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The Crystal and Molecular Structure of Dichlorobis(2,6-lutidine N-oxide)zinc(II)

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The crystal structure of dichlorobis(2,6-lutidine N-oxide)zinc(II), $(C_7H_9NO)_2ZnCl_2$, has been determined by single-crystal X-ray diffraction methods. Multiple-film equiinclination Weissenberg photographs were used to collect 991 nonzero reflections. The complex crystallizes in the monoclinic space group C2/c with four monomeric molecules per unit cell of dimensions a = 14.167 (8), b = 8.419 (5), c = 14.625 (8) Å, and β = 96° 16 (5)′. The observed and calculated densities are 1.50 and 1.47 g/cm^3, respectively. Positional and isotropic thermal parameters were refined by least-squares methods to a conventional R factor of 11.6%. The zinc atoms lie on twofold symmetry axes and are tetrahedrally coordinated to two chlorine atoms and two oxygen atoms from the 2,6-lutidine N-oxide groups. The tetrahedral geometry is distorted slightly owing to differences in atomic size; the Cl–Zn–Cl angle is larger than the normal tetrahedral angle of 109° 28′ and the O–Zn–O angle is smaller. The structure is somewhat similar to that of the yellow form of the corresponding copper(II) complex of 2,6-lutidine N-oxide, but the geometry about the metal ion is different in that the copper complex has a configuration intermediate between tetrahedral and *cis* square planar.

Introduction

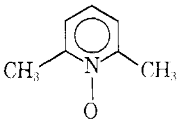
The interesting magnetic and structural properties of aromatic N-oxide complexes of copper(II) halides have been the subject of a number of studies.[1–4] The studies have been mostly concerned with dimeric complexes having strong metal–metal interactions. These interactions are found in most complexes having a 1:1 ratio of N-oxide to copper(II) chloride. The antiferromagnetic behavior and crystal structure of di-μ-(pyridine N-oxide)-bis[dichlorocopper(II)] have been reported,[5,6] and we have recently completed the crystal structure determination of Cu_3Cl_6(2-picoline N-oxide)$_2 \cdot 2H_2O$.[7]

In continuing our study of methyl-substituted pyridine N-oxide complexes, we have become interested in complexes containing two ligands per metal halide. Several 2:1 complexes of copper(II) chloride and zinc(II) chloride were made and characterized.[8] The 2:1 copper(II) complexes, with the exception of the pyridine N-oxide complex, are paramagnetic, whereas the zinc complexes are diamagnetic. We are interested in investigating the 2:1 N-oxide copper(II) complexes by single-crystal electron paramagnetic resonance techniques. Because of strong dipole–dipole interactions in the pure copper(II) complex, it is necessary to dilute magnetically the copper complexes in a diamagnetic host. The zinc N-oxide complexes have been found to serve as adequate host crystals to dilute the paramagnetic centers. The electron paramagnetic resonance spectrum of single crystals of monomeric dichlorobis(2,6-lutidine N-oxide)zinc(II) containing a small amount of the copper(II) complex has been obtained and hyperfine interactions due to the chlorine nuclei were observed. Before the data can be completely interpreted, however, the crystal structure of the zinc complex must be known.

The 2:1 zinc chloride complexes of pyridine N-oxide and the three picoline N-oxides are also monomeric. It seems likely that the structure of dichlorobis(2,6-lutidine N-oxide)zinc(II) is representative of these other 2:1 zinc complexes. The structure of the yellow form of dichlorobis(2,6-lutidine N-oxide)copper(II) has been determined recently.[9] The geometry about the copper atom lies between tetrahedral and *cis* square planar. The 1:1 zinc chloride complex of 1,10-phenanthroline also exhibits a lack of symmetry;[10] the plane of the zinc and chlorine atoms makes an angle of 79° with the plane of the zinc and the 1,10-phenanthrene molecule. In order to determine the geometry about the zinc, as well as interpret the electron spin resonance data, a complete crystal structure determination of dichlorobis(2,6-lutidine N-oxide)zinc(II) was done. We now wish to report the details of this structure.

Experimental Section

The 2,6-lutidine N-oxide (I), obtained from Reilly Tar & Chemical Corp., was purified by vacuum distillation. Colorless crystals of the zinc complex precipitated immediately on mixing ethanol solutions of zinc chloride and ligand in a 1:2 molar ratio. Crystals suitable for X-ray diffraction investigations were obtained by recrystallization from an ethanol solution. A crystal having the dimensions 0.16 × 0.45 × 0.20 mm was used in collecting all intensity data. The 0.45-mm dimension was parallel with the spindle axis of the camera.



