151	150
10	140	132
-1	487	462
-2	283	251
-3	344	289
-4	518	-520
-5	110	-90
-6	317	294
-7	78	58
-8	685	-643
-9	110	144
-10	95	100
-11	335	-324
-14	246	232
-16	96	-99
-17	206	221
2,6,L		
0	138	120
1	1523	-1530
2	216	-210
3	1134	1202
4	79	74
5	631	-666
6	66	-83
7	650	662
9	220	-227
15	131	124
-1	748	840
-2	105	-94
-3	426	-503
-5	311	349
-7	597	-579
-8	285	249
-9	972	959
-11	444	-409
-14	179	-171
-15	216	-206
-17	222	240
2,7,L		
0	245	-236
1	72	-94
4	131	-114
5	295	-270
6	126	109
7	95	80
8	179	168
11	146	146
12	129	-120
13	130	-126
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-2	111	-81
-3	218	172
-4	169	-158
-5	408	349
-6	461	422
-8	308	-290
-9	293	-250
-10	451	479
-11	104	-100
-14	109	-118
-15	102	106
-16	108	-118
-18	66	95
2,8,L		
0	1112	-1194
1	239	-214
2	1053	1058
3	121	99
4	253	-290
6	95	90
8	259	-250
10	398	372
12	190	-160
14	127	143
-1	147	135
-2	279	318
-4	455	-449
-6	762	754
-8	1007	-1100
-9	150	124
-10	873	915
-16	118	-124
2,9,L		
0	303	280
2	192	195
3	239	-196
4	254	-236
5	111	101
10	105	108
-1	107	98
-3	175	174
-4	154	-144
-5	155	-155
-6	101	-87
-7	310	297
-9	458	-429
-10	117	-137
-11	114	122
-14	183	182
-15	84	86
-17	56	-75
2,10,L		
0	201	-194
1	976	956
2	212	192
3	721	-744
4	98	-92
5	232	225
7	105	-92
9	332	324
11	281	-263
13	95	100
-1	631	-579
-5	169	-173
-7	572	572
-9	429	-419
-10	106	117
-11	125	133
-14	144	-172
2,11,L		
3	138	-142
5	173	-165
6	124	166
7	176	174
12	131	-116
-2	235	-221
-3	443	424
-4	149	153
-5	109	-110
-6	107	-103
-7	104	87
-8	221	191
-11	228	-213
-13	104	-117
-14	86	-84
-15	85	114
-16	47	59
2,12,L		
0	157	161
1	102	76
2	383	-411
3	108	-106
4	430	422
6	296	-299
8	276	293
10	196	-201
12	144	148
-6	272	-232
-8	304	272
-11	97	96
-12	160	148
-14	89	-89
-15	54	-79
2,13,L		
0	105	-100
-2	208	192
-3	110	99
-4	105	-113
-5	110	89
-6	129	-139
-7	212	-201
-13	71	81
2,14,L		
1	105	-85
3	154	146
5	284	-298
7	287	289
9	109	-112
11	64	98
-1	114	109
-2	114	-118
-3	286	-282
-4	105	90
-5	317	305
-7	163	-167
-9	130	136
-11	96	-111
-13	70	99
2,15,L		
7	86	-91
8	85	91
9	112	128
10	59	-65
-1	215	-206
-2	146	-150
-3	316	311
-9	84	-79
-11	68	59
2,16,L		
0	177	-184
2	94	107
4	207	-187
5	85	-79
6	241	254
8	114	-128
-2	181	197
-4	211	-209
-6	89	62
-9	72	64
-10	81	95
-11	53	-77
2,17,L		
2	84	103
-3	85	79
-8	64	58
-9	54	-58
2,18,L		
0	75	-88
1	162	171
2	76	68
3	166	-184
4	61	-80
5	165	173
-1	202	-224
-3	137	147
-5	110	-116
-6	75	87
-7	176	195
3,0,L		
2	53	-49
10	104	92
-4	140	165
-6	169	-195
-8	156	-125
-12	340	351
-14	207	-199
-16	102	110
3,1,L		
0	58	121
1	369	468
2	704	-759
3	874	-1015
4	676	741
5	412	446
6	270	-300
7	233	-246
8	290	267
9	340	334
10	297	-276
11	266	-247
12	252	249
13	190	165
-2	275	-406
-3	334	409
-4	459	501
-5	403	-444
-6	365	-420
-7	150	201
-8	184	-123
-9	230	181
-11	214	206
-12	362	351
-13	308	-294
-14	205	-200
-15	106	80
-17	100	-105
3,2,L		
0	304	-247
1	46	-44
4	695	-659
6	595	588
8	263	254
9	100	94
11	108	-89
12	183	-188
13	146	134
-1	45	55
-2	628	-641
-3	211	-219
-4	750	761
-5	304	335
-6	144	-130
-8	105	-86
-9	83	-55
-10	293	-266
-11	115	-121
-12	167	159
-13	186	195
-14	156	-154
-15	147	-137
-18	157	177
3,3,L		
0	452	470
1	439	-475
2	415	-465
3	268	289
4	295	297
5	334	-323
6	370	-350
7	357	358
8	349	345
9	197	-169
10	237	-222
11	225	220
12	218	202
13	298	-311
-1	410	449
-2	522	-562
-3	1042	-1136
-4	1096	1197
-5	939	1016
-6	482	-542
-7	110	-154
-8	102	140
-9	262	266
-10	106	-114
-11	242	-227
-13	289	270
-14	176	-153
-15	241	-276
-16	128	117
-17	90	-90
3,4,L		
0	109	-109
1	116	-97
3	297	245
5	132	108
9	158	-145
11	125	-121
13	257	250
14	99	-101
-1	264	254
-2	142	143
-3	716	-686
-4	384	-382
-5	64	-56
-6	224	219
-7	229	190
-8	129	-131
-9	108	102
-10	231	209
-11	249	-231
-12	168	-144
-13	395	363
-14	311	318
-15	165	-151
-16	158	-171
-17	87	-77
3,5,L		
0	635	-656
1	702	-774
2	470	480
3	422	469
4	396	-379
5	636	-627
6	542	528
7	489	491
8	292	-287
9	151	-157
12	142	-136
13	133	-112
14	149	162
-1	655	724
-2	605	678
-3	722	-770
-4	704	-695
-5	619	646
-6	141	154
-7	256	-264
-8	299	-301
-9	454	455
-10	382	384
-11	333	-322
-12	316	-304
-13	250	252
-14	401	390
-15	309	-329
-16	123	-142
-17	108	129
3,6,L		
0	119	84
1	96	81
2	154	-162
6	100	-85
8	380	377
-1	169	-157
-2	402	359
-3	143	132
-4	231	-197
-5	104	-97
-7	134	144
-8	103	-86
-9	226	-231
-10	100	-59
-11	283	267
-12	131	-106
-13	273	-297
-15	211	225
-17	79	-94
3,7,L		
0	729	-744
1	392	391
2	337	359
3	296	-298
4	469	-445
5	300	282
