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The Crystal Structures of Bis[2,2′-iminobis(acetamidoxime)]nickel(II) Chloride Dihydrate and Bis[2,2′-iminobis(acetamidoxime)]copper(II) Chloride

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Received September 15, 1969

The crystal structures of two complexes with a new potentially tridentate ligand, 2,2′-iminobis(acetamidoxime), IBO, $C_4H_{11}N_5O_2$, have been determined. The intensities of 2259 reflections (2023 observed) for $Ni(IBO)_2Cl_2 \cdot 2H_2O$ and 3958 reflections (3500 observed) for $Cu(IBO)_2Cl_2$ were collected by diffractometer methods using niobium-filtered Mo Kα radiation. The space group for both compounds is $P2_1/a$. Cell dimensions for the nickel compound are a_0 = 10.049 (1), b_0 = 12.366 (1), c_0 = 8.207 (1) Å, and β = 103.45 (1)° with two molecules in the unit cell, while for the copper compound they are a_0 = 13.453 (2), b_0 = 16.121 (2), c_0 = 8.835 (1) Å, and β = 114.66 (1)° with four molecules in the unit cell. The observed densities are 1.631 and 1.742 g/cm^3. Both compounds were refined by full-matrix least-squares methods to conventional R values of 0.032 and 0.040 for the nickel and copper complexes, respectively. The nickel compound consists of discrete $Ni(IBO)_2^{2+}$ cations and chloride anions. The cation is a centrosymmetric, slightly distorted octahedral complex with bonding through the central amine nitrogen atom and the two oxime nitrogen atoms. Neither the chloride ion nor the water molecule is involved in coordination. The Ni–N(amine) distance is 2.115 (2) Å, while the Ni–N(oxime) distances are 2.081 (2) and 2.068 (2) Å. The copper compound consists of discrete $Cu(IBO)_2^{2+}$ cations and chloride anions. The cation is a distorted square-pyramidal pentacoordinate complex. One ligand molecule is tridentate, bonded through the amine nitrogen atom and the two oxime nitrogen atoms, these three donor atoms filling three of the four positions in the basal plane. The other ligand molecule is bidentate with one oxime nitrogen atom occupying the apical position. The remaining acetamidoxime group is not coordinated. The three Cu–N(oxime) distances are 1.951 (3), 1.960 (3), and 1.976 (3) Å. The Cu–N(amine) distances are 2.014 (3) Å for the equatorial bond and 2.357 (4) Å for the apical bond.

Introduction

Dr. L. P. Eddy of Western Washington State College has prepared a new potentially tridentate ligand, $C_4H_{11}N_5O_2$, IBO, 2,2′-iminobis(acetamidoxime),[1] and a number of its complexes. A schematic representation of this ligand is shown in Figure 1. In order to investigate the mode of coordination, we have determined the crystal structures of two of the complexes, $Ni(IBO)_2Cl_2 \cdot 2H_2O$ and $Cu(IBO)_2Cl_2$.

Experimental Section

Samples of both complexes were provided by Dr. Eddy. The crystals of bis[2,2′-iminobis(acetamidoxime)]nickel(II) chloride dihydrate are violet monoclinic rods elongated along *c* and bounded by {110}, and those of bis[2,2′-iminobis(acetamidoxime)]copper(II) chloride are dark blue monoclinic plates on {010}. From the density measurement and eventual solution of the structure, the crystals are the dihydrate. The crystal of the former used for intensity measurements was cut from a large crystal by cleaving on (001) and had the approximate dimensions 0.40 × 0.42 × 0.27 mm in the directions of *a*, *b*, and *c*, respectively. It was mounted parallel to the *b* axis. The shape of the crystal of the copper complex used for intensity measurements did not conform to the space group symmetry. It was bounded by {001}, (10$\bar{1}$), and ($\bar{4}$01). The approximate dimensions of this crystal were 0.21 mm along [104] and 0.11 mm along [010], while the mean distance in the direction of [100] was 0.40 mm. It was mounted parallel to the *b* axis.

Systematic absence of 0*k*0 for *k* odd and of *h*0*l* for *h* odd in Weissenberg photographs indicated the space group $P2_1/a$ (C_{2h}^5) for both compounds.

All data for the nickel complex were collected on a Picker manual diffractometer and those for the copper complex on a Picker automated (card controlled) diffractometer, using Mo Kα radiation (λ 0.71069 Å) filtered by a 0.001-in. thickness of niobium metal foil. Cell dimensions were determined by least squares, minimizing the differences between observed and calculated 2θ values for 19 reflections. Crystal data are listed in Table I. Densities were measured by the flotation method using a mixture of carbon tetrachloride and *sym*-tetrabromoethane.

TABLE I

CRYSTAL DATA

	$Ni(IBO)_2Cl_2 \cdot 2H_2O$	$Cu(IBO)_2Cl_2$
a_0, Å	10.049 (1)	13.453 (2)
b_0, Å	12.366 (1)	16.121 (2)
c_0, Å	8.207 (1)	8.835 (1)
β, deg	103.45 (1)	114.66 (1)
Space Group	$P2_1/a$	$P2_1/a$
Vol of unit cell, Å^3	991.9	1741.2
Density(calcd), g/cm^3	1.631	1.742
Density(obsd), g/cm^3	1.62 (2)	1.74 (1)
Z	2	4

Intensity data were collected by the θ–2θ scan method, monitoring the intensity scale by remeasuring a group of standard reflections every 3 or 4 hr. The intensity, I, and its estimated standard deviation, σ_I, for each reflection were calculated by

$$I = S - \frac{t_S}{2t_B}(B_1 + B_2)$$

$$\sigma_I^2 = \left[S + \left(\frac{t_S}{2t_B}\right)^2 (B_1 + B_2)\right] + K^2\left[S + \frac{t_S}{2t_B}(B_1 + B_2)\right]^2$$

where S is counts measured in scan of time t_S, B_i is counts measured at background in time t_B, and K is an empirical constant (0.01 for nickel complex; 0.0033 for copper complex).

A reflection was coded as unobserved if its intensity was less than or equal to twice the standard deviation of its intensity. For the nickel complex, 236 of the 2259 measured reflections were coded as unobserved and assigned "intensities" equal to $2\sigma_I$. For the copper complex, 458 of the 3958 measured reflections were coded as unobserved and assigned intensities equal to I +

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[1] L. P. Eddy, W. W. Levenhagen, and S. K. McEwen, *Inorg. Syn.*, **11**, 89 (1968).

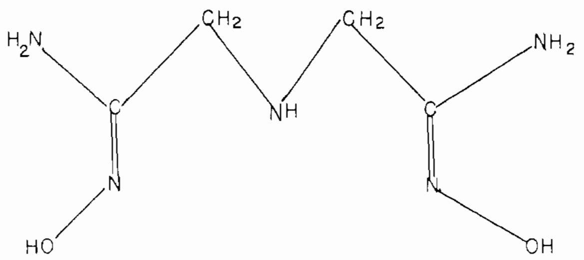

Figure 1.—The potentially tridentate ligand 2,2′-iminobis-(acetamidoxime).

$2\sigma_I$. For the nickel complex, an approximate calculation of the absorption correction by the method of Busing and Levy[2] as programmed by Burnham[3] gave a range of values from 1.35 to 1.41. Because of this small range, absorption corrections were neglected. For the copper complex, absorption correction factors calculated by the method of DeMeulenaer and Tompa[4] ranged from 1.27 to 1.70 and were therefore applied to the measured intensities.

Determination of the Structures

Both structures were determined and refined by normal procedures, consisting of the following steps: (a) application of Lorentz and polarization factors and calculation of observed structure factors, F_o, and their estimated standard deviations, σ_F; (b) determination of positions of metal ions; (c) determination of positions of other nonhydrogen atoms from three-dimensional Fourier maps; (d) refinement of scale factors, positions, and thermal (first isotropic, then anisotropic) parameters of nonhydrogen atoms; (e) determination of positions of hydrogen atoms from three-dimensional difference Fourier maps; (f) final refinement of scale factors, positions of all atoms, and anisotropic thermal parameters of nonhydrogen atoms and isotropic thermal parameters of hydrogen atoms. Refinements in steps d and f were carried out by the full-matrix least-squares method, minimizing $\Sigma w(F_o - F_c)^2$, with w equal to the reciprocal of σ_F^2 for each reflection, except that in each cycle any unobserved reflection having $|F_c| < |F_o|$ was assigned $w = 0$ for that cycle. Agreement factors quoted are $R = \Sigma|F_o - F_c|/\Sigma|F_o|$ and $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$. Examination of the structure factors by the method of Housty and Clastre[5] showed no evidence for secondary extinction in either compound.

$Ni(IBO)_2Cl_2 \cdot 2H_2O$.—Scattering factors for nickel(II) ion, chloride ion, and carbon, nitrogen, and oxygen atoms were taken from ref 6; those for the hydrogen atom were from Stewart, Davidson, and Simpson.[7] No anomalous dispersion terms were used.

In step b, the nickel ion is required to be at a center of symmetry, selected to be 0, 0, 0. In step e, the hydrogen atoms of the water molecule could not be located. Since the oxygen atom [O(3)] of the water molecule has high thermal parameters (*e.g.*, $B_{11} = 21.2$ Å^2), indicating either very large thermal motion or disorder, the failure to locate the hydrogen atoms is not surprising. They have not been included in the final calculations.

During the final cycle of refinement, the maximum shift was less than 0.5σ for all parameters of all nonhydrogen atoms. Five positional parameters and three thermal parameters of the hydrogen atoms had shifts of 1.0–1.5σ, but it was not felt to be worthwhile to continue refinement. Final values of R and R_w were 0.032 and 0.038, respectively.

The final list of F_o and F_c values is given in Table II. The final positional and thermal parameters are listed in Table III, and the root-mean-square displacements for the nonhydrogen atoms are listed in Table IV.

$Cu(IBO)_2Cl_2$.—Scattering factors for copper(II) ion, chloride ion, and carbon, nitrogen, and oxygen atoms were taken from Cromer and Waber;[8] those for the hydrogen atom were from Stewart, Davidson, and Simpson.[7] No anomalous dispersion terms were used.

In step b, the positions of the copper ions were found from a three-dimensional origin-removed sharpened Patterson synthesis. Because of the large number of parameters, the refinement cycles in step f were carried out in blocks. One of the hydrogen atoms, H(6), failed to refine and was therefore fixed at its position from the difference synthesis. During the final cycle of refinement, the maximum shift in any parameter was 0.06σ. Final values of R and R_w were 0.040 and 0.041, respectively.

The final list of F_o and F_c values is given in Table V. Table VI lists the final positional and thermal parameters, and Table VII lists the root-mean-square displacements for the nonhydrogen atoms.

Description of Structures and Discussion

A. Coordination Geometry in $Ni(IBO)_2Cl_2 \cdot 2H_2O$.—

The structure of bis[2,2′-iminobis(acetamidoxime)]-nickel(II) chloride dihydrate is shown in Figure 2. It consists of discrete $Ni(IBO)_2^{2+}$ cations, chloride anions, and water molecules. The cation is centrosymmetric, displaying a distorted octahedral coordination. Bonding is through the two oxime nitrogen atoms and the central amine nitrogen atom, a *trans*-facial configuration. The chloride ions are 4.07 Å and the water molecules are 4.86 Å from the nickel ion, so that none of these is involved in coordination.

The coordination octahedron is slightly distorted. The N(oxime)–Ni–N(amine) intrachelate angles are 78.9 (1) and 79.2 (1)° instead of the ideal 90°. The N(1)(oxime)–Ni–N(3)(oxime) angle is 88.4(1)°.

The Ni–N(oxime) bond lengths are 2.068 (2) and 2.081 (2) Å. On the basis of the standard deviations, this difference in Ni–N(oxime) distances may be significant. No other octahedral nickel structures involving coordination through oxime nitrogen atoms have been reported. All previously reported structures have been square planar with Ni–N(oxime) bond dis-

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(2) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(3) C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

(4) J. DeMeulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

(5) J. Housty and J. Clastre, *ibid.*, **10**, 695 (1957).

(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 201–207.

(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(8) D. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

TABLE II
LIST OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BIS[2,2'-IMINOBIS(ACETAMIDOXIME]NICKEL(II) CHLORIDE DIHYDRATE[a]