I

The unit cell dimensions at room temperature were determined

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $(C_7H_9NO)_2ZnCl_2$

h	l	|Fo|	|Fc|
k = 0			
6	0	201	103
8	0	203	178
14	0	26	29
16	0	31	31
2	2	0	6
-4	2	0	4
4	2	87	72
-6	2	21	18
6	2	141	141
-8	2	92	100
8	2	107	100
-10	2	43	44
12	2	23	33
-12	2	0	5
-14	2	37	44
14	2	61	63
16	2	26	32
-16	2	31	40
0	4	125	118
-2	4	143	140
2	4	67	37
-4	4	12	9
4	4	97	93
-6	4	21	13
6	4	168	151
-8	4	95	96
8	4	84	80
10	4	52	64
-10	4	75	82
12	4	68	72
-12	4	0	14
-14	4	0	17
14	4	53	52
-16	4	37	41
16	4	25	28
-18	4	28	27
0	6	73	75
-2	6	156	159
2	6	0	12
-4	6	96	87
4	6	26	35
-6	6	21	10
6	6	94	79
-8	6	56	71
8	6	25	26
10	6	36	30
-10	6	91	97
-12	6	0	2
12	6	0	13
-14	6	0	6
14	6	45	39
-16	6	34	35
-18	6	27	26
0	8	41	39
-2	8	116	125
2	8	0	12
-4	8	109	106
4	8	101	91
-6	8	62	55
6	8	91	83
-8	8	55	55
10	8	23	26
-10	8	74	87
12	8	47	45
-12	8	71	80
-18	8	26	30
0	10	35	30
2	10	64	60
-2	10	60	59
-4	10	83	86
4	10	104	85
-6	10	37	37
6	10	62	53
-8	10	21	21
8	10	0	10
-10	10	41	54
10	10	27	29
-12	10	31	33
12	10	53	48
0	12	37	36
-2	12	117	118
2	12	43	45
-4	12	97	105
4	12	104	97
-6	12	31	31
6	12	54	50
-8	12	20	22
8	12	0	10
-10	12	34	42
10	12	23	26
12	12	26	25
-12	12	31	36
0	14	0	4
-2	14	21	18
2	14	43	47
-4	14	25	31
4	14	39	38
-6	14	21	29
6	14	0	4
-8	14	0	5
8	14	0	12
10	14	39	35
12	14	28	26
0	16	0	12
-2	16	0	11
2	16	47	45
-4	16	41	42
4	16	24	30
-6	16	33	36
6	16	0	6
10	16	32	28
-2	18	0	10
4	18	0	7
-6	18	34	35
k = 1			
3	0	30	9
5	0	46	29
7	0	53	50
9	0	58	62
11	0	0	0
13	0	0	13
15	0	25	38
-3	1	132	152
3	1	100	87
-5	1	79	80
5	1	112	112
-7	1	111	113
7	1	65	63
-9	1	83	92
9	1	44	46
11	1	43	48
-11	1	40	38
13	1	38	43
-13	1	20	15
15	1	23	34
-3	2	47	35
3	2	60	61
-5	2	0	10
5	2	35	24
-7	2	83	87
7	2	94	100
-9	2	65	63
9	2	22	22
11	2	23	17
13	2	18	17
-13	2	0	3
15	2	23	28
-15	2	27	28
-17	2	28	26
-1	3	124	92
1	3	86	73
-3	3	75	64
3	3	33	30
-5	3	44	49
5	3	99	86
-7	3	34	32
7	3	99	102
-9	3	31	32
9	3	43	44
-11	3	24	32
11	3	30	30
13	3	43	41
-13	3	26	30
-15	3	25	33
15	3	32	30
-17	3	28	24
-1	4	183	190
1	4	81	67
-3	4	100	96
3	4	71	60
5	4	39	39
-5	4	0	8
-7	4	46	45
7	4	56	102
-9	4	85	95
9	4	0	0
11	4	35	29
-11	4	32	35
13	4	32	30
-13	4	0	4
15	4	28	26
-1	5	65	53
1	5	110	101
-3	5	0	1
3	5	114	108
5	5	67	62
-5	5	0	9
-7	5	38	37
7	5	70	63
-9	5	44	41
9	5	83	80
11	5	47	51
-11	5	0	15
13	5	27	25
-13	5	0	16
15	5	24	21
-15	5	26	23
-1	6	120	101
1	6	32	26
-3	6	61	62
3	6	21	16
5	6	122	121
-5	6	0	12
-7	6	35	29
7	6	40	41
-9	6	44	46
9	6	21	16
11	6	31	29
-11	6	0	19
13	6	44	41
-1	7	58	52
-3	7	126	118
3	7	0	3