6	334	319
7	203	-203
8	166	-155
9	199	190
10	291	268
11	236	-228
12	315	-309
13	171	164
14	141	160
-1	737	-761
-2	856	876
-3	477	442
-4	172	-185
-5	145	-162
-6	315	344
-7	449	449
-8	472	-490
-9	367	-381
-10	450	423
-11	374	367
-12	445	-446
-13	228	-206
-14	208	197
3,8,L		
0	140	114
1	84	-84
5	384	338
7	213	-195
11	103	-105
12	136	-135
13	119	126
14	73	63
-2	240	-208
-4	85	77
-5	177	-170
-6	193	-183
-7	154	144
-8	266	248
-9	102	-108
-10	232	-209
-11	176	159
-12	331	331
-14	109	-112
-15	93	-74
3,9,L		
0	498	499
1	403	417
2	232	-243
3	326	-324
4	175	183
5	157	158
7	107	120
9	107	77
10	199	-174
11	319	-296
12	166	157
13	178	200
-1	891	-885
-2	549	-507
-3	621	592
-4	118	126
-5	239	-239
-6	216	-221
-7	465	470
-8	259	235
-9	295	-288
-10	272	-277
-11	342	347
-12	267	253
-13	297	-299
3,10,L		
4	136	-102
8	137	109
10	100	112
13	71	82
-1	122	116
-2	238	209
-3	181	-157
-4	281	-250
-6	279	256
-7	104	-106
-8	249	-259
-11	172	-171
-13	173	188
-16	65	77
3,11,L		
0	277	261
1	270	-248
2	343	-329
3	246	256
4	332	331
5	201	-196
6	229	-214
7	107	76
8	185	158
9	146	-135
10	213	-205
11	132	143
12	160	182
-1	130	140
-2	244	-208
-3	105	-105
-4	239	222
-7	138	106
-10	138	-132
-12	177	158
-14	109	-131
-15	70	-67
3,12,L		
1	199	-192
5	112	103
-1	152	141
-4	106	-96
-10	103	73
-11	99	65
-12	92	-82
-14	87	127
3,13,L		
1	162	-147
2	112	111
3	173	151
4	107	-101
5	181	-166
6	146	126
7	263	249
8	154	-126
9	146	-139
-3	347	-318
-4	226	-236
-5	359	372
-6	184	175
-8	125	-135
-9	106	99
-10	98	83
-11	109	-114
-13	113	114
-14	77	106
3,14,L		
0	183	182
2	106	-117
4	103	87
-1	107	-84
-2	278	-257
-3	175	161
-4	185	155
-5	126	-115
-6	121	109
-8	207	-194
3,15,L		
0	277	-269
1	125	133
2	273	263
3	121	-115
4	202	-193
5	128	109
6	207	214
7	130	-133
8	163	-176
-1	112	-128
-2	283	289
-3	111	121
-4	273	-275
-5	139	-131
-6	130	137
-7	103	91
-10	78	-83
3,16,L		
1	128	135
3	97	-101
7	105	123
-1	139	-143
-3	103	94
-5	172	-171
-7	110	106
3,17,L		
0	147	150
1	168	202
2	84	-101
3	165	-187
4	73	66
5	133	153
6	62	-77
-1	219	-221
-2	146	-129
-3	163	150
-4	114	104
-5	159	-148
-6	133	-130
-7	162	198
-8	73	96
-9	113	-112
3,18,L		
-2	70	-69
-4	91	102
-7	77	-80
3,19,L		
0	133	159
-1	59	61
-2	122	-137
4,0,L		
0	162	211
2	52	-116
4	912	1005
6	135	-199
8	200	191
10	322	-298
-6	387	-446
-8	1056	1119
-10	533	-515
-12	227	217
-14	328	-324
-16	165	166
-18	241	-266
4,1,L		
2	182	184
3	383	-371
4	487	-458
5	353	348
6	182	154
7	99	-94
8	86	-65
9	111	96
-1	63	71
-2	54	89
-3	326	-371
-4	217	189
-5	170	181
-6	171	177
-7	219	-255
-8	403	-392
-9	171	170
-10	294	294
-13	207	184
-15	93	-81
-16	147	-150
-17	87	89
-18	143	166
-19	107	-154
4,2,L		
1	371	-414
3	381	436
5	479	-531
7	377	390
9	370	-350
11	217	193
-1	900	1020
-3	993	-1182
-4	179	-161
-5	703	801
-6	94	87
-7	654	-932
-9	523	520
-10	102	-90
-11	151	-143
-12	183	-171
-13	128	106
-14	141	143
-15	155	-152
-17	189	188
-19	94	-107
4,3,L		
0	212	-207
1	107	-94
3	281	-253
4	279	246
5	121	95
6	90	63
7	222	197
9	106	-107
11	93	73
-1	42	-38
-2	368	357
-3	214	-205
-4	701	-684
-5	301	242
-6	595	583
-8	312	-310
-9	89	-89
-10	129	128
-11	142	-128
-12	332	-314
-13	340	338
-14	293	274
-16	178	-185
-17	193	-141
-18	77	105
4,4,L		
0	797	-816
1	99	-82
2	631	635
4	158	-149
6	746	745
7	85	66
8	583	-578
10	180	183
12	221	-215
-1	49	55
-2	535	587
-3	50	-53
-4	907	-924
-5	73	-59
-6	887	900
-8	352	-324
-10	235	240
-11	145	134
-12	229	-207
-13	279	-278
-14	182	175
-15	118	130
-16	345	-348
-18	103	114
4,5,L		
0	85	75
2	201	-200
3	94	86
4	99	79
8	91	-63
11	155	148
-1	56	-43
-2	198	-215
-3	146	-114
-4	303	261
-5	241	-236
-7	149	136
-8	206	198
-10	120	-117
-11	193	185
-13	184	-166
-15	274	281
-17	177	-201
4,6,L		
0	97	-97
1	825	807
2	105	103
3	485	-471
5	485	491
6	86	87
7	807	-860
8	96	-83
9	686	727
11	402	-424
13	129	128
-1	484	-517
-3	292	313
-4	79	-68
-5	639	-579
-7	324	318
-8	79	-81
-9	286	-300
-10	95	79
-11	203	235
-13	165	-142
-15	185	180
-17	70	-78
4,7,L		
0	119	119
1	126	-120
3	77	90
8	133	-111
10	138	143
-2	102	-106
-4	215	191
-5	130	-105
-6	347	-320
-7	165	128
-8	228	216
-9	115	126
-10	114	-122
-11	123	-128
-13	175	161
-16	76	68
4,8,L		
0	616	636
1	122	104
2	543	-518
4	268	261
8	402	415
9	93	85
10	518	-524
12	170	170
-1	80	-84
-2	581	-587
-3	75	61
-4	482	451
-6	329	-323
-8	481	470
-10	343	-326
-12	157	141
-13	95	-102
-14	113	-93
4,9,L		
0	209	-192
6	93	-103
10	86	-95
12	70	66
-2	217	219
-4	270	-273
-5	146	-127
-6	286	267
-8	111	-85
-9	122	151
-10	94	106