0,0,L		
1	1085	1116
2	522	-587
3	444	-437
4	337	349
5	444	461
6	533	554
7	401	406
8	97	94
9	64	-69
10	120	92
2,0,L		
-10	22*	-13
-9	218	218
-8	447	446
-7	373	378
-6	325	323
-5	99	-101
-4	230	220
-3	324	343
-2	644	632
-1	1234	1084
0	709	674
1	556	530
2	229	-219
3	735	743
4	653	650
5	116	126
6	90	86
7	148	151
8	72	72
9	107	104
4,0,L		
-10	98	100
-9	211	216
-8	156	158
-7	52	68
-6	151	136
-5	573	608
-4	199	206
-3	415	425
-2	128	-128
-1	156	-167
0	268	259
1	491	477
2	584	580
3	377	392
4	212	215
5	68	70
6	36	-47
7	203	200
8	234	234
9	70	66
6,0,L		
-10	21*	17
-9	21*	-10
-8	24	21
-7	110	104
-6	300	289
-5	649	636
-4	466	478
-3	451	-433
-2	344	-330
-1	420	412
0	752	757
1	530	531
2	41	-30
3	68	-65
4	99	105
5	277	216
6	338	338
7	208	201
8	30	32
8,0,L		
-9	46	42
-8	269	264
-7	198	193
-6	86	76
-5	130	126
-4	152	159
-3	226	216
-2	406	413
-1	516	520
0	129	136
1	210	-210
2	142	143
3	303	301
4	229	232
5	173	175
6	105	107
10,0,L		
-8	65	66
-7	21*	26
-6	20*	16
-5	161	143
-4	324	324
-3	302	299
-2	242	239
-1	125	132
0	64	64
1	118	125
2	150	150
3	189	190
4	87	90
12,0,L		
-6	81	85
-5	169	172
-4	169	172
-3	82	91
-2	21*	-1
-1	110	113
0	206	208
1	136	136
0,1,L		
1	10*	-18
2	111	114
3	151	-156
4	13*	8
5	32	40
6	32	-45
7	157	151
8	21*	1
9	32	39
10	35	36
1,1,L		
-10	93	95
-9	172	170
-8	167	185
-7	251	254
-6	207	206
-5	219	223
-4	188	193
-3	760	782
-2	69	68
-1	785	845
0	745	695
1	676	599
2	537	546
3	595	594
4	321	334
5	55	-49
6	151	147
7	348	345
8	199	198
9	99	90
10	84	81
2,1,L		
-10	27	35
-9	71	62
-8	43	-43
-7	79	-75
-6	122	-128
-5	279	280
-4	77	78
-3	239	226
-2	301	308
-1	116	-139
0	185	-155
1	900	944
2	395	402
3	90	84
4	286	-275
5	26	-22
6	17*	-11
7	18*	5
8	141	140
9	72	77
3,1,L		
-10	140	139
-9	110	109
-8	19*	-14
-7	117	115
-6	538	548
-5	700	697
-4	263	279
-3	259	-258
-2	129	109
-1	67	72
0	1081	1149
1	1006	1066
2	376	366
3	54	-64
4	103	113
5	350	349
6	357	355
7	164	160
8	56	55
9	29	19
4,1,L		
-10	22*	-0
-9	20*	0
-8	24	32
-7	24	28
-6	19	13
-5	117	110
-4	199	196
-3	81	-85
-2	357	-367
-1	77	69
0	238	228
1	352	361
2	383	384
3	183	-187
4	115	-105
5	100	-106
6	28	-20
7	61	58
8	34	38
9	24*	20
5,1,L		
-10	21*	-8
-9	30	31
-8	278	273
-7	318	311
-6	351	342
-5	128	126
-4	113	114
-3	264	266
-2	459	469
-1	366	405
0	190	188
1	297	300
2	306	313
3	233	236
4	347	338
5	229	223
6	112	108
7	118	122
8	96	97
6,1,L		
-10	22*	-9
-9	38	-36
-8	77	84
-7	63	67
-6	35	-40
-5	29	-24
-4	16*	11
-3	245	-236
-2	104	-101
-1	15*	-18
0	75	76
1	62	-63
2	16*	13
3	95	91
4	106	-108
5	39	-39
6	21*	-1
7	45	-42
8	22*	-16
7,1,L		
-10	76	74
-9	127	130
-8	197	196
-7	114	120
-6	19*	-9
-5	246	242
-4	410	385
-3	335	335
-2	323	319
-1	230	236
0	87	78
1	63	62
2	273	275
3	329	375
4	187	183
5	102	102
6	87	85
7	88	94
8,1,L		
-9	22*	12
-8	28	-23
-7	30	-13
-6	19*	-0
-5	65	-64
-4	18*	-9
-3	25	16
-2	135	-137
-1	125	-126
0	137	-139
1	22	26
2	93	90
3	19*	-10
4	20*	-8
5	40	-36
6	21*	-10
9,1,L		
-9	67	65
-8	48	-49
-7	27	-22
-6	179	173
-5	376	380
-4	389	389
-3	116	116
-2	55	-56
-1	105	103
0	251	245
1	330	326
2	231	233
3	24	24
4	20*	-4
5	79	35
10,1,L		
-8	32	-31
-7	21*	4
-6	21*	15
-5	26	20
-4	20*	4
-3	26	18
-2	28	-31
-1	90	-90
0	25*	36
1	32	34
2	20*	-11
3	23	0
4	21*	-9
11,1,L		
-7	200	200
-6	151	157
-5	25	26
-4	20*	2
-3	125	118
-2	214	215
-1	224	222
0	176	178
1	44	47
2	29	16
3	68	75
12,1,L		
-6	32	20
-5	22*	12
-4	22*	4
-3	21*	6
-2	51	49
-1	66	69
0	24*	-5
1	23*	-15
0,2,L		
0	702	639
1	720	749
2	51	-21
3	316	-325
4	118	123
5	491	508
6	530	527
7	161	153
8	57	-52
9	37	32
10	122	171
1,2,L		
-10	22*	-0
-9	115	109
-8	106	-107
-7	200	-200
-6	26	19
-5	222	220
-4	133	124
-3	374	-359
-2	398	373
-1	140	188
0	223	-261
1	165	179
2	513	484
3	269	-272
4	111	-103
5	274	-268
6	147	144
7	116	115
8	70	72
9	21*	10
10	22*	-9
2,2,L		
-10	58	54
-9	144	139
-8	251	244
-7	262	253
-6	129	125
-5	62	-46
-4	19	20
-3	828	835
-2	1233	1248
-1	278	252
0	339	-355
1	175	-168
2	650	654
3	628	632
4	480	475
5	343	344
6	122	119
7	40	44
8	109	107
9	164	165
3,2,L		
-10	48	45
-9	35	-31
-8	59	59
-7	127	-130
-6	95	85
-5	127	118
-4	136	-136
-3	339	-338
-2	271	259
-1	174	190
0	149	141
1	11*	-24
2	399	390
3	69	-64
4	214	-209
5	21	19
6	102	-106
7	19*	11
8	77	77
9	38	42
4,2,L		
-10	179	181
-9	184	184
-8	87	81
-7	63	70
-6	182	183
-5	312	315
-4	593	575
-3	746	736
-2	634	632
-1	56	64
0	153	-153
1	632	626
2	758	779
3	520	546
4	226	234
5	56	52
6	94	90
7	157	162
8	213	207
5,2,L		
-10	22*	8
-9	67	65
-8	89	89
-7	24	20
-6	193	-203
-5	17*	17
-4	155	143
-3	166	-156
-2	172	-169
-1	245	232
0	187	-197
1	15*	-6
2	195	177
3	236	246
4	86	-99
5	193	-192
6	19*	-7
7	20*	0
8	22*	7
6,2,L		
-10	163	160
-9	46	47
-8	22	-8
-7	141	140
-6	417	423
-5	532	534
-4	303	305
-3	132	130
-2	37	44
-1	272	274
0	650	663
1	659	653
2	310	317
3	57	-54
4	28	28
5	266	270
6	249	250
7	140	136
7,2,L		
-9	44	49
-8	48	-42
-7	65	-64
-6	19*	-5
-5	108	107
-4	39	34
-3	36	-30
-2	159	-155
-1	113	-110
0	99	-99
1	70	-64
2	273	261
3	119	116
4	124	-120
5	59	-65
6	21*	-2
7	22*	2
8,2,L		
-9	67	66
-8	186	186
-7	293	294
-6	170	176
-5	27	-12
-4	49	48
-3	291	288
-2	442	441
-1	258	257
0	43	46
1	94	92
2	140	144
3	207	218
4	207	210
5	115	113
6	36	38
9,2,L		
-9	37	-32
-8	85	-84
-7	54	55
-6	149	149
-5	21*	-8
-4	79	-73
-3	42	-48
-2	18*	7
-1	42	-51
0	30	-26
1	47	45
2	48	-37
3	20*	5
4	25	29
5	31	27
10,2,L		
-8	72	76
-7	44	49
-6	49	48
-5	94	92
-4	193	193
-3	236	234
-2	99	94
-1	19*	-5
0	42	43
1	140	141
2	205	212
3	143	145
4	76	74
11,2,L		
-7	21*	-15
-6	29	-23
-5	35	-35
-4	20*	-9
-3	103	107
-2	77	77
-1	29*	-1
0	61	-68
1	93	-86
2	22*	0
3	23*	28
12,2,L		
-6	114	116
-5	173	175
-4	153	156
-3	41	40
-2	33	-28
-1	22*	27
0	163	163
1	201	205
0,3,L		
1	574	-590
2	635	-621
3	21	-17
4	220	227
5	113	117
6	60	-45
7	27*	-0
8	98	-97
9	28*	-20
10	41	37
1,3,L		
-10	134	132
-9	155	156
-8	139	137
-7	55	53
-6	92	95
-5	254	253
-4	650	653
-3	452	454
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3,3,L		
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5,3,L		
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8,3,L		
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3	160	169
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9,3,L		
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3	22*	8
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6	406	411
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1,4,L		
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4,4,L		
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3	35	26
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3	155	153
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11,4,L		
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7	158	160
8	216	204
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2,5,L		
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3,5,L		
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12,5,L		
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7	107	114
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4,7,L		
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10,7,L		
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2	443	448
3	269	266
4	35	-12
5	96	95
6	191	190
7	197	197
8	91	86
3,8,L		
-9	65	-60
-8	29	37
-7	69	72
-6	20*	-6
-5	183	-183
-4	329	-324
-3	78	-73
-2	121	114
-1	266	266
0	100	102
1	283	-280
2	246	-279
3	18*	-11
4	81	86
5	155	152
6	35	-25
7	66	-76
8	72	-75
4,8,L		
-9	73	77
-8	55	52
-7	226	230
-6	299	305
-5	244	237
-4	21*	-25
-3	200	194
-2	318	308
-1	234	238
0	126	125
1	395	403
2	243	243
3	92	92
4	187	186
5	233	230
6	133	131
7	50	53
5,8,L		
-8	44	47
-7	50	-48
-6	172	-170
-5	137	-143
-4	28	31
-3	148	143
-2	81	81
-1	81	-80
0	153	-143
1	24	19
2	47	54
3	130	128
4	80	79
5	41	-44
6	21*	-11
7	32	-26
6,8,L		
-8	66	75
-7	87	93
-6	123	122
-5	228	226
-4	283	289
-3	219	219
-2	116	111
-1	57	42
0	135	131
1	214	209
2	262	265
3	167	167
4	114	117
5	130	124
6	85	87
7,8,L		
-8	22*	-16
-7	82	-82
-6	21*	13
-5	118	118
-4	94	87
-3	20*	20
-2	83	-81
-1	103	-97
0	57	43
1	99	97
2	132	127
3	20*	12
4	21*	-15
5	22*	11
8,8,L		
-7	85	85
-6	120	120
-5	184	186
-4	229	230
-3	131	129
-2	116	114
-1	109	110
0	85	87
1	153	153
2	211	206
3	125	127
4	35	37
9,8,L		
-7	65	65
-6	111	105
-5	40	45
-4	66	-68
-3	117	-113
-2	52	52
-1	108	110
0	38	30
1	34	-30
2	96	-89
3	30	-16
10,8,L		
-6	109	111
-5	69	77
-4	112	113
-3	166	170
-2	131	126
-1	98	100
0	129	123
1	115	117
2	75	79
11,8,L		
-4	23*	14
-3	81	86
-2	49	47
-1	25	-34
0,9,L		
1	363	-359
2	254	-249
3	74	72
4	140	143
5	100	93
6	24*	-12
7	24*	-6
8	52	-39
1,9,L		
-8	64	69
-7	229	231
-6	273	272
-5	250	257
-4	111	112
-3	186	185
-2	314	313
-1	369	369
0	428	425
1	490	407
2	168	168
3	253	259
4	116	116
5	158	158
6	240	242
7	160	160
8	81	83
2,9,L		
-8	21*	0
-7	119	-122
-6	186	-182
-5	19*	-16
-4	51	45
-3	165	167
-2	83	80
-1	31	-18
0	209	-209
1	34	36
2	172	171
3	101	101
4	114	-118
5	82	-80
6	29*	-31
7	27	26
8	88	85
3,9,L		
-8	79	85
-7	112	114
-6	314	322
-5	236	239
-4	36	33
-3	168	164
-2	297	282
-1	248	244
0	259	256
1	344	342
2	239	242
3	51	-50
4	124	126
5	206	204
6	169	173
7	102	100
4,9,L		
-8	34	-37
-7	72	-73
-6	21*	-23
-5	72	79
-4	74	57
-3	115	-110
-2	142	-140
-1	31	-23
0	146	143
1	130	130
2	125	119
3	53	-51
4	82	-87
5	77	-73
6	52	49
7	48	48
5,9,L		
-8	76	76
-7	86	94
-6	136	139
-5	134	134
-4	117	121
-3	177	158
-2	275	273
-1	23	73
0	132	131
1	272	272
2	201	195
3	83	85
4	88	83
5	140	141
6	93	91
6,9,L		
-8	46	48
-7	62	74
-6	73	70
-5	36	-42
-4	134	-139
-3	176	-175
-2	58	61
-1	214	205
0	65	65
1	148	-147
2	75	-71
3	84	83
4	76	79
5	46	44
7,9,L		
-7	94	96
-6	153	154
-5	161	157
-4	140	135
-3	57	60
-2	80	74
-1	219	220
0	189	186
1	210	207
2	160	158
3	45	65
4	81	79
5	118	117
8,9,L		
-7	35	-41
-6	71	-73
-5	46	-40
-4	21*	21
-3	114	117
-2	46	44
-1	110	-110
0	174	-183
1	32	-36
2	90	97
3	103	107
4	35	33
9,9,L		
-6	82	89
-5	80	85
-4	93	96
-3	160	154
-2	180	180
-1	148	146
0	151	150
1	121	121
2	93	92
10,9,L		
-5	70	71
-4	73	70
-3	22*	12
-2	63	-62
-1	101	-101
0	61	-37
1	25	26
0,10,L		
0	167	169
1	207	209
2	183	176
3	298	295
4	282	288
5	138	140
6	122	124
7	78	79
8	104	115
1,10,L		
-8	76	-83
-7	117	-120
-6	24	34
-5	143	155
-4	38	29
-3	68	-66
-2	61	-62
-1	128	-125
0	147	151
1	244	243
2	205	200
3	157	-160
4	160	-162
5	19*	5
6	119	119
7	87	86
2,10,L		
-8	46	47
-7	71	69
-6	163	168
-5	302	314
-4	244	249
-3	181	170
-2	87	85
-1	112	116
0	403	401
1	325	318
2	228	223
3	70	60
4	83	83
5	122	127
6	176	172
7	202	202
3,10,L		
-8	27	21
-7	73	73
-6	77	79
-5	72	-78
-4	74	-67
-3	60	-66
-2	171	176
-1	154	147
0	61	62
1	65	54
2	33	-22
3	53	-53
4	91	94
5	80	78
6	10	-40
7	53	-53
4,10,L		
-8	114	112
-7	127	134
-6	196	201
-5	119	125
-4	61	59
-3	65	67
-2	286	283
-1	399	401
0	327	320
1	184	179
2	58	-55
3	50	50
4	196	194
5	211	208
6	144	144
5,10,L		
-7	22*	-13
-6	151	-152
-5	21*	-20
-4	129	128
-3	120	121
-2	118	-122
-1	97	-99
0	57	-63
1	19*	25
2	142	141
3	123	125
4	66	-63
5	97	-102
6	80	-79
6,10,L		
-7	59	63
-6	21*	21
-5	122	124
-4	124	125
-3	221	216
-2	216	222
-1	215	212
0	143	141
1	136	128
2	157	158
3	146	142
4	141	139
5	100	99
7,10,L		
-7	30	-27
-6	34	-19
-5	48	50
-4	60	53
-3	79	-83
-2	163	-164
-1	110	-109
0	21*	-2
1	87	90
2	69	69
3	21*	-12
4	82	-78
8,10,L		
-6	96	102
-5	145	149
-4	152	151
-3	77	68
-2	95	96
-1	123	127
0	158	157
1	195	193
2	153	152
3	101	92
9,10,L		
-5	51	-51
-4	95	-95
-3	24*	-32
-2	22*	-12
-1	22*	10
0	46	42
1	24*	-27
2	72	-67
10,10,L		
-3	32	38
-2	74	73
-1	145	145
0,11,L		
1	68	76
2	49	-57
3	21*	21
4	80	79
5	29	25
6	45	-47
7	36	-32
1,11,L		
-7	72	78
-6	159	157
-5	106	105
-4	166	163
-3	161	164
-2	254	254
-1	172	171
0	119	115
1	69	60
2	113	115
3	166	165
4	211	213
5	234	234
6	99	102
7	71	73
2,11,L		
-7	56	-57
-6	35	-28
-5	20*	2
-4	37	33
-3	139	146
-2	41	-43
-1	192	-185
0	171	-125
1	223	223
2	166	159
3	62	-55
4	36	-32
5	20*	3
6	62	-63
3,11,L		
-7	79	82
-6	21*	11
-5	103	108
-4	201	213
-3	316	322
-2	248	247
-1	253	245
0	137	128
1	112	113
2	98	99
3	262	258
4	218	219
5	125	121
6	99	97
4,11,L		
-7	22*	-1
-6	54	-53
-5	56	62
-4	120	116
-3	20*	18
-2	139	-146
-1	166	-162
0	35	55
1	171	168
2	45	42
3	37	-45
4	60	-61
5	21*	-12
6	22*	-6
5,11,L		
-7	33	45
-6	61	62
-5	161	169
-4	234	236
-3	230	233
-2	211	219
-1	184	186
0	174	173
1	170	171
2	242	237
3	179	177
4	98	97
5	46	47
6,11,L		
-6	23*	26
-5	43	-46
-4	21*	-8
-3	73	-75
-2	61	-64
-1	76	71
0	56	70
1	46	-45
2	46	-44
3	28	-24
4	36	36
7,11,L		
-6	189	181
-5	137	140
-4	60	56
-3	50	52
-2	156	156
-1	195	182
0	215	211
1	189	185
2	102	103
3	57	56
8,11,L		
-5	91	-89
-4	29	31
-3	92	94
-2	21*	6
-1	78	-81
0	23*	-13
1	22*	13
2	22*	17
9,11,L		
-3	66	71
-2	116	114
-1	123	120
0	74	75
0,12,L		
0	150	-150
1	64	66
2	297	301
3	343	349
4	176	173
5	143	140
6	25*	3
1,12,L		
-6	42	46
-5	87	93
-4	20*	-19
-3	95	-103
-2	111	-110
-1	69	-77
0	24*	17
1	89	85
2	20*	6
3	45	-53
4	52	-43
5	21*	-9
6	22*	7
2,12,L		
-7	45	51
-6	63	66
-5	170	171
-4	292	296
-3	217	225
-2	99	95
-1	60	61
0	113	112
1	245	250
2	255	252
3	140	139
4	116	117
5	68	71
6	134	131
3,12,L		
-6	27	24
-5	30	-36
-4	107	-111
-3	74	-76
-2	62	64
-1	50	48
0	79	-76
1	163	-160
2	99	-102
3	26*	15
4	121	117
5	44	47
4,12,L		
-6	115	116
-5	82	90
-4	113	118
-3	129	129
-2	218	220
-1	303	291
0	266	265
1	22*	10
2	62	65
3	158	156
4	164	164
5	146	144
5,12,L		
-6	73	-77
-5	23*	-9
-4	83	85
-3	69	70
-2	21*	24
-1	77	-78
0	103	-113
1	46	-44
2	83	81
3	59	65
4	21*	2
6,12,L		
-6	43	41
-5	22*	17
-4	115	122
-3	236	241
-2	257	253
-1	126	121
0	22*	9
1	90	91
2	142	143
3	179	183
7,12,L		
-5	26	30
-4	38	41
-3	31	22
-2	22*	-9
-1	24*	32
0	23*	35
1	39	40
2	22*	11
8,12,L		
-4	97	104
-3	128	131
-2	40	40
-1	22*	16
0	100	106
1	163	164
0,13,L		
1	67	-84
2	24*	-3
3	48	53
4	78	89
5	24*	3
6	25	-27
1,13,L		
-6	117	124
-5	105	101
-4	98	102
-3	138	140
-2	217	220
-1	281	280
0	217	223
1	122	119
2	120	122
3	198	196
4	218	221
5	175	176
2,13,L		
-6	38	-36
-5	22*	-9
-4	21*	6
-3	54	-58
-2	20*	8
-1	28	-16
0	26	-28
1	101	-107
2	29	-29
3	59	60
4	38	38
5	21*	-5
3,13,L		
-6	22*	-7
-5	30	28
-4	193	203
-3	208	214
-2	177	169
-1	151	146
0	107	100
1	29	34
2	109	105
3	253	256
4	160	158
4,13,L		
-5	23*	27
-4	22*	5
-3	21*	10
-2	24	28
-1	29	23
0	120	-112
1	63	-69
2	21*	15
3	35	37
4	27*	15
5,13,L		
-5	106	115
-4	169	169
-3	135	136
-2	24	11
-1	92	92
0	98	102
1	115	111
2	128	129
3	135	130
6,13,L		
-4	51	-60
-3	22*	4
-2	46	46
-1	51	57
0	24*	-16
1	29	-36
2	25	-27
7,13,L		
-3	49	48
-2	91	100
-1	132	136
0	183	177
0,14,L		
0	117	114
1	148	151
2	223	220
3	175	183
4	121	123
5	44	47
1,14,L		
-5	40	-32
-4	26	26
-3	21*	-5
-2	66	-71
-1	33	13
0	54	50
1	67	66
2	22*	-26
3	21*	7
4	22*	24
2,14,L		
-5	132	138
-4	140	147
-3	90	97
-2	44	36
-1	125	123
0	195	196
1	245	244
2	177	179
3	104	103
4	22*	19
3,14,L		
-4	42	-39
-3	22*	15
-2	43	39
-1	86	98
0	47	37
1	70	-73
2	36	-41
3	43	49
4,14,L		
-4	22*	20
-3	22*	14
-2	94	95
-1	205	205
0	193	182
1	69	64
2	50	46
3	65	68
5,14,L		
-4	23*	20
-3	29	25
-2	38	35
-1	52	-55
0	23*	-36
1	49	40
2	23*	26
6,14,L		
-2	163	161
-1	93	90
0	46	44
0,15,L		
1	23*	8
2	25*	23
3	23*	7
1,15,L		
-3	22*	10
-2	148	159
-1	219	219
0	170	165
1	114	110
2	58	59
3	60	63
2,15,L		
-3	28	-24
-2	30	-19
-1	54	49
0	112	106
1	25*	13
2	23*	-18
3,15,L		
-3	136	140
-2	188	184
-1	81	77
0	26*	19
1	97	101
2	222	224
4,15,L		
-2	23*	15
-1	26	34
0	31	23
0,16,L		
0	88	82