-5	7	110	116
5	7	42	43
-7	7	76	68
7	7	19	19
-9	7	79	70
9	7	0	8
-11	7	71	80
11	7	0	13
-13	7	40	46
13	7	26	25
-15	7	24	23
-1	8	76	69
-3	8	110	105
3	8	34	28
-5	8	17	14
5	8	82	82
-7	8	35	36
7	8	45	40
-9	8	48	50
9	8	0	0
-11	8	22	38
11	8	24	20
13	8	35	28
-13	8	25	16
1	9	73	69
-1	9	79	79
-3	9	75	71
3	9	74	64
5	9	49	47
-5	9	38	39
7	9	45	38
-7	9	43	43
-9	9	46	51
9	9	32	35
11	9	25	28
-11	9	26	28
13	9	26	23
-1	10	0	4
1	10	40	39
3	10	39	43
-3	10	77	76
-5	10	25	25
5	10	50	51
7	10	0	11
-7	10	21	14
9	10	0	6
-9	10	25	29
-11	10	32	41
11	10	27	24
13	10	28	14
1	11	78	67
-1	11	68	65
-3	11	51	48
3	11	67	62
5	11	58	63
-5	11	45	50
7	11	44	45
-7	11	40	42
9	11	23	27
-9	11	26	22
11	11	22	19
-1	12	24	21
-3	12	29	32
3	12	45	42
5	12	0	18
-5	12	38	53
7	12	0	3
9	12	0	8
11	12	28	23
-1	13	18	17
1	13	42	34
-3	13	46	45
-5	13	36	40
5	13	21	23
7	13	0	18
9	13	28	24
11	13	30	25
-1	14	0	6
3	14	40	38
-3	14	28	32
-5	14	30	35
5	14	21	16
7	14	0	3
9	14	0	10
11	14	22	14
0	15	22	0
-1	15	0	19
1	15	26	20
-3	15	0	16
3	15	30	25
-5	15	25	19
5	15	24	22
-1	16	0	2
1	16	0	16
3	16	27	23
k = 2			
4	0	197	206
6	0	47	40
8	0	0	3
10	0	50	51
12	0	36	37
-4	1	18	19
4	1	0	11
6	1	29	29
-6	1	96	84
8	1	62	67
-8	1	65	61
10	1	37	45
-10	1	25	36
12	1	34	38
-12	1	17	23
14	1	31	34
-14	1	29	36
-16	1	32	37
2	2	162	121
-2	2	113	114
4	2	98	97
-4	2	100	99
6	2	30	23
-6	2	64	57
-8	2	69	50
8	2	0	9
10	2	67	64
-10	2	0	5
12	2	34	34
-12	2	56	55
0	3	169	129
-2	3	211	199
2	3	54	50
4	3	77	70
-4	3	110	105
6	3	72	68
-6	3	74	71
8	3	50	51
-8	3	85	92
10	3	19	20
-10	3	57	61
-12	3	24	34
12	3	0	1
-14	3	24	26
14	3	20	16
0	4	14	13
-2	4	24	19
2	4	104	103
4	4	53	52
-4	4	78	91
-6	4	78	79
6	4	0	7
8	4	42	47
-8	4	0	7
10	4	78	70
-10	4	0	14
-12	4	43	58
12	4	34	38
-14	4	24	26
0	5	109	109
2	5	53	42
-2	5	110	107
4	5	65	59
-4	5	91	83
-6	5	74	68
6	5	74	93
-8	5	75	66
8	5	30	32
-10	5	81	74
10	5	0	12
12	5	47	44
-12	5	31	42
14	5	33	33
0	6	60	57
2	6	80	79
-2	6	18	21
-4	6	16	21
4	6	13	13
6	6	36	24
-6	6	88	91
-8	6	22	24
8	6	0	4
-10	6	22	30
10	6	24	21
12	6	0	2
-12	6	0	12
-14	6	20	29
0	7	65	60
2	7	77	73
-2	7	81	81
4	7	98	92
-4	7	37	40
6	7	78	74
-6	7	26	22
-8	7	44	45
8	7	55	62
10	7	48	46
12	7	28	30
-12	7	0	4
14	7	24	25
-14	7	27	22
0	8	66	67
-2	8	0	0
2	8	83	77
4	8	0	5
-4	8	16	18
6	8	0	4
-6	8	77	74
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8	8	53	57
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16	8	26	19
0	9	56	58
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4	9	51	48
-4	9	49	50
-6	9	30	27
6	9	45	48
8	9	23	22
-8	9	20	22
-10	9	42	42
10	9	29	24
12	9	31	26
-12	9	24	31