-12	119	-131
-14	102	100
-17	49	85
4,10,L		
0	99	105
1	471	-465
2	99	-83
3	406	425
5	213	-172
7	199	183
9	273	-298
11	157	174
13	89	-95
-1	498	498
-2	85	-100
-3	399	-371
-4	156	142
-5	88	97
-6	211	-187
-7	91	-93
-8	93	87
-9	163	163
-11	194	-193
-13	130	126
-15	56	65
4,11,L		
0	112	-115
1	118	-134
2	148	139
3	149	152
-2	135	122
-5	234	-221
-7	265	258
-10	92	93
-11	90	122
-13	79	-71
-15	60	75
4,12,L		
0	171	-150
2	98	91
4	133	-96
6	342	321
7	87	72
8	223	-233
10	73	91
-2	231	222
-4	375	-372
-5	94	82
-6	405	399
-7	98	-105
-8	289	-273
-10	283	276
-12	179	-179
4,13,L		
2	93	115
5	89	-42
-3	112	122
-5	224	-208
-7	199	192
-9	194	-194
-11	140	134
4,14,L		
0	92	-101
1	187	166
5	203	192
7	173	-177
-1	254	-253
-2	100	106
-3	315	327
-5	419	-397
-7	311	302
-9	179	-180
4,15,L		
-1	98	110
-3	87	-109
-4	87	70
-6	172	-151
-7	81	64
-8	122	126
4,16,L		
0	252	277
2	218	-215
4	215	237
6	149	-172
-1	83	-91
-2	257	-264
-4	170	157
-6	196	-183
-8	213	209
4,17,L		
0	88	107
1	67	-62
-1	69	81
-5	79	82
-6	67	-72
-7	141	-159
-9	85	96
4,18,L		
1	62	-72
-1	80	106
-2	55	-58
-3	81	-91
-5	130	118
5,0,L		
0	82	78
2	121	102
-4	77	-90
-6	169	185
-9	357	-382
-10	440	467
-12	345	-350
-14	125	116
-16	159	-160
-18	177	206
5,1,L		
0	109	61
1	284	-337
2	574	622
3	650	687
4	453	-454
5	311	-324
6	250	268
7	232	213
9	122	128
10	156	-161
-1	158	-121
-2	163	226
-3	180	-252
-4	339	-398
-5	315	354
-6	270	318
-7	586	-626
-8	428	-445
-9	630	626
-10	461	458
-11	483	-470
-12	242	-217
-13	241	215
-15	92	-93
-16	110	-90
-17	158	172
-18	93	102
-19	94	-111
5,2,L		
0	169	155
1	101	92
2	154	138
3	63	-75
4	75	-62
6	112	-93
8	294	-332
-1	55	-58
-2	696	751
-3	92	167
-4	633	-642
-5	345	-343
-6	294	-259
-7	296	303
-8	306	291
-9	259	-282
-11	301	286
-13	172	-171
-15	91	82
-17	122	-116
-19	91	128
5,3,L		
0	478	-488
1	329	370
2	351	377
3	431	-450
4	612	-616
5	594	592
6	451	406
7	161	-140
10	93	69
11	123	-106
12	116	-103
-1	373	-374
-2	185	203
-3	547	567
-4	514	-534
-5	712	-734
-6	650	661
-7	234	256
-8	250	-267
-9	256	-231
-10	141	125
-11	263	248
-12	180	-165
-13	202	-200
-14	111	92
-15	151	154
-16	85	-61
-18	82	93
-19	48	57
5,4,L		
0	129	114
1	213	-189
3	173	-167
5	328	304
7	475	-454
9	204	190
-1	240	245
-2	51	-57
-3	422	397
-4	186	185
-5	78	-87
-6	324	-307
-7	250	-230
-8	79	75
-9	166	-135
-11	202	193
-12	193	185
-13	149	-148
-14	204	-203
-15	93	101
-16	84	73
5,5,L		
0	241	243
1	303	297
2	215	-203
3	416	-400
4	493	493
5	648	624
6	436	-417
7	266	-275
8	168	166
9	229	245
10	200	-206
11	151	-156
-1	270	-333
-2	109	-113
-3	177	170
-4	281	270
-5	507	-482
-6	264	-265
-7	373	344
-11	149	144
-12	158	161
-13	219	-216
-14	171	-169
-15	105	108
-16	88	89
5,6,L		
1	70	-70
2	115	100
3	78	60
6	227	-236
8	130	-126
10	115	103
12	75	-83
-1	128	124
-2	128	93
-3	147	-143
-5	208	205
-7	227	-216
-8	80	-87
-9	84	81
-10	236	202
-11	91	-100
-12	108	-111
-13	163	168
-15	86	-79
-17	68	-88
-18	53	-55
5,7,L		
0	362	357
1	353	-319
2	540	-529
3	391	383
4	457	454
5	250	-249
6	344	-329
7	307	313
8	402	404
9	276	-290
10	247	-247
11	154	163
12	136	140
-1	349	352
-2	547	-529
-3	398	-388
-4	384	362
-5	317	305
-6	309	-297
-7	345	-334
-8	349	325
-9	165	155
-10	175	-177
-12	142	142
-14	89	-93
-18	61	109
5,8,L		
0	94	-87
1	106	99
2	105	99
3	147	-141
7	140	-146
9	89	85
11	87	-91
-2	178	166
-4	127	-133
-5	137	125
-6	89	82
-7	285	-287
-8	197	-182
-10	113	107
-14	86	60
5,9,L		
0	298	-273
1	463	-437
2	335	315
3	473	459
4	184	-183
5	196	-188
6	97	92
7	182	177
8	141	-122
9	119	-108
-1	442	416
-2	301	286
-3	416	-403
-4	84	-70
-7	131	-127
-8	219	-221
-9	280	259
-10	211	190
-11	120	-118
-12	128	-102
-13	110	103
-14	88	82
5,10,L		
1	101	100
4	119	126
6	202	-197
-1	120	-116
-3	134	138
-4	218	233
-6	212	-209
-7	92	95
-9	174	-177
-10	117	92
-11	116	124
-12	108	-90
-13	107	-110
-14	76	87
-15	66	67
5,11,L		
0	308	-294
1	189	174
2	227	202
3	178	-165
4	363	-351
5	233	233
6	296	314
7	137	-127
8	124	-128
9	68	92
10	96	106
11	51	-59
-1	265	-238
-2	313	292
-3	189	166
-4	254	-248
-5	96	-88
-6	229	244
-7	122	121
-8	271	-281
-9	221	-201
-10	257	255
-11	232	209
-12	157	-147
-13	155	-150
-14	69	75
5,12,L		
1	237	231
5	138	-139
7	93	84
9	80	-91
-1	206	-192
-3	223	207
-4	93	79
-5	148	-140
-6	127	-135
-8	159	150
-9	147	-121
-10	165	-165
-11	197	185
-12	117	121
-13	129	-132
-14	59	-70
5,13,L		
4	90	60
5	191	193
6	82	-77
-1	93	-81
-2	124	-108
-3	182	161
-4	229	230
-5	354	-359
-6	272	-269
-7	275	265
-8	159	162
-9	180	-179
-10	171	-166
-11	176	182