[a] Columns are l, $10|F_o|$, and $10F_c$. Unobserved reflections are indicated by an asterisk (the values given for F_o for these reflections are the F's obtained from the assigned intensities, equal to $2\sigma_I$).

TABLE III

BIS[2,2-IMINOBIS(ACETAMIDOXIME)]NICKEL(II) CHLORIDE DIHYDRATE[a]

Positional Parameters ($\times10^4$) and Thermal Parameters ($\times10^2$)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	207 (1)	144 (1)	201 (1)	−1 (1)	46 (1)	−24 (1)
Cl	1547 (1)	4667 (1)	1743 (1)	297 (2)	336 (2)	365 (2)	34 (2)	133 (2)	38 (1)
C(1)	1662 (2)	1247 (2)	2714 (2)	297 (8)	267 (8)	237 (6)	−43 (6)	37 (6)	−31 (6)
C(2)	247 (2)	1663 (2)	2643 (3)	360 (10)	413 (11)	347 (10)	60 (8)	37 (8)	−194 (9)
C(3)	−1028 (3)	2247 (2)	−166 (3)	401 (10)	246 (9)	409 (10)	103 (7)	172 (8)	31 (7)
C(4)	−241 (2)	2128 (1)	−1500 (2)	255 (8)	216 (8)	289 (8)	19 (6)	35 (6)	24 (6)
N(1)	1784 (1)	533 (1)	1634 (2)	215 (6)	279 (7)	271 (6)	11 (5)	48 (5)	−44 (5)
N(2)	2678 (3)	1629 (2)	3936 (3)	365 (10)	499 (12)	386 (9)	−34 (8)	−21 (8)	−184 (8)
N(3)	−726 (2)	1367 (1)	1076 (2)	238 (7)	210 (6)	297 (7)	−13 (5)	87 (5)	−36 (5)
N(4)	−181 (2)	2983 (3)	−2481 (3)	547 (11)	256 (8)	424 (9)	102 (7)	180 (8)	98 (7)
N(5)	269 (2)	1196 (1)	−1654 (2)	308 (7)	230 (7)	257 (6)	34 (5)	105 (5)	7 (5)
O(1)	3151 (2)	163 (1)	1912 (2)	277 (7)	564 (10)	317 (7)	97 (6)	46 (5)	−20 (7)
O(2)	920 (2)	1168 (1)	−3021 (2)	556 (9)	403 (8)	323 (7)	150 (7)	224 (6)	80 (6)
O(3)	1517 (4)	3706 (2)	5257 (3)	2121 (31)	529 (13)	502 (11)	−579 (16)	630 (16)	−175 (10)

Positional Parameters ($\times10^3$) and Thermal Parameters ($\times10$)

Atom	x/a	y/b	z/c	B
H(1)	337 (4)	−1 (3)	88 (5)	115 (15)
H(2)	339 (3)	144 (2)	399 (3)	40 (6)
H(3)	250 (3)	215 (2)	464 (4)	39 (6)
H(4)	25 (3)	236 (3)	300 (3)	55 (7)
H(5)	−14 (4)	138 (3)	367 (5)	93 (12)
H(6)	−147 (3)	114 (2)	129 (3)	36 (6)
H(7)	−89 (2)	296 (2)	27 (3)	39 (5)
H(8)	−201 (3)	226 (2)	−61 (4)	57 (7)
H(9)	31 (3)	293 (2)	−327 (3)	47 (7)
H(10)	−36 (3)	372 (3)	−217 (4)	63 (7)
H(11)	163 (3)	72 (3)	−265 (4)	63 (8)

[a] Estimated standard deviations in parentheses. The temperature factor is defined as: $\exp(-{}^1/_4\Sigma_{i=1}\Sigma_{j=1}B_{ij}h_ia_i^*a_j^*)$.

TABLE IV

ROOT-MEAN-SQUARE DISPLACEMENTS (Å) FOR PRINCIPAL AXES OF THERMAL ELLIPSOIDS OF BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]NICKEL(II) CHLORIDE DIHYDRATE[a]

	Axis 1	Axis 2	Axis 3
Ni	0.130	0.162	0.164
Cl	0.177	0.198	0.229
C(1)	0.160	0.188	0.205
C(2)	0.149	0.207	0.282
C(3)	0.155	0.205	0.251
C(4)	0.159	0.181	0.200
N(1)	0.164	0.185	0.237
N(2)	0.163	0.234	0.281
N(3)	0.158	0.167	0.200
N(4)	0.161	0.220	0.277
N(5)	0.163	0.172	0.205
O(1)	0.177	0.201	0.276
O(2)	0.172	0.199	0.294
O(3)	0.205	0.208	0.542

[a] Orientation of thermal ellipsoids may be seen by reference to Figures 2 and 8.

tances averaging 1.86 Å.[9,10] This phenomenon of bonds involving nickel(II) in the triplet state being longer than those involving that ion in the singlet state is a common occurrence.[11]

The Ni–N(amine) bond distance is 2.115 (2) Å. This is in good agreement with the distances in other octahedral nickel(II) complexes.[11] The Ni–N(amine) distance is significantly longer than the average Ni–N(oxime) distance of 2.07 Å. A similar effect is noted in bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate,[9] which is a square-planar complex also containing oxime and amine functional groups. In this complex the average Ni–N(amine) bond length of 1.91 (1) Å is significantly longer than the Ni–N(oxime) distance of 1.86 (1).

B. Coordination Geometry in Cu(IBO)$_2$Cl$_2$.—The structure of bis[2,2′-iminobis(acetamidoxime)]copper(II) chloride consists of discrete Cu(IBO)$_2^{2+}$ cations and chloride anions. The cation, which is shown in Figure 3, is best described as a distorted square-pyramidal pentacoordinate complex. Unlike the nickel compound, in which both ligand molecules are tridentate, only one ligand molecule in the copper complex is tridentate, filling three of the four positions in the basal plane. It is bonded to the metal ion through the central amine nitrogen atom and the two oxime nitrogen atoms. The other ligand molecule is bidentate with an oxime nitrogen atom filling the fourth position in the basal plane and the central amine nitrogen atom occupying the apical position.

The remaining acetamidoxime group is not coordinated. The oxygen atom of this group seems to fill the sixth position of an octahedron on the neighboring cation, since it forms an angle of 79.3° with the basal plane and an angle of 164.2° with the Cu–N(8) bond in this cation. However, this oxygen atom is 3.26 Å from the copper ion, far too distant to be considered a bonding distance. The chloride ions are located 4.598 and 4.600 Å from the copper ion and are not involved in the coordination.

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(11) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

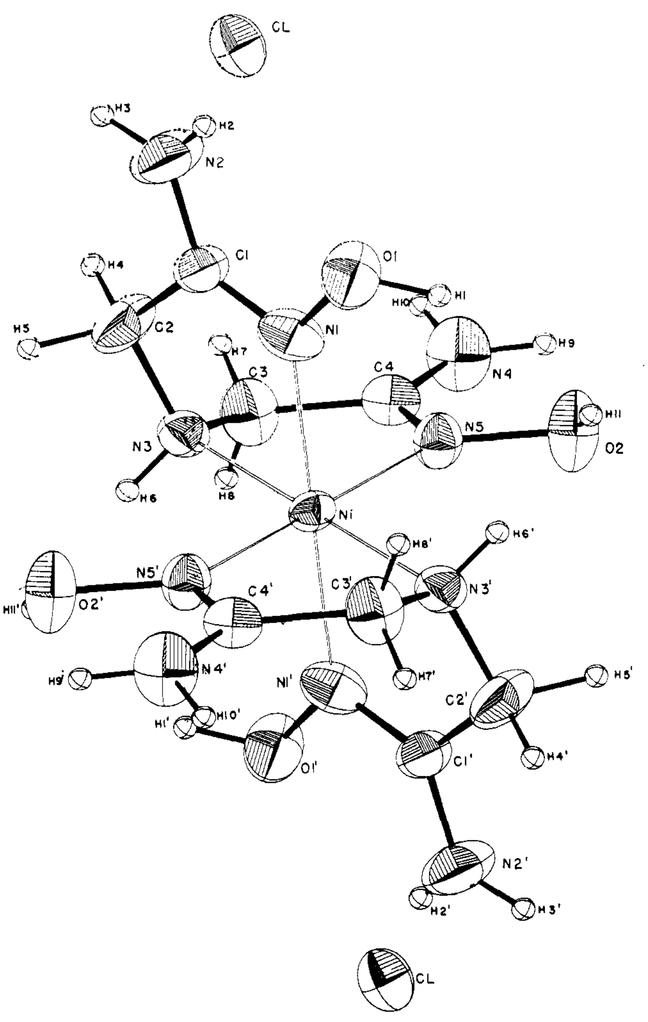

Figure 2.—Structure of bis[2,2′-iminobis(acetamidoxime)]-nickel(II) chloride. Thermal ellipsoids of nonhydrogen atoms drawn for 50% probability. Thermal ellipsoids of hydrogen atoms not drawn to scale.

Comparison of this complex with other pentacoordinate structures and its nickel analog yield some very interesting conclusions. Of primary interest is the difference in coordination between the IBO complexes of copper and nickel. Very few other X-ray determinations, in which the same ligand has different coordination numbers for different central metal ions, have been reported. The most notable cases are the tren–thiocyanate complexes (tren = β,β',β''-triaminotriethylamine): Ni(tren)$(SCN)_2$ is *cis* octahedral,[12] while [Cu(tren)(NCS)]SCN[13] and [Zn(tren)(NCS)]-SCN[14] are trigonal-bipyramidal pentacoordinate complexes. However, it is important to note that relatively little change is needed in the configuration of the tren molecule to fit either of these configurations. The arms of the tren molecule need only move enough so that the N–metal–N angles, where N are the terminal nitrogen atoms, are 120° for the pentacoordinate structures instead of 90° in the octahedral complex. In the $Ni(IBO)_2^{2+}$ cation the two chelate rings of each ligand molecule, as defined by the planes of the metal atom and the two coordinated nitrogen atoms, are approximately perpendicular, forming an angle of 89.5°, while in the $Cu(IBO)_2^{2+}$ cation the angle between chelate rings of the tridentate molecule is 13.5°.

The phenomenon of a potentially tridentate ligand not attaining its full coordination is also uncommon. One such case is in the series of compounds bis(β-R,R′-aminoethyl-X-salicylaldiminato)nickel(II), which have been extensively studied by Sacconi and his coworkers.[11] The compound with $R = R' = C_2H_5$, X = 5-chloro has been found to be a square-pyramidal complex, with only one ligand molecule attaining the full tridentate coordination.[15] The other ligand molecule is bidentate with the β-nitrogen atom uncoordinated. This is undoubtedly due to the steric effects of the ethyl groups, since with other substituents, octahedral and planar complexes are obtained.[11] No such steric effects are present in the IBO molecule.

Since the structure of the $Cu(IBO)_2^{2+}$ cation is not a perfect square pyramid, it is necessary to define a basal plane, so that details of the coordination may be described. This plane is defined as the unweighted least-squares plane determined by the four coordinated equatorial nitrogen atoms. The equation of this plane in the monoclinic system is: $0.120x + 0.253y - 0.671z + 0.483 = 0$. Several interesting details of the structure may be noted. (1) The copper atom is 0.18 Å above the basal plane. (2) There is some tetrahedral distortion of the basal plane. N(3) and N(6) are 0.07 and 0.05 Å, respectively above the plane, while N(1) and N(5) are 0.06 Å below the plane. (3) The Cu–N(8) bond length of 2.357 (4) Å is considerably longer than the other four Cu–N bonds. (4) The Cu–N(8) bond is not perpendicular to the basal plane but is tipped 16.9° from the normal to this plane. (5) As in $Ni(IBO)_2Cl_2 \cdot 2H_2O$ and in previously reported four- and five-coordinate copper(II) complexes, the M–N(amine) bond is significantly longer than the M–N(oxime) distance.