-12	176	175
-13	98	-101
-14	45	-60
5,14,L		
8	60	-77
-4	89	66
-5	110	100
-6	112	-119
-9	77	66
-11	107	-109
-12	77	82
-13	70	89
5,15,L		
0	107	116
1	124	-129
2	275	-284
3	173	166
4	235	265
5	114	-119
6	149	-179
7	59	78
-2	83	-86
-4	177	179
-5	131	120
-6	130	-127
-7	76	-59
-10	71	-75
-11	54	-56
5,16,L		
1	71	-64
3	139	148
5	124	-150
-5	72	62
-7	93	-92
-10	43	54
5,17,L		
1	87	-90
2	70	89
3	150	162
-5	93	113
-6	73	79
-7	125	-134
-8	84	-98
6,0,L		
0	826	-978
2	758	804
4	426	-446
8	123	-126
-4	194	194
-6	239	255
-8	773	-820
-10	501	513
-12	111	-82
-14	174	148
-16	155	-135
-18	123	135
6,1,L		
1	381	409
2	56	31
4	82	68
5	94	102
6	171	183
7	82	-89
8	90	69
9	193	-188
-1	184	-235
-3	176	249
-4	214	-244
-5	49	-57
-6	299	-301
-7	82	-62
-8	503	521
-9	171	-155
-10	309	-325
-12	162	154
-14	204	-187
-16	138	144
-17	69	-74
-18	82	-107
-19	61	83
6,2,L		
0	46	36
1	873	989
3	687	-768
5	220	218
7	119	-99
9	398	431
-1	792	-942
-2	35	-25
-3	461	601
-4	181	196
-5	267	-307
-6	114	98
-7	560	595
-8	177	-168
-9	487	-542
-10	73	59
-11	247	234
-13	183	-162
-14	102	97
-15	168	159
-16	107	-103
-17	98	-102
-19	52	61
6,3,L		
0	195	196
1	55	-0
2	159	-148
3	66	61
4	163	156
5	341	359
6	362	-358
7	190	-180
8	84	-61
9	138	-148
-1	108	117
-2	248	-255
-3	163	127
-4	428	445
-5	214	-192
-6	108	-106
-7	241	-233
-8	96	90
-9	94	86
-10	212	-200
-12	175	175
-13	121	100
-14	96	-99
-15	162	-159
-17	110	111
-19	37	-45
6,4,L		
0	321	337
1	84	71
2	464	-446
4	204	153
6	142	-126
8	312	289
10	164	-160
-1	65	-61
-2	487	-516
-4	340	355
-5	114	105
-6	150	-160
-8	96	70
-10	137	-124
-12	320	316
-14	241	-237
-15	97	77
-16	126	145
-17	84	-88
6,5,L		
0	227	-223
1	186	186
2	131	129
3	213	211
4	451	493
5	348	-348
6	169	-185
-2	89	94
-4	158	-152
-5	145	147
-6	164	-150
-7	169	-164
-10	207	205
-11	109	-89
-12	177	-169
-13	175	171
-14	131	133
-15	78	-73
-16	117	-131
6,6,L		
0	110	119
1	399	-378
4	78	-76
5	173	-162
7	354	350
9	225	-221
11	160	183
-1	540	547
-3	524	-527
-4	95	86
-5	559	550
-6	121	105
-7	221	-203
-9	155	125
-10	247	-246
-11	298	-300
-12	104	100
-13	222	224
-15	92	-85
6,7,L		
0	71	-66
1	194	172
3	246	244
4	195	-186
6	113	-115
7	212	-215
8	126	120
9	77	69
10	82	-83
11	84	-104
-1	89	-68
-2	198	198
-3	87	78
-4	203	-182
-6	379	356
-7	239	-212
-8	199	-172
-9	223	-210
-11	317	313
-12	83	-83
-14	93	87
-16	83	-86
6,8,L		
0	690	-674
1	99	-100
2	142	123
6	163	177
8	154	-144
10	129	118
-1	151	141
-2	485	471
-4	361	-330
-6	276	230
-7	116	121
-8	219	-189
-10	323	313
-11	109	-102
-12	210	-203
-14	108	101
-15	83	87
-16	74	-85
-17	46	-65
6,9,L		
0	220	196
1	81	78
3	109	111
4	315	286
5	174	-174
6	129	-128
-2	302	-294
-7	81	60
-9	214	-218
-11	209	206
-13	126	-122
-15	112	134
6,10,L		
0	148	-138
1	470	445
3	267	-255
5	169	159
7	284	-287
9	208	222
-1	560	-537
-2	186	184
-3	307	284
-6	97	89
-7	150	116
-9	369	-346
-11	281	276
-13	163	-168
-15	108	144
6,11,L		
0	185	172
1	106	103
3	228	232
4	187	-179
5	247	-246
-1	147	126
-2	104	-88
-3	153	-141
-5	96	97
-7	238	-223
-8	122	128
-10	270	-282
-12	148	162
-14	70	-89
6,12,L		
0	301	295
2	241	-219
4	81	66
6	134	-133
7	64	-58
8	207	252
9	44	52
-1	53	-76
-2	481	-463
-3	98	91
-4	358	346
-5	83	-75
-6	251	-245
-7	116	113
-8	307	302
-10	223	-228
-12	120	131
-14	62	-91
6,13,L		
0	83	81
4	95	-83
6	108	122
-1	174	164
-3	127	-128
-4	81	-70
-6	98	77
-7	78	-69
-9	115	104
-11	95	-94
-13	47	64
6,14,L		
1	246	-239
2	77	-70
3	188	180
5	145	-158
7	81	66
-1	223	211
-3	163	-151
-4	76	65
-5	158	145
-7	83	-71
-11	61	-83
6,15,L		
2	63	65
3	71	75
4	83	-89
-5	68	-59
-7	63	-65
-11	45	71
6,16,L		
0	194	-216
1	65	-73
2	214	264
3	54	60
-2	60	48
-6	89	92
-8	46	-59
6,17,L		
1	49	57
-5	48	-64
-6	37	52
7,0,L		
0	165	157
2	103	-143
-6	234	-266
-8	357	401
-10	96	-89
-14	69	-55
-16	107	97
-18	92	-108
7,1,L		
0	502	568
1	524	584
2	522	-565
3	355	-353
4	183	170
5	106	88
6	222	-188
7	359	-382
8	343	363
9	259	272
-1	343	-390
-2	300	-385
-3	228	334
-4	143	170
-5	232	-273
-6	311	-357
-7	511	571
-8	360	374
-9	409	-430
-10	133	-127
-11	90	70
-13	115	-94
-15	101	89
-16	100	79
-17	56	-50
-18	55	-63
-19	26	49
7,2,L		
0	303	312
1	170	-172
2	91	-88
3	75	67
4	81	73
6	162	151
8	152	-136
-1	197	222
-3	195	-236
-4	155	-164
-5	283	319
-7	306	-334
-8	228	-230
-9	211	218
-11	138	-123
-13	124	117
-14	119	122
-15	119	-111
-17	97	108
7,3,L		
0	387	427
1	274	-282
2	148	-144
3	122	111
4	259	259
5	347	-354
6	419	-446
7	240	221
8	180	186
9	118	-117
10	139	-138
-1	303	319
-2	332	-334
-3	227	-214
-4	462	495
-5	448	496
-6	365	-373
-7	205	-231
-8	114	122
-9	160	157
-10	102	-84
-11	255	-260
-12	154	137
-13	100	84
-14	167	-158
-15	86	-79
-16	70	70
-17	88	88
-18	55	-64
7,4,L		
0	64	-61
1	56	42
2	59	-56
3	63	50
5	197	190
7	111	-112
-1	389	-399
-2	79	80
-3	182	186
-4	236	-240
-5	130	149
-6	184	190
-7	176	-165
-8	87	78
-9	247	227
-10	99	80
-11	120	-107
-12	200	-188
-14	192	184
-16	138	-143
-18	59	72
7,5,L		
0	152	139
1	257	265
2	145	-150
4	257	-230
5	451	-438
6	278	282
7	165	150
9	62	-57
10	70	75
-1	148	151
-3	321	-334
-4	403	-415
-5	414	414
-6	289	276
-9	138	-132
-10	109	78
-11	229	-205
-12	135	-124
-13	230	208
-14	140	133
-15	107	-104
-16	89	-82
-17	77	88
7,6,L		
0	199	186
1	118	-118
2	435	438
4	114	-119
6	70	-45
8	88	72
10	79	-85
-1	78	-67
-2	231	-225
-3	246	252
-4	251	-244
-5	260	-270
-6	119	104
-7	107	93
-8	140	-110
-10	140	-148
-11	169	151
-12	152	148
-13	209	-204
-14	99	88
-15	146	149
-16	54	-53
-17	74	-85
7,7,L		
0	262	271
1	171	-153
2	67	-36
3	229	-217
4	315	-319
5	190	167
6	145	144
7	84	-82
8	111	-113
-2	426	430
-3	497	482
-4	501	-492
-5	378	-372
-6	287	267
-7	219	212
-8	137	-136
-9	68	-42
-10	115	103
-12	176	-168
-13	157	-156
-14	74	81
-15	157	164
-17	66	-84
7,8,L		
0	110	-125
3	92	-92
7	109	121
-2	150	-133
-4	203	197
-5	184	-162
-6	96	-91
-7	175	156
-8	113	102
-12	97	93
-13	155	-140
-14	154	-165
-15	121	120
-16	81	92
-17	39	-57
7,9,L		
0	126	-113
1	72	-65
2	108	-103
3	324	-320
4	206	204
5	218	202
6	153	-134
7	209	-201
8	111	110
-1	123	159
-2	111	-92
-3	324	292
-4	166	137
-5	157	-129
-6	129	-112
-7	93	88
-8	134	120
-9	122	-131
-10	69	-65
-12	129	120
-13	91	-87
-14	140	-139
-15	111	121
-16	59	74
7,10,L		
0	132	118
2	249	234
3	98	78
6	94	-93
8	108	123
-2	185	-165
-3	146	-133
-4	107	-88
-5	159	145
-7	105	-99
-9	119	101
-10	100	-94
-12	151	157
-13	124	130
-15	119	-162
7,11,L		
0	208	194
1	170	-157
2	232	-208
3	104	88
4	274	268
5	216	-206
6	315	-336
7	161	174
8	148	145
-1	242	228
-2	189	-163
-3	204	-188
-4	455	433
-5	222	204
-6	384	-381
-7	135	-120
-8	204	194
-9	118	98
-10	94	-87
-11	145	-151
-13	63	59
-14	92	-116
7,12,L		
0	67	-56
2	70	54
3	175	-188
7	120	133
-1	300	280
-2	68	41
-3	187	-181
-4	239	-238
-5	117	-102
-6	262	262
-7	118	136
-8	95	-81
-9	63	48
-10	60	40
-11	118	-122
-14	39	64
7,13,L		
0	181	-178
1	133	-123
3	71	55
4	59	-33
5	203	-230
6	112	113
-1	252	241
-2	219	212
-3	233	-200
-4	162	-153
-5	394	385
-6	78	63
-7	215	-212
-13	28	35
7,14,L		
1	55	51
2	63	-58
3	49	-43
4	62	72
-1	74	-63
-2	105	108
-3	60	42
-4	59	-52
-5	143	-146
-6	144	-142
-7	94	89
-11	52	51
7,15,L		
0	149	-158
1	97	83
2	177	185
3	91	-104
-1	88	-106
-2	168	169
-3	101	102
-4	109	-100
-6	127	141
-8	84	-97
-9	60	-72
-10	52	64
7,16,L		
0	44	54
1	39	-59
-2	47	-59
-5	47	-52
-6	43	-55
-7	65	70
8,0,L		
0	488	601
2	535	-568
6	131	-107
-2	98	-95
-8	273	334
-10	413	-527
8,1,L		
1	300	-326
2	77	-66
-1	170	181
-2	80	75
-4	162	-241
-5	159	-199
-6	220	236
-8	218	-203
-9	345	358
-10	331	331
-11	109	-96
-12	89	-76
8,2,L		
1	512	-546
3	339	340
5	141	-124
7	180	175
-1	487	548
-2	70	-62
-3	324	-361
-4	169	199
-5	152	146
-6	210	-229
-7	306	-327
-9	486	538
-11	334	-332
-12	117	118
-13	117	106
8,3,L		
0	121	-161
3	287	-291
4	251	233
5	280	282
6	140	-162
7	129	-149
-1	144	-143
-3	332	382
-4	282	333
-5	329	-365
-6	89	-94
-7	148	140
-8	353	-389
-10	251	263
-11	221	211
-12	113	-96
-13	165	-147
8,4,L		
0	189	-163
2	177	144
3	100	76
4	366	-369
6	163	154
8	197	-193
-1	73	66
-2	380	424
-3	203	-215
-5	154	159
-6	194	174
-7	88	96
-8	325	-305
-9	130	-136
-10	172	153
-11	89	-67
-12	300	-288
-13	89	91
-14	85	73
8,5,L		
2	161	-148
4	93	72
6	152	-147
7	118	109
-1	102	-103
-2	204	-173
-3	206	-194
-4	275	274
-5	73	69
-7	311	301
-9	165	-151
-10	88	-61
-11	97	89
-12	240	218
-14	84	-83
8,6,L		
1	409	347
3	382	-340
5	284	288
7	108	-92
-1	295	-272
-3	190	198
-4	132	-127
-5	315	-320
-7	364	348
-9	224	-203
-10	103	88
-11	173	167
-12	102	-90
-13	114	-118
8,7,L		
0	139	115
1	88	-76
2	171	-183
3	161	-133
4	192	193
-3	83	-66
-4	83	81
-5	134	126
-6	253	-244
-8	151	137
-9	174	175
-11	110	-102
8,8,L		
0	377	309
2	522	-478
4	255	259
6	165	-183
-2	236	232
-4	216	187
-6	365	-349
-8	248	231
-10	193	-186
8,9,L		
0	90	-66
1	141	-126
3	154	156
-2	175	-166
-3	89	-60
-4	247	234
-5	238	204
-7	205	-165
-9	179	165
8,10,L		
1	396	-361
3	414	410
5	182	-211
-2	110	91
-3	125	117
-4	180	-179
-5	214	188
-7	338	-342
-9	233	223
8,11,L		
0	132	-106
2	102	102
-2	143	121
-3	192	-181
-4	185	-158
-5	104	92