The first three points are quite common in previously reported tetragonal-pyramidal copper(II) structures. Indeed the phenomenon of a long axial bond is universal in such complexes. The deviations of the copper atom from the basal plane and the tetrahedral distortion of the coordinating atoms from that plane are not always found but are still present in the majority of complexes of this type.

The deviation of the Cu–N(8) bond from the normal to the basal plane is easily explained since N(8) is part of a chelate ring and is therefore constrained. The angle N(6)–Cu–N(8) is only 76.5°. A similar distortion from the idealized square-pyramidal geometry is seen for the equatorial ligand, where instead of the idealized angles of 90° the angles N(1)–Cu–N(3) and N(1)–Cu–N(5) are 79.9 and 82.1°, respectively.

The last point mentioned involves the differences in bond lengths for the metal–nitrogen bonds. As was the

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(15) L. Sacconi, P. L. Orioli, and M. Di Vaira, *ibid.*, **87**, 2059 (1965).

TABLE V

LIST OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]COPPER(II) CHLORIDE[a]

case in $Ni(IBO)_2^{2+}$, the Cu–N(amine) equatorial bond length of 2.014 (3) Å is significantly longer than the Cu–N(oxime) distances of 1.950 (3), 1.959 (3), and 1.976 (3) Å. The differences in bond lengths between the metal atoms and the two different types of nitrogen functional groups would seem to indicate the oxime nitrogen atom is a stronger coordinating agent than the amine nitrogen atoms. If this is true, it provides a possible rationale for the unusual structure of the $Cu(IBO)_2^{2+}$ cation.

TABLE V (*Continued*)

15,7,L		
-3	176	-184
-2	44	-20
-1	124	123
16,7,L		
-6	171	-157
-5	115	-135
-4	45	-52
-3	67	88
0,8,L		
0	987	1015
1	602	620
2	638	668
3	59	25
4	90	-62
5	49*	4
6	197	-184
7	322	-317
8	179	-165
9	213	-209
1,8,L		
-9	80	79
-8	238	223
-7	84	-79
-6	295	-289
-5	102	-104
-4	240	-252
-3	461	-476
-2	360	-358
-1	118	108
0	52	-65
1	112	113
2	26*	22
3	155	160
4	275	295
5	50	-28
6	38	6
7	67	-60
8	90	-88
9	73	-69
2,8,L		
-10	102	101
-9	90	91
-8	235	-230
-7	291	-284
-6	59	21
-5	845	-870
-4	794	-821
-3	261	261
-2	120	109
-1	77	43
0	464	485
1	70	58
2	710	735
3	927	963
4	40	-8
5	92	90
6	51	-26
7	383	-387
8	170	-179
3,8,L		
-10	45	38
-9	140	130
-8	144	125
-7	37*	-26
-6	194	212
-5	168	159
-4	241	-231
-3	429	-412
-2	411	-403
-1	426	-437
0	470	-476
1	395	-391
2	309	-301
3	241	248
4	56	45
5	85	-91
6	267	251
7	86	78
8	51	28
4,8,L		
-10	56	36
-9	70	61
-8	116	116
-7	300	-278
-6	303	-312
-5	404	-417
-4	721	-704
-3	211	-186
-2	486	-470
-1	381	-366
0	157	-133
1	476	484
2	363	378
3	304	299
4	73	48
5	127	125
6	39	-23
7	47	-25
8	56*	-50
5,8,L		
-10	64	-53
-9	61	50
-8	191	183
-7	111	139
-6	66	51
-5	253	236
-4	82	89
-3	314	-306
-2	41*	9
-1	37*	5
0	118	-125
1	266	-267
2	213	-216
3	148	141
4	34*	-8
5	86	83
6	170	173
7	117	112
6,8,L		
-10	210	209
-9	247	237
-8	52*	31
-7	327	328
-6	132	132
-5	399	-405
-4	168	-172
-3	186	-185
-2	897	-890
-1	217	-225
0	96	-97
1	442	-441
2	160	155
3	245	241
4	159	156
5	458	441
6	127	130
7	135	-115
7,8,L		
-10	44	-52
-9	150	146
-8	76	79
-7	19*	5
-6	247	245
-5	419	421
-4	37*	20
-3	65	73
-2	126	130
-1	234	-236
0	137	-94
1	238	-234
2	45*	-19
3	272	277
4	53	-39
5	49	60
8	166	159
8,8,L		
-10	44*	-22
-9	318	328
-8	246	247
-7	168	160
-6	384	389
-5	76	-51
-4	199	-179
-3	72	-78
-2	288	-292
-1	313	-314
0	62*	8
1	275	-273
2	89	82
3	267	268
4	280	279
5	143	133
6	75	48
9,8,L		
-10	62*	-50
-9	70	-79
-8	56*	-20
-7	70	-65
-6	125	123
-5	380	387
-4	121	120
-3	106	104
-2	160	171
-1	222	230
0	115	102
1	272	-266
2	106	-99
3	106	-103
4	208	-188
5	44	-33
10,8,L		
-10	59*	35
-9	56	46
-8	192	182
-7	220	218
-6	87	99
-5	85	100
-4	343	346
-3	128	-132
-2	170	-167
-1	42*	29
0	382	-383
1	367	-362
2	126	117
3	84	-80
4	46	50
11,8,L		
-10	53*	-24
-9	43*	-14
-8	58	-62
-7	115	-127
-6	214	212
-5	157	153
-4	98	-102
-3	206	205
-2	163	168
-1	44*	12
0	180	-176
1	281	-282
2	52*	-36
3	45	-56
12,8,L		
-9	85	62
-8	108	-111
-7	117	130
-6	316	332
-5	93	92
-4	217	229
-3	103	111
-2	316	-309
-1	53	24
0	143	-140
1	337	-331
2	192	-198
3	74	-71
13,8,L		
-9	97	-96
-8	124	-125
-7	157	-168
-6	41	33
-5	40*	2
-4	46	27
-3	106	104
-2	64	55
-1	164	152
0	65	50
1	42*	-6
2	50	15
14,8,L		
-8	62*	17
-7	43	17
-6	71	68
-5	209	208
-4	81	92
-3	42*	-15
-2	194	195
-1	131	121
0	299	-297
15,8,L		
-7	143	-177
-6	44*	-19
-5	121	-125
-4	99	-91
-3	59	51
-2	151	166
-1	140	176
16,8,L		
-5	49	34
-4	273	296
0,9,L		
1	57	21
2	373	-396
3	616	-657
4	484	-506
5	76	-67
6	106	118
7	90	88
8	67	51
9	212	212
1,9,L		
-9	42*	9
-8	189	-181
-7	195	185
-6	116	-94
-5	415	-420
-4	219	205
-3	566	-575
-2	219	215
-1	652	644
0	539	-555
1	425	436
2	918	943
3	178	176
4	104	-116
5	107	-107
6	80	-67
7	206	-198
8	196	-183
9	91	-81
2,9,L		
-9	270	-270
-8	231	-227
-7	260	-258
-6	51	-41
-5	312	303
-4	356	356
-3	614	616
-2	478	473
-1	442	440
0	509	518
1	358	357
2	578	-589
3	340	-353
4	190	-207
5	308	-305
6	253	-255
7	92	-97
8	63*	42
3,9,L		
-10	171	156
-9	67	67
-8	159	-163
-7	58	36
-6	48*	-34
-5	320	-327
-4	509	-510
-3	197	-187
-2	604	571
-1	229	-230
0	84	85
1	851	846
2	30*	9
3	192	193
4	41*	-24
5	251	-248
6	45*	17
7	67	-75
8	332	-317
4,9,L		
-10	65	-82
-9	76	-68
-8	109	-111
-7	213	-209
-6	320	-316
-5	310	-320
-4	161	-158
-3	436	442
-2	616	604
-1	617	590
0	598	608
1	294	313
2	90	89
3	54	49
4	177	-180
5	331	-332
6	226	-211
7	179	-189
5,9,L		
-10	223	214
-9	120	-110
-8	53*	38
-7	242	242
-6	472	-464
-5	39*	24
-4	344	-353
-2	387	376
-1	64	-59
0	590	-591
1	256	265
2	295	297
3	136	124
4	197	181
5	147	143
6	40	-34
7	42*	-35
6,9,L		
-10	45*	-7
-9	50*	-26
-8	69	-65
-7	389	-394
-6	465	-470
-5	115	-116
-4	124	127
-3	79	53
-2	276	266
-1	223	224
0	444	462
1	308	317
2	259	255
3	48*	7
4	155	-153
5	245	-235
6	164	-158
7	64	-82
7,9,L		
-10	205	203
-9	40*	-11
-8	53*	31
-7	299	298
-6	118	121
-5	57	-57
-4	396	-395
-3	141	-132
-2	303	-302
-1	676	-682
0	130	-140
1	35*	12
2	189	197
3	265	243
4	131	142
5	98	94
6	248	233
8,9,L		
-10	90	92
-9	115	114
-8	70	-83
-7	226	-219
-6	177	-164
-5	504	-491
-4	525	-519
-3	299	-305
-2	210	-202
-1	164	175
0	536	534
1	208	207
2	169	172
3	244	246
4	61	-68
5	42	-18
9,9,L		
-10	77	87
-9	62*	-11
-8	350	366
-7	40*	18
-6	80	80
-5	245	241
-4	382	-388
-3	224	-225
-2	236	236
-1	262	-264
0	193	-191
1	57	50
2	63	-60
3	45*	6
4	200	188
5	63	53
10,9,L		
-9	182	174
-8	135	124
-7	189	-183
-6	199	-216
-5	178	-192
-4	457	-463
-3	327	-327
-2	42*	-39
-1	43*	17
0	153	-166
1	147	135
2	262	276
3	251	248
4	132	126
11,9,L		
-9	141	-131
-8	62	53
-7	201	212
-6	272	274
-5	187	192
-4	205	238
-3	168	171
-2	39*	-10
-1	184	-180
0	313	-307
1	173	-174
2	79	-68
3	49*	-7
12,9,L		
-9	184	180
-8	64	59
-7	144	158
-6	57	57
-5	205	-210
-4	231	-229
-3	205	-212
-2	336	-343
-1	128	-127
0	50*	-10
1	79	81
2	215	196
13,9,L		
-8	45	48
-7	54*	-20
-6	242	263
-5	157	159
-4	125	-122
-3	134	138
-2	119	118
-1	115	-116
0	44	-39
1	46	-46
14,9,L		
-8	189	210
-7	164	190
-6	235	225
-5	72	79
-4	113	-133
-3	114	-133
-2	72	-75
-1	217	-238
0	147	-144
15,9,L		
-6	55*	-25
-5	85	71
-4	72	59
-3	107	105
-2	164	159
0,10,L		
0	907	-903
1	531	-569
2	124	-129
3	68	-67
4	38	40
5	186	186
6	134	109
7	193	169
8	284	270
9	50	-28
1,10,L		
-9	170	-160
-8	189	-178
-7	138	-136
-6	234	-243
-5	52	50
-4	467	471
-3	244	254
-2	539	535
-1	299	289
0	446	-438
1	146	-140
2	139	-144
3	486	-514
4	428	-438
5	134	125
6	296	-291
7	71	55
8	222	199
2,10,L		
-9	44*	-8
-8	42*	-22
-7	159	155
-6	350	337
-5	47*	-16
-4	86	80
-3	187	190
-2	393	-392
-1	116	-106
0	108	130
1	463	-477
2	80	-60
3	53	-57
4	554	-566
5	47*	33
6	327	320
7	94	90
8	182	180
3,10,L		
-9	40*	6
-8	384	-383
-7	51*	-40
-6	155	-155
-5	258	-252
-4	56	56
-3	410	410
-2	89	-93
-1	389	370
0	419	416
1	31	-9
2	199	201
3	267	-271
4	592	-585
5	182	-186
6	215	-219
7	125	-113
8	58	-54
4,10,L		
-9	49*	12
-8	102	100
-7	51*	-42
-6	294	304
-5	375	385
-4	68	53
-3	434	426
-2	414	383
-1	184	-193
0	81	-65
1	348	-362
2	525	-533
3	180	-163
4	44	45
5	46	-47
6	54	-67
7	219	197
5,10,L		
-9	90	-85
-8	118	-120
-7	114	-128
-6	267	-256
-5	238	-244
-4	214	-214
-3	273	231
-2	513	500
-1	446	444
0	270	274
1	487	492
2	440	446
3	363	-366
4	44*	-31
5	159	-156
6	299	-288
7	175	-148
6,10,L		
-10	95	-93
-9	216	-209
-8	190	-185
-7	115	111
-6	169	161
-5	181	177
-4	458	430
-3	334	326
-2	338	335
-1	576	582
0	93	-96
1	198	-202
2	338	347
3	280	-270
4	532	-520
5	114	-113
6	160	-156
7,10,L		
-10	151	151
-9	55	-40
-8	56*	-23
-7	53	58
-6	218	-219
-5	548	-559
-4	99	105
-3	39	-3
-2	45	-33
-1	250	244
0	126	131
1	380	385
2	471	464
3	64	-72
4	123	121
5	57*	44
6	87	-98
8,10,L		
-9	50*	17
-8	98	-104
-7	182	-195
-6	110	111
-5	117	-112
-4	48	-27
-3	475	478
-2	131	125
-1	190	196
0	391	384
1	48	24
2	125	-132
3	76	-71
4	168	-166
5	256	-241
9,10,L		
-9	54	106
-8	61*	18
-7	68*	10
-6	170	-98
-5	612	-611
-4	191	-193
-3	277	-268
-2	265	-275
-1	136	-132
0	49*	-38
1	414	411
2	192	185
3	185	146
4	239	224
10,10,L		
-9	186	-182
-8	275	-267
-7	254	-256
-6	194	-201
-5	91	-92
-4	40*	-29
-3	56	-55
-2	256	266
-1	356	352
0	47*	-12
1	274	211
2	240	226
3	118	-121
4	82	-62
11,10,L		
-9	58*	-3
-8	128	176
-7	277	276
-6	165	-179
-5	158	-159
-4	98	-107
-3	344	-369
-2	148	-152
-1	125	-133
0	188	-188
1	190	188
2	52*	-10
3	42*	19
12,10,L		
-8	167	-158
-7	54	-60
-6	80	-82
-5	369	-372
-4	171	-167
-3	100	-102
-2	99	-108
-1	126	140
0	156	160
1	103	95
2	191	186
13,10,L		
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-7	256	261
-6	59	-38
-5	42*	2
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-3	47*	-23
-2	108	-95
-1	211	-206
0	107	-115
1	102	-92
14,10,L		
-7	58	-75
-6	93	-104
-5	130	-133
-4	146	-155
-3	106	-112
-2	42*	12
-1	42*	-20
15,10,L		
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-4	55*	48
-3	76	-93
0,11,L		
1	690	720
2	46*	-30
3	447	462
4	335	351
5	212	-209
6	85	87
7	92	93
8	249	-233
1,11,L		
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-8	61*	34
-7	363	354
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-5	270	273
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-3	161	148
-2	171	-176
-1	78	-78
0	523	-516
1	695	-707
2	43	0
3	258	-265
4	326	-325
5	241	235
6	275	257
7	132	130
8	142	135
2,11,L		
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-8	320	314
-7	354	351
-6	156	-161
-5	35*	-8
-4	355	-363
-3	614	-624
-2	345	-347
-1	484	-463
0	465	-465
1	31*	1
2	185	190
3	257	249
4	89	73
5	484	489
6	298	295
7	78	-69
8	119	-82
3,11,L		
-9	44*	-5
-8	57	48
-7	61	47
-6	409	408
-5	384	381
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-3	760	773
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-1	224	-225
0	186	-199
1	313	-319
2	393	-404
3	461	-472
4	114	-114
5	134	-139
6	113	113
7	83	84
4,11,L		
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-8	161	145
-7	63	47
-6	235	227
-5	215	209
-4	309	-307
-3	230	223
-2	413	-407
-1	1004	-995
0	195	-194
1	367	-353
2	205	-203
3	432	436
4	73	76
5	44	47
6	439	429
7	61	56
5,11,L		
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-8	210	-205
-7	126	-139
-6	110	137
-5	68	69
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-3	140	143
-2	258	243
-1	351	340
0	60	-27
1	34*	24
2	57	45
3	286	-276
4	236	-231
5	161	-166
6	56	-56
6,11,L		
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-8	325	339
-7	179	183
-6	252	259
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-3	58	61
-2	114	113
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0	348	-360
1	71	-7
2	115	-107
3	335	-336
4	45*	12
5	242	225
6	221	191
7,11,L		
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-8	267	-275
-7	114	-125
-6	56*	-67
-5	378	-379
-4	39	35
-3	298	296
-2	343	337
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0	162	167
1	124	129
2	180	-173
3	169	-162
4	273	-283
5	136	-126
8,11,L		
-9	81	-55
-8	59	61
-7	126	136
-6	400	398
-5	163	159
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-3	600	606
-2	54	-54
-1	164	-166
0	109	-117
1	503	-492
2	214	-199
3	48	-42
4	237	-235
5	106	99
9,11,L		
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-8	163	-174
-7	188	-196
-6	260	-259
-5	107	-106
-4	39*	-37
-3	52*	25
-2	101	103
-1	43	39
0	129	127
1	209	216
2	56	51
3	80	75
4	71	-85
10,11,L		
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-7	74	-79
-6	174	189
-5	131	139
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-3	435	444
-2	187	189
-1	136	-129
0	99	86
1	107	113
2	219	-216
3	189	-187
11,11,L		
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-7	96	107
-6	113	-114
-5	43	-77
-4	106	-115
-3	150	-160
-2	57	46
-1	161	165
0	218	220
1	162	148
2	199	186
12,11,L		
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-7	71	-83
-6	111	-113
-5	50	-48
-4	216	223
-3	241	247
-2	95	102
-1	206	207
0	72	53
1	112	-112
13,11,L		
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-6	49*	-16
-5	120	-130
-4	179	-180
-3	48*	20
-2	53*	19
-1	55*	-10
0	116	115
14,11,L		
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-5	111	-115
-4	49*	-13
-3	172	172
-2	48*	35
-1	63	37
0,12,L		
0	580	593
1	529	552
2	170	171
3	87	88
4	107	-114
5	308	-303
6	403	-399
7	116	-129
8	171	-167
1,12,L		
-8	262	255
-7	255	250
-6	133	129
-5	194	-190
-4	386	-393
-3	376	-378
-2	489	-499
-1	385	-381
0	425	-416
1	506	519
2	587	603
3	158	-153
4	448	455
5	478	491
6	57	61
7	96	92
8	50*	2
2,12,L		
-8	54	-45
-7	185	-179
-6	455	-455
-5	67	-51
-4	81	-78
-3	182	-179
-2	49*	21
-1	190	145
0	108	110
1	463	467
2	160	165
3	45*	-5
4	312	319
5	46	46
6	175	-176
7	119	-115
3,12,L		
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-8	131	141
-7	428	428
-6	214	218
-5	436	-427
-4	174	173
-3	239	234
-2	677	-661
-1	331	-331
0	226	-229
1	107	-113
2	65	60
3	102	104
4	266	273
5	406	403
6	202	216
7	42	-29
4,12,L		
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-8	167	140
-7	53*	7
-6	94	-91
-5	136	-128
-4	317	-305
-3	647	-671
-2	332	-338
-1	46	-43
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1	221	228
2	269	265
3	263	256
4	423	416
5	41	25
6	52*	62
7	55*	-37
5,12,L		
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-8	198	138
-7	299	308
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-5	295	280
-4	214	225
-3	50	-37
-2	199	-207
-1	715	-715
0	496	-475
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2	257	-290
3	173	-159
4	245	236
5	162	155
6	97	113
6,12,L		
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-8	220	230
-7	44	57
-6	122	-125
-5	217	-210
6,12,L		
-4	164	-163
-3	380	-381
-2	136	-139
-1	211	-214
0	269	-260
1	90	97
2	83	84
3	232	225
4	305	305
5	116	108
6	87	78
7,12,L		
-9	169	-168
-8	55	-44
-7	403	412
-6	80	-70
-5	57	19
-4	545	537
-3	55	48
-2	82	-72
-1	45*	3
0	311	-299
1	312	-308
2	186	-189
3	296	-282
4	69	-69
5	141	138
8,12,L		
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-8	73	76
-7	48	33
-6	97	106
-5	261	244
-4	42	-7
-3	189	-189
-2	198	-192
-1	390	-400
0	288	-281
1	45	51
2	189	-187
3	54	42
4	98	98
9,12,L		
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-8	124	-135
-7	47	50
-6	121	121
-5	126	116
-4	155	167
-3	390	396
-2	89	93
-1	318	-308
0	97	-98
1	111	-124
2	231	-235
3	177	-167
4	74	-82
10,12,L		
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-7	290	264
-6	72	66
-5	182	193
-4	45*	-3
-3	130	-130
-2	51	-60
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0	176	-159
1	160	-159
2	175	-185
3	42*	9
11,12,L		
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-3	149	145
-2	225	220
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0	50*	-24
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2	104	-99
12,12,L		
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-6	77	61
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-3	186	185
-2	120	112
-1	180	-186
0	53*	-33
1	106	-114
13,12,L		
-7	49	-41
-6	41*	-9
-5	102	-109
-4	91	90
-3	209	211
-2	102	100
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14,12,L		
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-4	68	91
-3	104	104
0,13,L		
1	200	-217
2	442	-444
3	327	-339
4	71	-69
5	350	-349
6	138	-144
7	41*	21
8	63	-47
1,13,L		
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-6	267	-262
-5	250	-242
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-1	220	209
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1	40	41
2	367	-363
3	131	123
4	52*	17
5	71	-64
6	189	-184
7	264	-260
2,13,L		
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-7	48*	-34
-6	188	-179
-5	179	-184
-4	492	498
-3	443	439
-2	321	314
-1	412	409
0	168	163
1	141	143
2	125	133
3	287	-287
4	368	-365
5	211	-211
6	177	-187
7	136	-135
3,13,L		
-8	50*	39
-7	228	-226
-6	223	-217
-5	98	-98
-4	44*	-2
-3	230	-226
-2	327	-311
-1	69	76
0	425	428
1	70	72
2	333	336
3	489	471
4	158	156
5	50*	42
6	156	-168
7	124	-140
4,13,L		
-8	157	-174
-7	338	-345
-6	87	-85
-5	120	-123
-4	41	-34
-3	137	114
-2	251	254
-1	210	222
0	449	445
1	332	337
2	111	-107
3	44*	-22
4	134	-124
5	156	-155
6	48*	-3
5,13,L		
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-7	45	-35
-6	45	23
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-4	123	-118
-3	84	-85
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0	486	490
1	64	-62
2	206	195
3	309	290
4	142	144
5	217	213
6	87	74
6,13,L		
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-7	91	-86
-6	405	-399
-5	251	-252
-4	173	-171
-3	297	-294
-2	64	60
-1	192	183
0	35*	-9
1	267	259
2	230	230
3	153	166
4	46	64
5	43	20
7,13,L		
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-7	80	-70
-6	40*	-7
-5	50*	39
-4	89	-80
-3	230	-232
-2	359	-362
-1	49*	-45
0	124	-119
1	161	-146
2	183	195
3	193	174
4	225	233
5	222	215
8,13,L		
-8	55*	-52
-7	56*	31
-6	132	-132
-5	240	-231
-4	226	-229
-3	51	-55
-2	77	-86
-1	43*	8
0	201	187
1	108	110
2	224	225
3	184	181
4	118	-92
9,13,L		
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-7	182	181
-6	233	235
-5	42	-56
-4	45*	18
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0	217	-215
1	276	-261
2	58	-54
3	47*	-29
10,13,L		
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-7	44*	-13
-6	50	-29
-5	60	43
-4	171	-182
-3	85	-88
-2	50*	8
-1	194	-193
0	40*	9
1	133	118
2	108	120
11,13,L		
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-6	78	74
-5	57*	52
-4	141	155
-3	47*	-19
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-1	94	-85
0	230	-235
1	147	-149
12,13,L		
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-6	49	48
-5	42	-22
-4	57*	-48
-3	175	-188
-2	171	-173
-1	40*	-2
0	89	-91
13,13,L		
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-4	307	312
-3	66*	59
-2	59*	-36
0,14,L		
0	237	-228
1	78	-66
2	96	-105
3	47	-63
4	215	221
5	182	182
6	246	255
7	92	91
1,14,L		
-7	172	-168
-6	167	-160
-5	214	210
-4	188	185
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-1	99	97
0	60*	23
1	45*	-27
2	214	-224
3	290	-285
4	177	-172
5	245	-264
6	87	-92
7	42*	18
2,14,L		
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-7	217	212
-6	104	98
-5	217	217
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-3	198	-197
-2	60	56
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0	331	-334
1	58	-60
2	303	-307
3	171	-167
4	158	152
5	51	18
6	41	29
7	132	133
3,14,L		
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-7	110	-110
-6	97	-86
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0	377	374
1	77	-73
2	50*	-37
3	166	-163
4	354	-354
5	206	-219
6	93	-84
4,14,L		
-8	141	-146
-7	97	96
-6	38*	-3
-5	62	51
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0	171	-158
1	80	-76
2	305	-302
3	290	-270
4	239	-246
5	117	-108
6	48	39
5,14,L		
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-6	244	-240
-5	88	-82
-4	275	-278
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0	267	269
1	268	261
2	87	-91
3	43*	56
4	56	-55
5	247	-253
6,14,L		
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-7	62*	-35
-6	68	-85
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1	44*	16
2	371	-379
3	267	-269
4	45	-55
5	84	-84
7,14,L		
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-6	211	-217
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-2	91	-92
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1	322	316
2	314	322
3	132	138
4	68	-62
8,14,L		
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-5	40*	27
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0	195	197
1	51	52
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9,14,L		
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-4	382	-399
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-2	48	44
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1	132	133
2	60	65
3	221	225
10,14,L		
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-6	128	-132
-5	47	-44
-4	57*	-23
-3	192	196
-2	102	97
-1	50*	54
0	287	281
1	200	204
2	43*	18
11,14,L		
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-6	58*	-43
-5	56	-36
-4	95	-104
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-2	169	-149
-1	175	-169
0	58*	-42
1	55	55
12,14,L		
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0,15,L		
1	208	198
2	41	20
3	37*	-11
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6	47*	4
7	58	60
1,15,L		
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0	182	-171
1	71	-71
2	237	-235
3	105	-99
4	133	148
5	52*	20
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2,15,L		
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-6	42*	-6
-5	78	-68
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-1	210	203
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1	158	-162
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3	44*	41
4	116	114
5	315	310
6	38*	15
3,15,L		
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-6	58	42
-5	150	139
-4	234	230
-3	52*	37
-2	45	39
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0	166	-162
1	243	-249
2	246	-243
3	380	-373
4	195	-195
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6	46*	29
4,15,L		
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-6	123	134
-5	133	-123
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-3	59	-50
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-1	98	-88
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1	50	-42
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3	96	89
4	139	142
5	68	64
5,15,L		
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-6	65	56
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-1	108	-98
0	77	68
1	57	-60
2	361	-363
3	184	-177
4	135	-149
5	155	-152
6,15,L		
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-4	129	120
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-2	92	-102
-1	37*	7
0	366	-354
1	213	-193
2	140	-139
3	208	-201
4	53*	34
7,15,L		
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-5	170	176
-4	189	188
-3	42	-9
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-1	212	207
0	203	190
1	116	106
2	88	-93
3	196	-196
8,15,L		
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-6	60	79
-5	83	79
-4	159	165
-3	120	-108
-2	156	-158
-1	53	52
0	221	-223
1	176	-174
2	66	-65
3	126	-122
9,15,L		
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-6	163	-156
-5	177	-180
-4	127	119
-3	167	163
-2	96	100
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0	345	331
1	45	37
2	48	51
10,15,L		
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-5	128	119
-4	115	104
-3	52*	29
-2	171	172
-1	92	77
0	59	-38
1	57	-47
11,15,L		
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-5	49*	-27
-4	90	-91
-3	53*	-27
-2	47*	29
-1	93	91
12,15,L		
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-3	43*	17
0,16,L		
0	459	453
1	53	-2
2	37*	-6
3	175	175
4	73	-84
5	123	-128
6	77	63
1,16,L		
-6	43	-57
-5	42*	11
-4	261	-260
-3	454	-452
-2	356	-359
-1	331	-307
0	74	-71
1	57	49
2	37	-0
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4	300	301
5	86	106
6	190	184
2,16,L		
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-6	153	-142
-5	100	-105
4,14,L		
-3	209	208
2,16,L		
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1	285	280
2	117	125
3	63	48
4	105	94
5	48*	16
6	129	-125
3,16,L		
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-6	169	156
-5	190	195
-4	179	-179
-3	357	-356
-2	311	-296
-1	417	-389
0	418	-407
1	310	-310
2	46	-51
3	281	269
4	151	142
5	166	170
4,16,L		
-7	51*	8
-6	99	-86
-5	259	-258
-4	52	-44
-3	55	-53
-2	335	-320
-1	126	136
0	50*	37
1	58	-56
2	273	285
3	191	195
4	123	-118
5	165	164
5,16,L		
-7	136	132
-6	290	275
-5	306	303
-4	40	-1
-3	46*	-7
-2	69	-69
-1	297	-283
0	98	-93
1	236	-241
2	197	-197
3	83	75
4	53*	-18
6,16,L		
-7	60	-52
-6	113	109
-5	41*	-10
-4	241	-248
-3	37*	5
-2	124	-119
-1	182	-181
0	134	120
1	151	152
2	60	-24
3	90	99
7,16,L		
-7	44	37
-6	179	176
-5	325	328
-4	210	201
-3	191	187
-2	112	115
-1	85	-72
0	209	-202
1	334	-331
2	128	-127
3	79	-83
8,16,L		
-6	55*	24
-5	62*	-68
-4	59*	37
-3	208	-204
-2	72	-72
0	177	-174
1	46*	-46
2	216	211
9,16,L		
-6	178	178
-5	225	223
-4	127	126
-3	176	179
-2	41*	-4
-1	57*	39
0	60*	47
1	173	-167
10,16,L		
-5	69	-73
-4	48*	12
-3	72	69
-2	151	-156
-1	202	-202
0	43*	-13
11,16,L		
-4	43*	7
-3	157	147
-2	201	195
0,17,L		
1	52*	-36
2	40*	-1
3	110	-130
4	233	-224
5	71	-61
6	69	-78
1,17,L		
-6	175	-172
-5	173	-173
-4	253	-235
-3	56*	-40
-2	331	322
-1	125	128
0	286	283
1	530	516
2	132	125
3	55*	57
4	119	172
5	160	-196
2,17,L		
-6	62	68
-5	77	64
-4	51	-61
-3	51*	46
-2	67	76
-1	171	158
0	117	113
1	39*	2
2	128	-148
3	55*	-39
4	58	-53
5	105	-108
3,17,L		
-6	228	-228
-5	142	-152
-4	57*	-27
-3	357	-356
-2	127	-117
-1	123	126
0	52*	-20
1	274	279
2	359	357
3	72	76
4	66	68
4,17,L		
-6	59	-55
-5	73	-64
-4	63	-57
-3	90	80
-2	159	149
-1	87	71
0	74	-85
1	107	106
2	181	172
3	51	-36
4	53*	23
5,17,L		
-6	50	-40
-5	209	-195
-4	415	-406
-3	278	-275
-2	243	-234
-1	224	-215
0	54*	37
1	159	158
2	91	96
3	263	265
6,17,L		
-6	44*	-6
-5	112	-116
-4	40*	-0
-3	46	34
-2	51*	-26
-1	40*	14
0	169	173
1	147	139
2	135	123
3	59*	15
7,17,L		
-6	59	-45
-5	82	79
-4	103	-115
-3	242	-241
-2	109	-103
-1	300	-296
0	291	-293
1	92	85
2	80	72
8,17,L		
-5	112	-107
-4	40*	-17
-3	40*	11
-2	40*	9
-1	53	-67
0	54*	38
1	151	142
9,17,L		
-5	69	79
-4	76	71
-3	92	-93
-2	164	-169
-1	180	-186
0	142	-145
10,17,L		
-3	67	-48
-2	111	-117
0,18,L		
0	59	-4
1	222	-216
2	109	-125
3	69	77
4	55	-66
5	47	32
1,18,L		
-5	57	-56
-4	175	173
-3	257	260
-2	119	122
-1	204	204
0	116	111
1	126	-136
2	165	-168
3	92	-88
4	197	-207
2,18,L		
-5	206	196
-4	119	115
-3	167	162
-2	45	-35
-1	134	-137
0	66	-68
1	158	-158
2	149	-149
3	158	-150
4	47*	-27
3,18,L		
-5	42	18
-4	59	17
-3	170	167
-2	294	290
-1	310	313
0	152	145
1	146	156
2	46*	-24
3	231	-221
4	195	-178
4,18,L		
-5	55*	52
-4	173	180
-3	149	140
-2	150	-143
-1	98	103
0	62	84
1	219	-226
2	92	-87
3	71	-71
5,18,L		
-5	128	-130
-4	88	84
-3	52*	25
-2	51*	47
-1	321	325
0	238	238
1	87	90
2	155	165
6,18,L		
-5	43*	-1
-4	54*	14
-3	217	205
-2	164	160
-1	85	80
0	46	63
1	48*	8
2	72	-65
7,18,L		
-5	200	-203
-4	213	-210
-3	138	-120
-2	90	82
-1	102	98
0	217	222
1	275	268
8,18,L		
-4	242	238
-3	58*	46
-2	53*	-56
-1	167	171
0	45	51
0,19,L		
1	45*	-40
2	65	63
3	45	63
4	57	47
1,19,L		
-4	82	68
-3	54*	13
-2	103	-90
-1	205	-199
0	242	-250
1	247	-247
2	310	-310
3	112	-113
2,19,L		
-4	195	-196
-3	41*	-7
-2	39*	18
-1	135	-146
0	51*	-19
1	190	193
2	135	-128
3	75	79
3,19,L		
-4	293	293
-3	138	132
-2	67	60
-1	46	21
0	157	-165
1	203	-203
2	160	-157
3	184	-188
4,19,L		
-4	84	70
-3	93	-95
-2	114	-107
-1	52	-36
0	93	-79
1	83	-85
2	123	-111
5,19,L		
-4	219	221
-3	163	168
-2	203	206
-1	142	137
0	47	49
1	97	-104
6,19,L		
-4	67	-63
-3	42*	-15
-2	53*	-39
-1	134	-128
0	66	63
7,19,L		
-2	300	298
-1	151	149
0,20,L		
0	120	102
1	110	98
2	64	-57
1,20,L		
-3	157	-136
-2	259	-259
-1	46*	-28
0	49	-36
1	96	-100
2	153	155
2,20,L		
-3	95	-91
-2	48	41
-1	46*	32
0	47*	20
1	146	147
2	53*	26
3,20,L		
-3	139	-147
-2	131	-124
-1	153	-158
0	219	-217
1	52*	-18
4,20,L		
-2	49*	-14
-1	54	45
0	122	106