[a] Columns are l, $10F_o$, and $10F_c$. Unobserved reflections are not reported. Reflections considered affected by extinction are marked with an E.

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 computer programs used in the calculations were as follows: reduction of intensities, structure factor calculation, Fourier summations, and block-diagonal least squares were performed on an IBM 1620 with programs written by Albano, Bellon, Pompa, and Scatturin.[8] The least-squares refinement of cell parameters, the calculation of the hydrogen positions, and the full-matrix least-squares refinement of the atom parameters were performed on the IBM 7090 of the CNUCE in Pisa with a set of programs written or adapted at the University of Washington and at the University of Maryland for the IBM 709/7090/7094.[7] The least-squares plane and the bond lengths and angles programs were local modifications of programs written by Damiani, *et al.*, for the IBM 1620.[9]

Table II reports the observed and calculated structure factors.

Discussion

The structure of bis(N-γ-dimethylaminopropylsalicylaldiminato)nickel(II) consists of discrete molecules (Figure 1) in which the nickel atom forms four bonds of normal length with the salicylaldimine donor atoms and two longer bonds with the γ nitrogen atoms. The coordination polyhedron can be described as a distorted octahedron with approximate C_{2h} symmetry. Bond lengths and angles in the coordination polyhedron, with their estimated standard deviations, are reported in Table III. The labeling of the atoms is also shown in Figure 1.

TABLE III

DISTANCES AND ANGLES IN THE COORDINATION GROUP WITH THEIR ESTIMATED STANDARD DEVIATIONS

Distance, A			Angle, deg		
Ni-O(1)	2.014	0.004	O(1)-Ni-N(3)	91.9	0.2
Ni-O(2)	1.996	0.004	O(2)-Ni-N(4)	92.2	0.2
Ni-N(1)	2.042	0.005	O(1)-Ni-N(4)	88.4	0.2
Ni-N(2)	2.058	0.006	O(2)-Ni-N(3)	87.4	0.2
Ni-N(3)	2.317	0.006	N(1)-Ni-N(3)	81.6	0.2
Ni-N(4)	2.285	0.005	N(2)-Ni-N(4)	81.5	0.2
Angle, deg			N(1)-Ni-N(4)	98.6	0.2
O(1)-Ni-N(1)	87.7	0.2	N(2)-Ni-N(3)	98.2	0.2
O(2)-Ni-N(2)	88.6	0.2	O(1)-Ni-O(2)	179.2	0.2
O(1)-Ni-N(2)	92.1	0.2	N(1)-Ni-N(2)	179.7	0.2
O(2)-Ni-N(1)	91.7	0.2	N(3)-Ni-N(4)	179.6	0.2

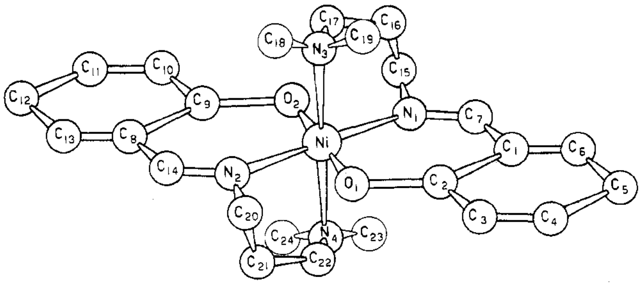

Figure 1.—A perspective drawing of the bis(N-γ-dimethylaminopropylsalicylaldiminato)nickel(II) structure showing also the labeling of the atoms.

Besides the nonequivalence of the six coordination bonds, the values of the angles also show large deviations from regularity, the four N-Ni-N angles being considerably different from 90°. The distortions in the octahedron are mainly caused by steric repulsion of the methyl groups attached to the γ nitrogen atoms and by the difficulty of the γ nitrogen atoms to reach the apical positions of the octahedron. Both effects are evident from the values of the intramolecular contacts (Table IV) and of the bond angles in the molecule (Table V). The methyl carbons, in fact, have short molecular contacts with the four equatorial ligands. Moreover, large strains are present in the trimethylene chains, as shown by the values of the angles at the carbon atoms, which are considerably higher than the expected tetrahedral value.

TABLE IV

INTRA- AND INTERMOLECULAR CONTACTS LESS THAN 3.6 A

Atom 1 (in x, y, z)	Atom 2	Distance, A	Molecule position
C(6)	C(13)	3.388	$x + 1, y, z$
C(6)	C(11)	3.551	$x + 1, {}^1/_2 - y, {}^1/_2 + z$
C(23)	C(23)	3.347	$-x, -y, -z$
C(18)	O(1)	3.019	x, y, z
C(18)	N(1)	3.245	x, y, z
C(19)	O(2)	3.505	x, y, z
C(19)	N(2)	3.181	x, y, z
C(23)	O(2)	3.027	x, y, z
C(23)	N(2)	3.212	x, y, z
C(24)	O(1)	3.531	x, y, z
C(24)	N(1)	3.171	x, y, z