[a] Columns are l, $10|F_o|$, and $10F_c$. Unobserved reflections are indicated by an asterisk (the values given for F_o for these reflections are the F's obtained from the assigned intensities, which are equal to $I + 2\sigma_I$).

Since the equatorial bonding positions in Cu(II) are more favorable than the apical ones, the first ligand molecule would be expected to fill three of the four equatorial positions. If the oxime nitrogen atom is a stronger coordinating agent than the amine nitrogen atom, it is likely that one of the oxime nitrogen atoms of the second ligand molecule would occupy the fourth equatorial position. The amine nitrogen atom of this second ligand molecule would have to fill an apical position. This leaves no place for the other oxime

TABLE VI

BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]COPPER(II) CHLORIDE[a]

Positional Parameters ($\times 10^4$) and Thermal Parameters ($\times 10^2$)

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	487 (1)	2393 (1)	−757 (1)	207 (2)	186 (2)	178 (2)	−2 (1)	51 (1)	24 (1)
Cl(1)	299 (1)	3843 (1)	3584 (1)	404 (5)	417 (5)	314 (4)	35 (4)	168 (4)	78 (4)
Cl(2)	2030 (1)	611 (1)	−3274 (1)	354 (4)	260 (4)	290 (4)	45 (3)	141 (3)	11 (3)
C(1)	696 (3)	4121 (2)	−831 (4)	196 (14)	215 (14)	240 (15)	17 (11)	126 (12)	−8 (12)
C(2)	−135 (3)	3937 (2)	−2562 (4)	247 (15)	195 (14)	258 (16)	−0 (12)	106 (13)	26 (12)
C(3)	−977 (3)	2661 (2)	−4208 (4)	277 (16)	267 (16)	190 (15)	−9 (13)	35 (13)	17 (13)
C(4)	−740 (3)	1750 (2)	−3961 (4)	189 (13)	271 (14)	231 (14)	−37 (11)	104 (11)	−22 (12)
C(5)	1594 (3)	1391 (2)	2187 (4)	279 (15)	203 (14)	183 (14)	−7 (11)	47 (12)	−4 (11)
C(6)	615 (3)	1620 (3)	2528 (5)	322 (18)	399 (20)	253 (17)	−27 (15)	132 (14)	83 (15)
C(7)	−1121 (3)	1304 (2)	203 (5)	296 (17)	273 (16)	341 (18)	−17 (13)	172 (15)	53 (14)
C(8)	−2022 (3)	1601 (2)	−1381 (4)	218 (13)	235 (14)	315 (16)	−30 (11)	174 (12)	−18 (12)
N(1)	976 (2)	3494 (2)	167 (3)	233 (12)	253 (12)	200 (12)	−10 (9)	60 (10)	−1 (9)
N(2)	1081 (3)	4889 (2)	−461 (5)	347 (16)	225 (14)	308 (16)	−42 (12)	101 (12)	−24 (12)
N(3)	−596 (2)	3100 (2)	−2581 (3)	314 (14)	269 (13)	288 (14)	−21 (11)	94 (11)	−15 (11)
N(4)	−1191 (3)	1264 (2)	−5274 (4)	349 (16)	306 (16)	284 (16)	−35 (13)	69 (13)	−53 (13)
N(5)	−86 (2)	1532 (1)	−2470 (3)	236 (12)	183 (11)	279 (13)	10 (9)	114 (10)	21 (9)
N(6)	1665 (2)	1727 (2)	919 (3)	242 (12)	267 (12)	251 (12)	33 (10)	110 (10)	51 (10)
N(7)	2355 (3)	872 (2)	3248 (4)	373 (16)	262 (13)	237 (14)	49 (11)	90 (12)	68 (11)
N(8)	−294 (2)	1929 (2)	1032 (3)	287 (13)	285 (13)	276 (13)	9 (10)	122 (11)	19 (10)
N(9)	−2515 (3)	1045 (2)	−2582 (5)	296 (15)	234 (14)	420 (18)	5 (12)	138 (13)	−51 (13)
N(10)	−2289 (2)	2369 (2)	−1506 (4)	245 (12)	284 (13)	325 (14)	19 (11)	112 (11)	−38 (11)
O(1)	1769 (2)	3685 (2)	1787 (3)	285 (12)	353 (13)	239 (12)	−36 (10)	46 (10)	−42 (10)
O(2)	83 (2)	661 (1)	−2287 (3)	386 (12)	192 (10)	416 (13)	14 (9)	175 (11)	26 (9)
O(3)	2635 (2)	1499 (2)	794 (4)	331 (13)	492 (15)	382 (14)	154 (11)	180 (11)	167 (12)
O(4)	−3174 (2)	2514 (2)	−3092 (4)	313 (12)	278 (13)	468 (15)	46 (10)	48 (10)	−8 (11)

Positional Parameters ($\times 10^3$) and Thermal Parameters ($\times 10$)

Atom	x/a	y/b	z/c	B
H(1)	141 (4)	377 (4)	220 (7)	80 (19)
H(2)	154 (3)	501 (2)	48 (5)	29 (9)
H(3)	89 (4)	532 (3)	−130 (6)	59 (12)
H(4)	19 (3)	400 (2)	−345 (5)	47 (10)
H(5)	−79 (3)	434 (3)	−277 (5)	60 (12)
H(6)	−11 (3)	315 (2)	−214 (4)	50 (12)
H(7)	−175 (3)	276 (2)	−485 (4)	28 (8)
H(8)	−66 (3)	288 (2)	−489 (4)	29 (8)
H(9)	−175 (3)	147 (2)	−626 (4)	22 (7)
H(10)	−105 (3)	78 (2)	−523 (5)	40 (12)
H(11)	92 (5)	47 (4)	−224 (8)	138 (22)
H(12)	252 (4)	173 (3)	10 (5)	74 (12)
H(13)	233 (3)	72 (2)	426 (4)	29 (8)
H(14)	300 (4)	96 (4)	326 (7)	98 (19)
H(15)	46 (3)	125 (2)	301 (5)	35 (10)
H(16)	83 (3)	215 (2)	350 (5)	54 (11)
H(17)	−44 (3)	236 (2)	136 (4)	31 (10)
H(18)	−69 (3)	83 (2)	−7 (4)	31 (8)
H(19)	−140 (3)	105 (2)	81 (4)	34 (9)
H(20)	−311 (3)	121 (2)	−371 (5)	48 (10)
H(21)	−223 (4)	65 (3)	−258 (5)	52 (13)
H(22)	−313 (3)	302 (3)	−323 (5)	46 (12)

[a] Estimated standard deviations in parentheses. Temperature factor is defined as: $\exp(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*)$.

group to coordinate. It might be expected to dimerize, filling the other apical position of a neighboring cation, but this does not happen.

In the case of $Ni(IBO)_2^{2+}$ all six positions are equivalent so no such situation should arise. As a result, other isomers besides the *trans* facial should exist. Professor Eddy has prepared what may be some of these isomers.[16] On the other hand, no evidence for other isomers of the copper complex has been found.

The copper–nitrogen bond lengths agree well with other reported values. The Cu–N(oxime) distances are in good agreement with the pentacoordinate copper–dimethylglyoxime structure[17] and also in agreement with those found in bis(salicylaldoximato)-copper(II)[18] and bis(5-chlorosalicylaldoximato)copper(II),[19] which are reported to be quasi-octahedral. The Cu–N(amine) equatorial distance is in good agreement with other reported distances, which average 2.00 Å.

C. Geometry and Bonding in the Ligand Molecule.—Bond lengths and angles for both the copper and

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[16] L. P. Eddy, personal communication.

[17] E. Frasson, R. Bardi, and S. Bezzi, *Acta Crystallogr.*, **12**, 201 (1959).

[18] M. A. Jarski and E. C. Lingafelter, *ibid.* **17**, 1109 (1964).

[19] P. L. Orioli, E. C. Lingafelter, and B. W. Brown, *ibid.*, **17**, 1113 (1964).

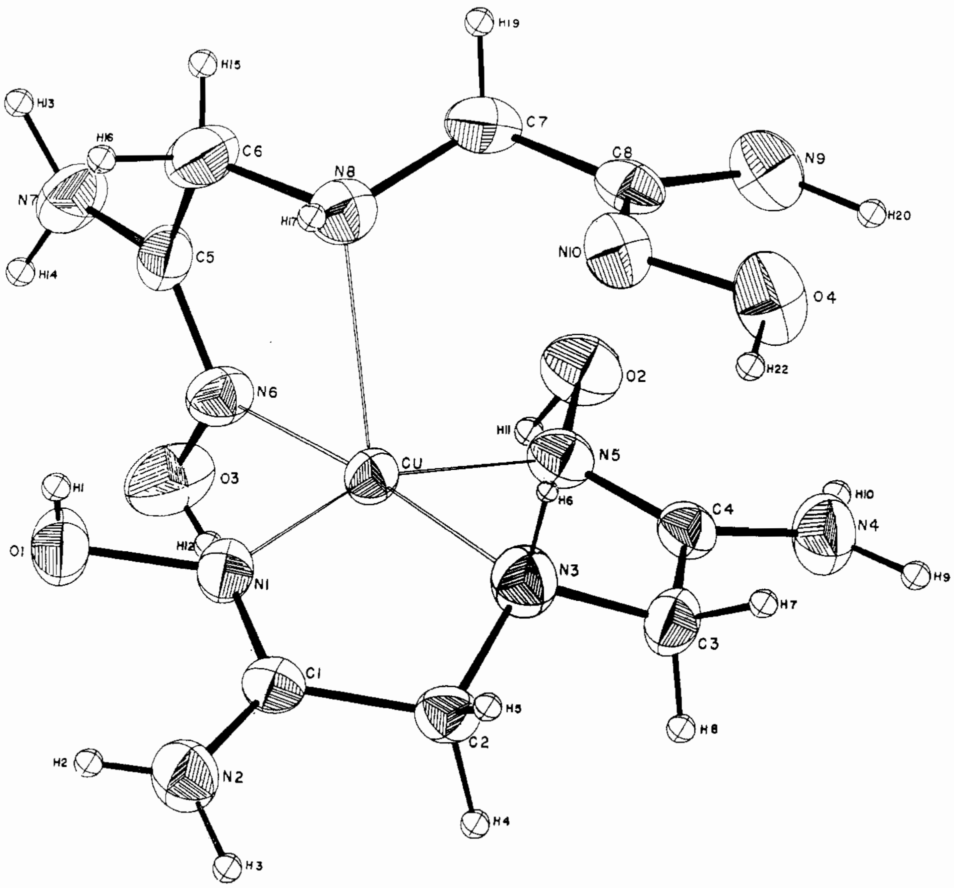

Figure 3.—Structure of cation in bis[2,2′-iminobis(acetamidoxime)]copper(II) chloride. Thermal ellipsoids of nonhydrogen atoms drawn for 50% probability. H(18) and H(21) are behind C(7) and N(9) and do not appear.

TABLE VII

ROOT-MEAN-SQUARE DISPLACEMENTS (Å) FOR PRINCIPAL AXES OF THERMAL ELLIPSOIDS FOR BIS[2,2′-IMINOBIS(ACETAMIDOXIME)]COPPER(II) CHLORIDE[a]

	Axis 1	Axis 2	Axis 3
Cu	0.141	0.155	0.179
Cl(1)	0.182	0.222	0.243
Cl(2)	0.175	0.189	0.217
C(1)	0.135	0.164	0.178
C(2)	0.152	0.176	0.185
C(3)	0.149	0.183	0.214
C(4)	0.143	0.167	0.191
C(5)	0.149	0.160	0.206
C(6)	0.162	0.201	0.235
C(7)	0.158	0.196	0.217
C(8)	0.132	0.172	0.206
N(1)	0.155	0.178	0.187
N(2)	0.162	0.198	0.225
N(3)	0.178	0.193	0.213
N(4)	0.169	0.209	0.234
N(5)	0.150	0.171	0.189
N(6)	0.161	0.172	0.199
N(7)	0.150	0.200	0.229
N(8)	0.181	0.188	0.195
N(9)	0.166	0.193	0.238
N(10)	0.169	0.185	0.215
O(1)	0.159	0.216	0.218
O(2)	0.155	0.219	0.230
O(3)	0.172	0.196	0.282
O(4)	0.176	0.199	0.179

[a] Orientation of thermal ellipsoids may be seen by reference to Figures 3 and 10.

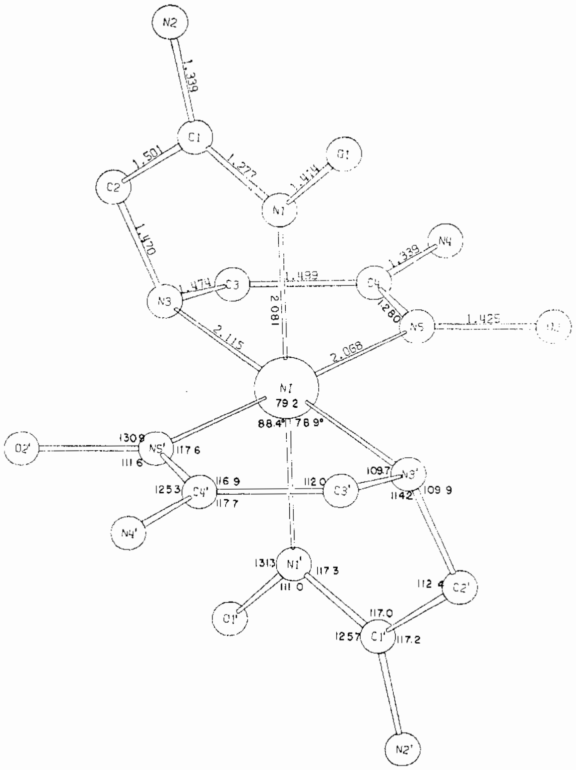

Figure 4.—Bond lengths and angles in $Ni(IBO)_2^{2+}$ cation.

TABLE VIII

BOND LENGTHS AND ANGLES

Atoms	$Cu(IBO)_2Cl_2$	$Ni(IBO)_2Cl_2 \cdot 2H_2O$
A. Bond Lengths, Å		
M–N(1)	1.951 (3)	2.081 (2)
M–N(3)	2.014 (3)	2.115 (2)
M–N(5)	1.960 (3)	2.068 (2)
M–N(6)	1.976 (3)	
M–N(8)	2.357 (4)	
C(1)–C(2)	1.500 (5)	1.501 (3)
C(3)–C(4)	1.500 (5)	1.499 (3)
C(5)–C(6)	1.514 (7)	
C(7)–C(8)	1.498 (5)	
C(1)–N(1)	1.290 (4)	1.277 (3)
C(4)–N(5)	1.290 (4)	1.280 (3)
C(5)–N(6)	1.284 (5)	
C(8)–N(10)	1.282 (4)	
C(1)–N(2)	1.331 (4)	1.340 (3)
C(4)–N(4)	1.320 (5)	1.339 (3)
C(5)–N(7)	1.351 (4)	
C(8)–N(9)	1.335 (5)	
C(2)–N(3)	1.483 (5)	1.470 (3)
C(3)–N(3)	1.488 (5)	1.474 (3)
C(6)–N(8)	1.464 (5)	
C(7)–N(8)	1.454 (5)	
N(1)–O(1)	1.417 (4)	1.414 (2)
N(5)–O(2)	1.422 (3)	1.425 (3)
N(6)–O(3)	1.403 (5)	
N(10)–O(4)	1.430 (5)	
C(2)–H(4)	1.06 (5)	0.92 (3)
C(2)–H(5)	1.05 (4)	1.07 (4)
C(3)–H(7)	0.98 (3)	0.95 (3)
C(3)–H(8)	0.94 (4)	0.98 (3)
C(6)–H(15)	0.82 (4)	
C(6)–H(16)	1.16 (4)	
C(7)–H(18)	1.05 (4)	
C(7)–H(19)	0.89 (4)	
N(2)–H(2)	0.83 (3)	0.74 (3)
N(2)–H(3)	0.97 (5)	0.91 (3)
N(3)–H(6)	1.07 (5)	0.86 (3)
N(4)–H(9)	0.95 (3)	0.91 (3)
N(4)–H(10)	0.79 (4)	0.98 (3)
N(7)–H(13)	0.94 (4)	
N(7)–H(14)	0.87 (7)	
N(9)–H(20)	1.03 (3)	
N(9)–H(21)	0.74 (5)	
O(1)–H(1)	0.73 (7)	0.95 (5)
O(2)–H(11)	1.15 (7)	0.90 (3)
O(3)–H(12)	0.68 (5)	
O(4)–H(22)	0.83 (4)	
N(8)–H(17)	0.81 (4)	
B. Bond Angles, Deg		
N(1)–M–N(3)	79.9 (1)	78.9 (1)
N(1)–M–N(5)	157.5 (1)	88.4 (1)
N(1)–M–N(6)	99.0 (1)	
N(1)–M–N(8)	100.1 (1)	
N(3)–M–N(5)	82.1 (1)	79.2 (1)
N(3)–M–N(6)	173.6 (2)	
N(3)–M–N(8)	109.9 (1)	
N(5)–M–N(6)	97.3 (1)	
N(5)–M–N(8)	98.6 (1)	
N(6)–M–N(8)	76.5 (1)	
C(2)–C(1)–N(1)	115.1 (3)	117.0 (2)
C(2)–C(1)–N(2)	118.8 (3)	117.3 (2)
N(1)–C(1)–N(2)	126.1 (3)	125.7 (2)
C(1)–C(2)–N(3)	108.7 (3)	112.4 (2)
C(4)–C(3)–N(3)	111.0 (3)	112.0 (2)
C(3)–C(4)–N(4)	117.6 (3)	117.8 (2)
C(3)–C(4)–N(5)	115.4 (3)	116.9 (2)
N(4)–C(4)–N(5)	127.0 (3)	125.3 (2)
C(6)–C(5)–N(6)	117.3 (3)	
C(6)–C(5)–N(7)	118.9 (4)	
N(6)–C(5)–N(7)	123.8 (4)	
C(5)–C(6)–N(8)	111.9 (4)	
C(8)–C(7)–N(8)	113.6 (3)	
C(7)–C(8)–N(9)	117.9 (3)	
C(7)–C(8)–N(10)	118.6 (3)	
N(9)–C(8)–N(10)	123.5 (3)	
M–N(1)–C(1)	118.4 (2)	117.3 (1)
M–N(1)–O(1)	126.9 (2)	131.3 (1)
C(1)–N(1)–O(1)	113.8 (8)	111.0 (2)
M–N(3)–C(2)	110.3 (2)	109.9 (1)
M–N(3)–C(3)	110.3 (2)	109.7 (1)
C(2)–N(3)–C(3)	114.7 (3)	114.2 (2)
M–N(5)–C(4)	118.4 (2)	117.6 (2)
M–N(5)–C(2)	128.3 (2)	130.1 (1)
C(4)–N(5)–C(2)	113.2 (3)	111.6 (2)
M–N(6)–C(5)	123.7 (3)	
M–N(6)–O(3)	124.4 (2)	
C(5)–N(6)–O(3)	111.6 (3)	
M–N(8)–C(6)	106.0 (3)	
M–N(8)–C(7)	110.2 (3)	
C(6)–N(8)–C(7)	113.2 (3)	
C(8)–N(10)–O(4)	109.4 (3)	
C(1)–C(2)–H(4)	112 (2)	112 (2)
C(1)–C(2)–H(5)	106 (2)	113 (2)
N(3)–C(2)–H(4)	112 (2)	118 (2)
N(3)–C(2)–H(5)	104 (2)	108 (2)
H(4)–C(2)–H(5)	113 (2)	92 (3)
C(4)–C(3)–H(7)	111 (2)	109 (2)
C(4)–C(3)–H(8)	109 (2)	113 (2)
N(3)–C(3)–H(7)	110 (2)	116 (2)
N(3)–C(3)–H(8)	113 (2)	108 (2)
H(7)–C(3)–H(8)	103 (3)	99 (2)
C(5)–C(6)–H(15)	111 (3)	
C(5)–C(6)–H(16)	111 (2)	
N(8)–C(6)–H(15)	115 (2)	
N(8)–C(6)–H(15)	106 (2)	
H(15)–C(6)–H(16)	101 (4)	
C(8)–C(7)–H(18)	109 (2)	
C(8)–C(7)–H(19)	109 (2)	
N(8)–C(7)–H(18)	105 (2)	
N(8)–C(7)–H(19)	117 (2)	
H(18)–C(7)–H(19)	103 (3)	
C(1)–N(2)–H(2)	121 (3)	120 (2)
C(1)–N(2)–H(3)	122 (2)	120 (2)
H(2)–N(2)–H(3)	117 (4)	120 (3)
M–N(3)–H(6)	100 (2)	104 (2)
C(2)–N(3)–H(6)	109 (2)	110 (2)
C(3)–N(3)–H(6)	112 (2)	109 (2)
C(4)–N(4)–H(9)	121 (2)	119 (2)
C(4)–N(4)–H(10)	122 (2)	123 (2)
H(9)–N(4)–H(10)	117 (3)	115 (3)
C(5)–N(7)–H(13)	120 (2)	
C(5)–N(7)–H(14)	111 (4)	
H(13)–N(7)–H(15)	117 (4)	
M–N(8)–H(17)	103 (3)	
C(6)–H(8)–H(17)	103 (2)	
C(7)–N(8)–H(17)	121 (3)	
C(8)–N(9)–H(20)	122 (2)	
C(8)–H(9)–H(21)	120 (3)	
H(20–N(9)–H(21)	120 (3)	
N(1)–O(1)–H(1)	100 (4)	111 (2)
N(5)–O(2)–H(11)	112 (3)	103 (2)
N(6)–O(3)–H(12)	93 (4)	
N(10)–O(4)–H(22)	103 (3)	

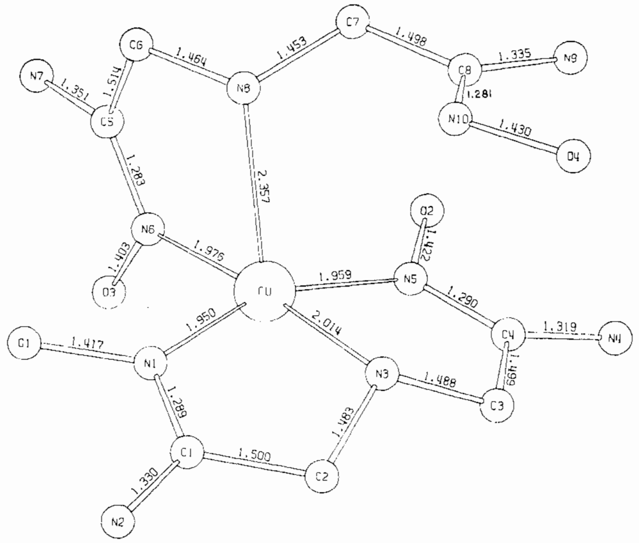

Figure 5.—Bond lengths in $Cu(IBO)_2^{2+}$ cation.

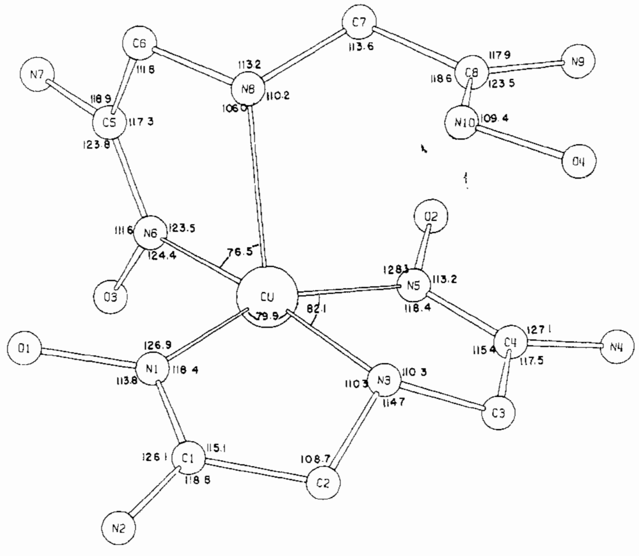

Figure 6.—Bond angles in $Cu(IBO)_2^{2+}$ cation.

nickel compounds are given in Table VIII and Figures 4–6. With the exception of the N–O distances, all bond lengths and angles agree with previously reported results. Carbon–nitrogen(amide) distances are in good agreement with the values found for several peptides (1.32 Å)[20] and for $K_2Cu(biuret)_2 \cdot 4H_2O$ (1.34 Å),[21] $Cu(biuret)_2$ (1.321 (6) Å),[22] bis(pyridine-2-carboxamido)-nickel(II) chloride (1.32 (2) Å),[23] and diaquobis(pyridine-2-carboxamido)nickel(II) chloride (1.311 (8) Å).[24] Similarly the carbon–nitrogen(amine) distances are in good agreement with the many amine complexes for which structures have been determined. The average C–N distance for several three-dimensional structure determinations of ethylenediamine complexes is 1.48 Å.[25]

Table IX gives a comparison of the IBO complexes with several three-dimensional structure determinations of oximes and oxime complexes. Examination of this table shows the C–C and C–N distances to agree. However there is a wide range of values for the N–O distances, with those in the IBO complexes being considerably longer than most of the others. We are unable to suggest an explanation for these differences.

TABLE IX

COMPARISON OF AVERAGE LIGAND BOND LENGTHS (Å)

	$C(sp^2)$–$C(sp^3)$	C–N(oxime)	N–O	Ref
$Ni(IBO)_2Cl_2 \cdot 2H_2O$	1.500 (3)	1.279 (2)	1.419 (2)	*a*
$Cu(IBO)_2Cl_2$	1.503 (2)	1.286 (4)	1.418 (4)	*a*
$Ni(DMG)_2$	1.51 (2)	1.30 (1)	1.36 (1)	*b*
$Pd(DMG)_2$	1.51 (4)	1.31 (1)	1.35 (2)	*c*
DMG	1.479 (15)	1.253 (11)	1.321 (21)	*d*
$Ni(G)_2$		1.303 (6)	1.347 (4)	*e*
		1.277 (7)		
		1.300 (10)	1.341 (7)	*f*
$Pd(G)_2$		1.321 (12)	1.337 (12)	*g*
		1.273 (13)	1.384 (12)	
		1.271 (15)	1.277 (13)	
		1.319 (16)	1.372 (12)	
G		1.284 (5)	1.397 (4)	*h*
$Ni(AO)_2Cl \cdot H_2O$	1.50 (2)	1.30 (1)	1.36 (1)	*i*
$Co(AO)_2Cl_2$	1.485 (10)	1.278 (10)	1.347 (10)	*j*
$Cu(salox)_2$		1.25 (2)	1.45 (2)	*k*
Cu(5-Cl-salox)		1.256 (14)	1.418 (14)	*l*
$Ni(salox)_2$		1.351 (10)	1.363 (9)	*m*
$(CoBF(DMG)_3BF)BF_4$	1.472 (6)	1.287 (6)	1.363 (4)	*n*
O-MeC(DMG)PyCo	1.51 (1)	1.28 (1)	1.37 (1)	*o*
	1.50			*p*
		1.29		*q*

[a] This work. [b] DMG = dimethylglyoxime; D. E. Williams, G. Wolhauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, **81,** 755 (1959). [c] C. Panattoni, E. Frasson, and R. Zannotti, *Gazz. Chim. Ital.*, **89,** 2132 (1959). [d] W. C. Hamilton, *Acta Crystallogr.*, **14,** 95 (1961). [e] G = glyoxime; M. Calleri, G. Ferraris, and D. Viterbo, *ibid.*, **22,** 468 (1967). [f] R. K. Murmann and E. O. Schlemper, *ibid.*, **23,** 667 (1967). [g] M. Calleri, G. Ferraris, and D. Viterbo, *Inorg. Chim. Acta*, **1,** 297 (1967). [h] M. Calleri, G. Ferraris, and D. Viterbo, *Acta Crystallogr.*, **20,** 73 (1966). [i] Bis-(2-amino-2-methyl-3-butanoneoximato)nickel(II) chloride monohydrate.[9] [j] E. O. Schlemper, S. J. LaPlaca, and W. C. Hamilton, Abstracts, American Crystallographic Association Meeting, Seattle, Wash., 1969, No. C6. [k] salox = salicylaldoxime.[18] [l] Reference 19. [m] Reference 10. [n] G. A. Zakrzewski, Ph.D. Dissertation, University of Washington, 1969. [o] Carboxymethylbis(O-methyldimethylglyoximato)pyridinecobalt(III); P. G. Lenhert, *Chem. Commun.*, 980 (1967). [p] Theoretical value for $C(sp^2)$–$C(sp^3)$: N. S. Ham, *Rev. Pure Appl. Chem.*, **11,** 159 (1961). [q] C–N distance in salicylaldimine chelates: E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88,** 2951 (1966).