TABLE V

BOND ANGLES (DEG) IN THE MOLECULE AND THEIR ESTIMATED STANDARD DEVIATIONS

Ni-O(1)-C(2)	129.4	0.4	Ni-O(2)-C(9)	129.2	0.4
Ni-N(1)-C(7)	126.6	0.4	Ni-N(2)-C(14)	125.8	0.4
Ni-N(1)-C(15)	116.0	0.4	Ni-N(2)-C(20)	115.4	0.4
C(7)-N(1)-C(15)	116.4	0.6	C(14)-N(2)-C(20)	117.5	0.5
Ni-N(3)-C(17)	110.4	0.5	Ni-N(4)-C(22)	110.6	0.4
Ni-N(3)-C(18)	110.8	0.5	Ni-N(4)-C(23)	111.6	0.4
Ni-N(3)-C(19)	109.7	0.4	Ni-N(4)-C(24)	110.2	0.4
C(17)-N(3)-C(18)	111.5	0.6	C(22)-N(4)-C(23)	109.8	0.5
C(17)-N(3)-C(19)	107.3	0.6	C(22)-N(4)-C(24)	107.0	0.5
C(18)-N(3)-C(19)	107.1	0.6	C(23)-N(4)-C(24)	107.5	0.5
C(2)-C(1)-C(6)	119.0	0.6	C(9)-C(8)-C(13)	119.1	0.6
C(2)-C(1)-C(7)	122.3	0.7	C(9)-C(8)-C(14)	123.3	0.6
C(6)-C(1)-C(7)	118.5	0.7	C(13)-C(8)-C(14)	117.3	0.6
O(1)-C(2)-C(1)	123.1	0.6	O(2)-C(9)-C(8)	123.2	0.5
O(1)-C(2)-C(3)	121.1	0.7	O(2)-C(9)-C(10)	120.6	0.6
C(1)-C(2)-C(3)	115.8	0.7	C(8)-C(9)-C(10)	116.3	0.6
C(2)-C(3)-C(4)	123.4	0.8	C(9)-C(10)-C(11)	122.2	0.7
C(3)-C(4)-C(5)	120.4	0.7	C(10)-C(11)-C(12)	122.2	0.7
C(4)-C(5)-C(6)	118.8	0.8	C(11)-C(12)-C(13)	116.3	0.7
C(1)-C(6)-C(5)	122.6	0.8	C(8)-C(13)-C(12)	123.7	0.7
N(1)-C(7)-C(1)	126.9	0.7	N(2)-C(14)-C(8)	127.0	0.6
N(1)-C(15)-C(16)	109.7	0.6	N(2)-C(20)-C(21)	109.7	0.6
C(15)-C(16)-C(17)	114.3	0.6	C(20)-C(21)-C(22)	115.2	0.5
N(3)-C(17)-C(16)	115.6	0.6	N(4)-C(22)-C(21)	116.2	0.6

Considering the salicylaldimine donor atoms, values for the Ni-O and Ni-N distances from octahedral nickel salicylaldimine chelates are not available for comparison. It is interesting to compare these distances with the analogous values from square-planar, tetrahedral, and five-coordinate nickel-salicylaldimine complexes. The results, taken from structures refined by three-dimensional X-ray analysis, are summarized in Table VI.[1b,1c,1d] (Values have been averaged in the case of more than one independent bond.)

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(8) (a) V. Albano, P. L. Bellon, and F. Pompa, *Ric. Sci., Suppl.*, **33**, 285 (1963); (b) V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *ibid.*, **33**, 1037 (1963).

(9) A. Damiani, P. De Santis, E. Giglio, and A. Ripamonti, *ibid.*, **32**, 195 (1962).

Table VI

Comparison of M–O and M–N Distances in Some Four-, Five-, and Six-Coordinate Nickel–Salicylaldimine Chelates

Complex	Stereochemistry	M–O, A	M–N, A	Ref
Bis(N-isopropyl-3-methylsalicylaldiminato)nickel	Planar	1.837 ± 0.002	1.920 ± 0.003	1b
Bis(N-isopropylsalicylaldiminato)nickel	Tetrahedral	1.896 ± 0.005	1.970 ± 0.007	1c
Bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel	Distorted square pyramidal	1.941 ± 0.015	1.987 ± 0.019	1d
Bis(N-γ-dimethylaminopropylsalicylaldiminato)-nickel	Octahedral	2.005 ± 0.004	2.050 ± 0.005	Present work

The increased length of the metal–ligand bonds in the high-spin complexes compared with the low-spin square complex can be mainly attributed to the presence of two unpaired electrons in the d antibonding orbitals. In the square complex the d antibonding orbital is empty, and this would then result in an increase of the σ-bond strength.

This explanation has been suggested by Cotton[10] in order to account for the different length of the metal–ligand bonds in square-planar and octahedral nickel(II) complexes.

Moreover, the repulsions between the ligands are undoubtedly an important factor in determining the increase of the metal–ligand bonds in the high-spin complexes, on going from four- to five- and to six-coordinate complexes.

From the octahedral and planar distances, using the corresponding values of the Pauling covalent radii for nickel(II) (1.39 and 1.22 A, respectively) we get for the covalent radii of oxygen and nitrogen 0.61 and 0.68 A, respectively (average). These values are slightly shorter than the usually quoted values of 0.66 and 0.70 A. With these values, we can get from the tetrahedral and five-coordinate metal–ligand distances, averaging over the M–O and M–N bond lengths, the values of 1.29 and 1.32 A, respectively, for the tetrahedral and the square-pyramidal radii of nickel(II).

Although the nickel atom does not lie on a crystallographic center of symmetry, the molecule is almost centrosymmetrical, the average deviations of the atomic positions from exact centrosymmetry being $\Delta x = 0.010$, $\Delta y = 0.011$, and $\Delta z = 0.014$ A. It is interesting to note that the largest deviation from centrosymmetry is shown by the pair of atoms C(6) and C(13) ($\Delta x = 0.018$, $\Delta y = 0.038$, $\Delta z = 0.038$ A) which are also found to be involved in one of the shortest molecular contacts (3.39 A).

The best least-squares planes passing through the salicylaldimine groups are almost parallel, the angle between them being 3° 12′. The perpendicular distance between the two planes is 0.80 A, the nickel atom being halfway between them. The equations of the planes are: salicylaldimine 1, $-0.3956x + 2.3559y + 2.9305z = 1$; salicylaldimine 2, $-0.5987x + 2.7865y + 3.8431z = 1$ (monoclinic coordinates). Deviations of the atoms from these planes are reported in Table VII.

Table VII

Distances (A) from Least-Squares Planes of Salicylaldimine Residues

C(1)	−0.0042	C(8)	−0.0300
C(2)	0.0001	C(9)	−0.0020
C(3)	0.0017	C(10)	−0.0008
C(4)	0.0117	C(11)	−0.0045
C(5)	0.0049	C(12)	0.0083
C(6)	−0.0167	C(13)	0.0104
C(7)[a]	−0.1103	C(14)	0.0074
C(15)[a]	−0.3936	C(20)[a]	0.1897
N(1)	0.0145	N(2)[a]	−0.1375
O(1)	−0.0121	O(2)	0.0112
Ni[a]	0.3936	Ni[a]	−0.4078

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

The four salicylaldimine donor atoms and the nickel atom lie in a plane having the equation: $-1.4007x + 3.2649y + 3.9166z = 1$ (monoclinic coordinates). Deviations of the atoms from this plane are all less than 0.01 A. The angles between the coordination plane and the planes through the salicylaldimines are 15° 18′ and 14° 30′, respectively, for salicylaldimine 1 and 2.