Since the IBO molecule contains both amine and oxime functional groups, the planarity of the chelate rings is of some interest. In all reported structures of ethylenediamine complexes the chelate rings have the *gauche* configuration. The degree of twist in the ring is often described by considering the dihedral angle between the plane defined by one nitrogen atom and the two carbon atoms, and the plane defined by the two carbon atoms and the other nitrogen atom. This

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(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 281.

(21) H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Crystallogr.*, **14,** 407 (1961).

(22) H. C. Freeman and J. E. W. L. Smith, *ibid.*, **20,** 153 (1966).

(23) S. C. Chang, D. Y. Park, and N. C. Li, *Inorg. Chem.*, **7,** 2144 (1968).

(24) A. Masuko, T. Nomura, and Y. Saito, *Bull. Chem. Soc. Jap.*, **40,** 511 (1967).

(25) J. R. Wiesner, Ph.D. Dissertation, University of Washington, 1966.

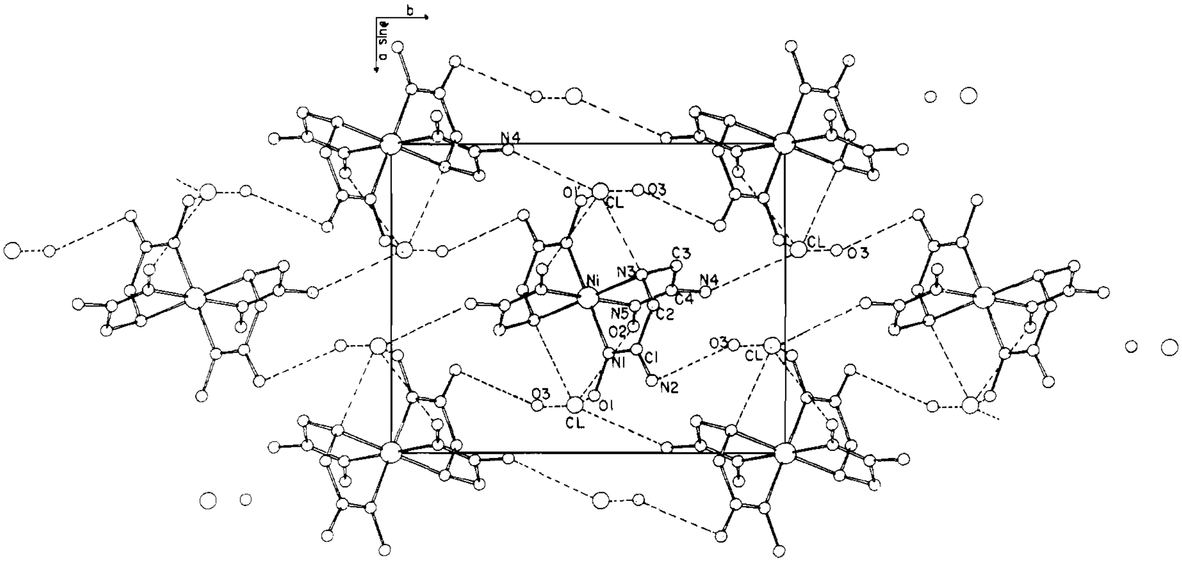

Figure 7.—Projection down 001 axis in $Ni(IBO)_2Cl_2 \cdot 2H_2O$. One layer of anions and cations and hydrogen bonds involving atoms in this layer are shown. The hydrogen bonds N(4)–O(3) and O(1)–O(3) which involve atoms in adjacent layers along the *z* axis are not shown.

angle ranges from 45 to 58° in ethylenediamine complexes.[26–28]

On the other hand the dioxime structures which have been reported are fairly planar. Nickel dimethylglyoxime was solved on the basis of only partial three-dimensional data and was assumed strictly planar by the authors.[29] More recently, nickel glyoxime was reported to show small but significant deviations from planarity.[30] The "*gauche*" angle, calculated as described above, is 1.3°.

The "*gauche*" angles in the IBO complexes are the following (atoms in plane 1, atoms in plane 2, angle): $Ni(IBO)_2^{2+}$: N(1)–C(1)–C(2), N(3)–C(1)–C(2), 14.5°; N(3)–C(3)–C(4), N(5)–C(3)–C(4), 17.5°. $Cu(IBO)_2^{2+}$: N(1)–C(1)–C(2), N(3)–C(1)–C(2), 11.6°; N(3)–C(3)–C(4), N(5)–C(3)–C(4), 12.5°; N(6)–C(5)–C(6), N(8)–C(5)–C (6), 21.1°; N (8)–C(7)–C(8), N(10)–C(7)–C(8), 30.8°. For the bidentate complex bis(2-amino-2-methyl-3-butanone oximato)nickel(II) chloride monohydrate,[9] which also contains oxime and amine groups, the angles are 17.2 and 19.0° for the two chelate rings.

Also of some interest is the "bite" distance, the distance between the coordinated nitrogen atoms. In the nickel complex both the N(1)–N(3) and N(3)–N(5) distances are 2.64 Å. In the copper complex there is less agreement. The distances for N(1)–N(3), N(3)–N(5), and N(6)–N(8) are 2.54, 2.61, and 2.60 Å, respectively. The N(8)–N(10) distance in the uncoordinated arm is 2.78 Å.

The hydrogen bonding in these IBO complexes is quite extensive. Lists of intermolecular distances for which hydrogen bonds are postulated are given for $Ni(IBO)_2Cl_2 \cdot 2H_2O$ in Table X and for $Cu(IBO)_2Cl_2$ in Table XI. The most significant feature of the hydrogen bonding in both compounds is the large degree of participation by the chloride ions. In the nickel compound four hydrogen–chloride distances are less than 3.0 Å, the sum of the van der Waals radii for hydrogen and chlorine.[31] Since the O(3)–Cl distance (O(3) belonging to the water of hydration) is 3.11 Å, well within the range of 2.86–3.21 Å listed by Pimentel and McClellan for O–H---Cl hydrogen-bonded distances,[32] a fifth hydrogen bond to the chloride ion may be assumed, although the positions of the hydrogen

TABLE X

A. Hydrogen Bonding in $Ni(IBO)_2Cl_2$

Atom A	Atom B	Hydrogen	A–B, Å	A–H, Å	H–B, Å	A–H–B, deg
N(4)	Cl	H(10)	3.328	0.981	2.381	162.2
N(3)	Cl	H(6)	3.184	0.862	2.328	172.9
O(1)	Cl	H(1)	3.145	0.947	2.211	168.7
O(2)	Cl	H(11)	3.128	0.900	2.228	177.0
O(3)	Cl	*a*	3.125			
N(2)	O(3)	H(3)	3.118	0.912	2.273	153.9
N(4)	O(3)	H(9)	2.938	0.908	2.128	143.9
O(3)	O(1)	*a*	2.897			

B. Hydrogen-Bond Angles (deg) around O(3) and Cl

Chloride ion		Water of hydration	
N(4)–Cl–N(3)	142.1	Cl–O(3)–N(2)	84.7
N(4)–Cl–O(1)	98.0	Cl–O(3)–N(4)	146.1
N(4)–Cl–O(2)	76.0	Cl–O(3)–O(1)	118.7
N(4)–Cl–O(3)	94.1	N(2)–O(3)–N(4)	106.7
N(3)–Cl–O(1)	68.7	N(2)–O(3)–O(1)	143.9
N(3)–Cl–O(2)	68.3	N(4)–O(3)–O(1)	70.0
N(3)–Cl–O(3)	101.5		
O(1)–Cl–O(2)	87.3		
O(1)–Cl–O(3)	168.0		
O(2)–Cl–O(3)	95.6		

[a] Bonding is through hydrogen atoms of water molecule which were not resolved.

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(26) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(27) D. L. Cullen and E. C. Lingafelter, *ibid.*, **9**, 1858 (1970).

(28) Mazar-ul-Haque, C. N. Caughlan, and K. Emerson, personal communication.

(29) D. E. Williams, G. Wolhauer, and R. E. Rundle, *J. Amer. Chem. Soc.*, **81**, 755 (1959).

(30) M. Calleri, G. Ferraris, and D. Viterbo, *Acta Crystallogr.*, **22**, 468 (1967).

(31) L. Pauling, ref 20, p 260.

(32) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., and London, 1960, p 290.

atoms of the water molecule were not resolved. The other O–Cl distances also lie in this range. Similarly the N–Cl distances lie within the range 2.91–3.41 Å listed in the same source.

Table X also summarizes the A–H–Cl (A = N or O) angles. These angles show that the hydrogen bonds are not strictly linear but fall in the range 144–177°.

The hydrogen-bonding scheme in the unit cell of the nickel compound can be seen by reference to the packing diagram (Figure 7) which shows one layer of anions and cations as viewed along the *c* axis and by reference to Figure 8. The scheme is best described as an infinite chain $(O(1)\text{–}Cl\text{–}O(3))_u$ with adjacent chains linked by two hydrogen bonds to N(4), which are approximately perpendicular to these chains. In addition, there are two more bonds to the chloride ion and one to O(3) that are not part of the chain.

There is also a large degree of hydrogen bonding involving the chloride ions in the copper compound. Here, however, Cl(1) has only two hydrogen bonds, while Cl(2) has five. The unusually short H(11)–Cl(2) distance quoted in Table XI is probably not significant, because of the large uncertainty in this hydrogen position. All A–Cl distances are within the range given by Pimentel and McClellan,[32] although the N(2)–Cl(2) distance is at the upper end of this range. There is more deviation from linearity in the A–H–Cl angles in the copper compounds than in the nickel complex.

TABLE XI

A. Hydrogen Bonding in $Cu(IBO)_2Cl_2$

			Å			
Atom A	Atom B	Hydrogen	A–B	A–H	H–B	A–H–B, deg
O(1)	Cl(1)	H(1)	3.019	0.727	2.297	172.8
N(2)	Cl(1)	H(3)	3.310	0.965	2.402	156.7
O(2)	Cl(2)	H(11)	3.087	1.152	2.057	147.0
O(4)	Cl(2)	H(22)	3.044	0.829	2.221	171.9
N(2)	Cl(2)	H(2)	3.422	0.828	2.601	171.8
N(4)	Cl(2)	H(10)	3.294	0.791	2.659	138.6
N(7)	Cl(2)	H(13)	3.306	0.940	2.384	167.0
N(4)	O(1)	H(9)	2.886	0.951	2.018	150.9
O(3)	N(10)	H(12)	2.765	0.678	2.120	159.7
N(9)	N(7)	H(21)	3.170	0.737	2.526	147.0

B. Hydrogen-Bond Angles (deg) around Atoms Involved in Two or More Bonds

Cl(1)	
O(1)–Cl(1)–N(2)	82.9

Cl(2)	
O(2)–Cl(2)–O(4)	81.6
O(2)–Cl(2)–N(2)	96.4
O(2)–Cl(2)–N(4)	86.6
O(2)–Cl(2)–N(7)	135.7
O(4)–Cl(2)–N(2)	109.6
O(4)–Cl(2)–N(4)	155.2
O(4)–Cl(2)–N(7)	88.5
N(2)–Cl(2)–N(4)	93.4
N(2)–Cl(2)–N(7)	127.4
N(4)–Cl(2)–N(7)	84.9

O(1)	
Cl(1)–O(1)–N(4)	96.2

N(2)	
Cl(2)–N(2)–Cl(1)	121.8

N(4)	
Cl(2)–N(4)–O(1)	68.5

As can be seen from Figure 9, the *c* axis projection of the unit cell of $Cu(IBO)_2Cl_2$, and from Figure 10, all but four of the listed hydrogen bonds are part of a finite cyclic arrangement, with the plane of each cycle approximately normal to the *z* axis. The O(4)–H(22)–Cl(2) and O(2)–H(11)–C(2) bonds could be considered as side arms to this cycle. The remaining two hydrogen bonds are approximately parallel to the *y* axis.

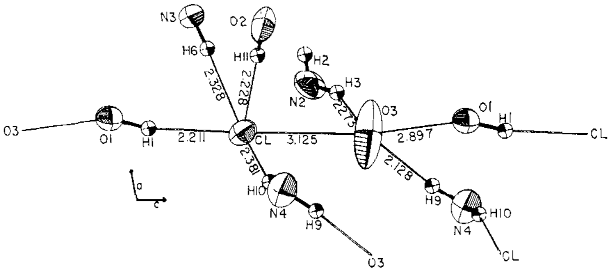

Figure 8.—Detail drawing of hydrogen-bonding scheme in $Ni(IBO)_2Cl_2 \cdot 2H_2O$ as viewed down the 010 axis.

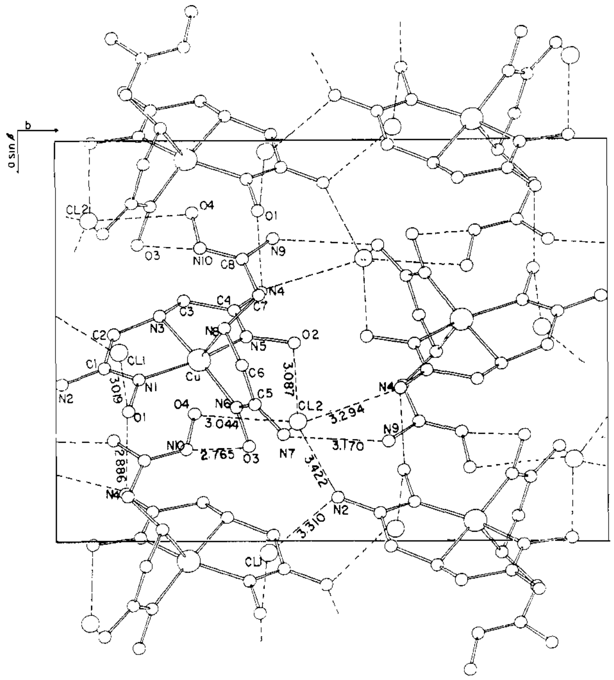

Figure 9.—Projection down 001 axis in $Cu(IBO)_2Cl_2$.

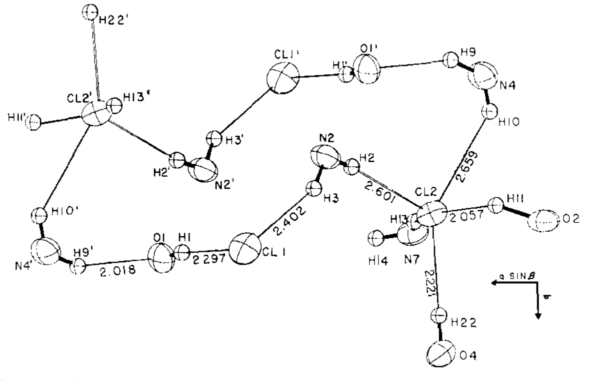

Figure 10.—Detailed drawing of the cyclic part of the hydrogen-bonding scheme as viewed down the 001 axis. The hydrogen bonds N(7)–N(9) and N(10)–O(3) are not shown.

Acknowledgment.—The authors wish to thank Professor L. P. Eddy for the samples used in this study and for valuable information about them. This work was supported in part by National Science Foundation Grant GP 7866.