Bond lengths and angles in the rest of the molecule (Tables V and VIII) are in agreement with values from other metal salicylaldiminates.[11]

Table VIII

Distances (A) in the Molecule, Not Involving the Nickel Atom, and Their Estimated Standard Deviations

O(1)–C(2)	1.290	0.009	O(2)–C(9)	1.293	0.008
C(1)–C(2)	1.436	0.011	C(8)–C(9)	1.433	0.010
C(2)–C(3)	1.408	0.009	C(9)–C(10)	1.425	0.009
C(3)–C(4)	1.350	0.013	C(10)–C(11)	1.348	0.011
C(4)–C(5)	1.406	0.014	C(11)–C(12)	1.419	0.013
C(5)–C(6)	1.340	0.011	C(12)–C(13)	1.374	0.011
C(6)–C(1)	1.415	0.011	C(13)–C(8)	1.403	0.010
C(1)–C(7)	1.436	0.009	C(8)–C(14)	1.425	0.008
N(1)–C(7)	1.277	0.009	N(2)–C(14)	1.274	0.008
N(1)–C(15)	1.466	0.008	N(2)–C(20)	1.463	0.007
C(15)–C(16)	1.500	0.012	C(20)–C(21)	1.497	0.010
C(16)–C(17)	1.543	0.013	C(21)–C(22)	1.535	0.012
N(3)–C(17)	1.469	0.009	N(4)–C(22)	1.485	0.008
N(3)–C(18)	1.475	0.009	N(4)–C(23)	1.474	0.008
N(3)–C(19)	1.454	0.012	N(4)–C(24)	1.458	0.011

The large deviations from the tetrahedral value of the angles at the carbon atoms in the trimethylene chains already have been correlated with the distortions in the coordination octahedron.

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(10) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

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

There are no abnormally short intermolecular distances (Table IV).

It is interesting to point out that the presence of a trimethylene chain allows the γ nitrogen atoms to reach the apical positions of the coordination octahedron, although with some difficulty, the *trans*-planar configuration being then possible for the salicylaldimine residues. In the structure of the square-pyramidal complex bis(N-β-diethylaminoethyl-5-chlorosalicylaldiminato)nickel(II)[1d] the β nitrogen atom of the bonded en chain coordinates in the basal plane of the square pyramid with the azomethine nitrogen atom and the oxygen atom of one salicylaldimine group. The two salicylaldimines must therefore coordinate in the *cis* position, the angle between the mean planes through them being 85° 6′.

Acknowledgment.—The authors wish to express their thanks to Professor L. Sacconi for suggesting the problem and for his continuous interest.

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Five-Coordinate Complexes. III. Structure and Properties of μ_4-Oxo-hexa-μ-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}[1]

BY J. A. BERTRAND[2]

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The preparation, structure, and properties of a cluster compound of copper(II), $Cu_4OCl_6(TPPO)_4$, are reported. The compound crystallizes as orange, cubic crystals (a = 12.22 A) of space group P$\bar{4}$3m with one formula unit per unit cell. In the structure, four copper atoms tetrahedrally surround an oxygen atom; chlorine atoms bridge adjacent copper atoms, and each copper atom is, thus, bonded to three chlorine atoms. The oxygen of the phosphine oxide completes a slightly distorted trigonal bipyramid about the copper atom. The linear Cu–O–P arrangement indicates π bonding and the high P–O stretching frequency (1194 cm^{-1}) indicates a higher bond order than in other phosphine oxide complexes. The spectral and magnetic properties of the complex are consistent with the formulation as trigonal-bipyramidal copper(II) and there is no indication of any interaction between the copper atoms.

Introduction

The preparation and properties of dichlorobis(triphenylphosphine oxide)copper(II) were reported[3] several years ago; it is a yellow compound which can be recrystallized from various solvents, including lower ketones. During further investigation of the complexes between copper(II) halides and triphenylphosphine oxide (hereafter abbreviated TPPO), an attempted recrystallization of $CuCl_2(TPPO)_2$ from methyl isobutyl ketone yielded orange, cubic crystals which were analyzed as $Cu_4OCl_6(TPPO)_4$. Further investigation has provided an alternate preparation, the structure, and some of the properties of this new compound, μ_4-oxo-hexa-μ-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}.

Experimental Section

Preparation.—Stoichiometric amounts of $CuCl_2$, CuO, and TPPO were mixed in nitromethane and refluxed for several hours; the solution was filtered while hot. Orange crystals slowly deposited over a period of several days. *Anal.* Calcd for $Cu_4Cl_6O_5P_4C_{72}H_{60}$: Cu, 15.92; Cl, 13.33; P, 7.76; C, 54.17; H, 3.80. Found: Cu, 16.21; Cl, 13.55; P, 7.41; C, 53.61; H, 3.64.

Spectral Measurements.—Visible and near-infrared spectra were measured using a Cary Model 14 spectrophotometer; acetone was used as solvent for the solution spectrum and a KBr pellet was used for the spectrum of the solid. The spectrum of a single crystal in the 10,000-cm^{-1} region was obtained with a microspectrophotometer; the crystal spectrum was identical with that obtained for the solid in a KBr pellet.

The infrared spectrum was measured using a Perkin-Elmer Model 21 spectrophotometer; a KBr pellet was used. Two peaks were found in the P–O stretching region, 1194 and 1125 cm^{-1}.

Magnetic Susceptibility Measurement.—The magnetic susceptibility (1909×10^{-6} cgs unit/g-atom of copper) was determined by the Gouy method at 25°, using $HgCo(CNS)_4$ as a calibrant. A correction for diamagnetism (221×10^{-6} cgs unit) was made, using published atomic values.[4] The value of μ_{eff} was found to be 2.2 (+0.1) BM.

Collection and Reduction of the X-Ray Data.—Optical examination of the crystals indicated that they were cubic; a crystal in the shape of a cube with edges of approximately 0.2 mm was mounted, and precession photographs were taken. Zero-level photographs confirmed the cubic system and a unit cell dimension, a, of 12.22 ($\pm$0.02) A was obtained. Assuming one formula unit of $Cu_4OCl_6(TPPO)_4$ per unit cell, the calculated density was 1.51; an experimental value of 1.49 was obtained by the flotation method. Precession photographs of the $hk0$ and $hk1$ zones showed fourfold symmetry; systematic absences were not observed on any of the diffraction photographs. Although either centric or acentric space groups were possible at this point, the acentric P$\bar{4}$3m was chosen from a consideration of the formula of the compound and the available special positions of the possible space groups.

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[1] Part II: J. A. Bertrand and J. A. Kelley, *J. Am. Chem. Soc.*, **88**, 4746 (1966).

[2] Alfred P. Sloan Research Fellow, 1966–1968.

[3] D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 2298 (1961).

[4] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., John Wiley and Sons, Inc., New York, N. Y., 1960, p 403.