0	10	45	40
-2	10	0	1
2	10	45	43
4	10	0	0
-4	10	0	3
6	10	0	3
-6	10	43	42
-8	10	27	36
8	10	38	35
-10	10	0	1
10	10	21	20
0	11	20	17
2	11	27	25
-2	11	24	24
4	11	46	45
-4	11	48	62
6	11	0	17
-6	11	27	27
-8	11	19	19
8	11	0	8
10	11	14	18
-10	11	21	36
12	11	24	24
-12	11	25	33
0	12	82	81
-2	12	46	45
2	12	35	37
4	12	0	0
-4	12	18	16
-6	12	35	40
6	12	32	32
-8	12	25	43
8	12	37	38
0	13	45	47
-2	13	38	37
2	13	30	31
-4	13	21	23
4	13	26	25
-6	13	31	31
6	13	22	24
8	13	23	21
-8	13	24	27
-10	13	25	22
0	14	32	30
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2	14	0	5
4	14	0	9
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-6	14	0	3
6	14	27	24
8	14	26	23
-8	14	25	26
0	15	25	22
-2	15	21	26
2	15	36	37
-4	15	46	48
4	15	30	27
6	15	24	14
-6	15	11	37
0	16	19	18
2	16	0	3
-2	16	34	30
4	16	0	12
6	16	10	26
0	17	0	14
2	17	20	20
4	17	21	21
0	18	0	7
-2	18	27	25
k = 3			
3	0	93	95
5	0	77	72
7	0	0	0
9	0	39	37
11	0	92	85
13	0	44	53
19	0	28	28
-3	1	26	28
3	1	53	43
-5	1	75	73
5	1	27	14
7	1	38	32
-7	1	21	12
9	1	0	0
-9	1	0	10
-11	1	19	18
11	1	24	26
3	2	129	133
-3	2	105	102
-5	2	119	117
5	2	151	118
-7	2	64	62
7	2	25	17
9	2	24	26
-9	2	32	25
11	2	69	63
-11	2	42	49
13	2	28	25
-13	2	42	48
-1	3	26	17
1	3	22	19
3	3	35	28
-3	3	24	20
-5	3	0	12
5	3	19	13
-7	3	0	5
7	3	25	21
-9	3	0	7
9	3	17	9
11	3	0	2
-11	3	0	1
13	3	23	18
1	4	149	134
3	4	145	132
-3	4	137	141
5	4	15	13
-5	4	143	158
7	4	0	11
-7	4	79	91
9	4	75	68
-9	4	49	59
-11	4	58	65
11	4	37	39
-13	4	57	56
1	5	34	30
-1	5	53	45
-3	5	40	38
3	5	26	29
-5	5	31	30
5	5	17	13
-7	5	0	11
7	5	18	13
9	5	18	13
-9	5	41	41
1	6	136	119
-1	6	19	10
-3	6	27	26
3	6	163	151
5	6	49	44
-5	6	118	126
7	6	31	28
-7	6	79	76
-9	6	0	0
9	6	92	81
-11	6	21	25
11	6	68	60
-13	6	37	52
17	6	24	24
-1	7	23	18
-3	7	17	8
3	7	0	9
-5	7	21	20
5	7	42	37
-7	7	43	40
7	7	26	25
-9	7	0	13
9	7	21	16
1	8	137	127
-1	8	78	71
3	8	79	65
-3	8	34	27
-5	8	65	53
5	8	36	31
7	8	92	79
-7	8	42	48
-9	8	0	11
9	8	89	72
-1	9	34	28
3	9	20	9
-3	9	0	10
-5	9	0	1
5	9	0	3
7	9	21	14
-7	9	0	8
-1	10	51	55
3	10	0	9
-3	10	0	7
5	10	0	3
-5	10	29	31
-7	10	69	69
7	10	47	35
9	10	35	33
-9	10	30	41
-13	10	23	31
15	10	24	23
1	11	22	16
-1	11	0	8
3	11	0	11
-3	11	0	10
5	11	0	7
-5	11	0	1
1	12	43	45
3	12	0	9
-3	12	0	11
5	12	0	17
7	12	39	42
-7	12	43	48
-9	12	26	34
9	12	31	30
1	13	0	6
-1	13	0	16
3	13	25	19
-3	13	0	15
5	13	0	5
-5	13	0	8
-1	14	57	63
1	14	32	39
3	14	24	22
-3	14	39	42
-5	14	0	14
5	14	24	29
7	14	26	29
-7	14	30	36
-9	14	32	46
1	15	0	0
-1	15	0	12
3	15	0	7
-3	15	0	9
5	15	0	3
-5	15	0	4
-1	16	34	39
1	16	0	18
-3	16	28	31
3	16	0	7
-5	16	0	18
5	16	30	25
-7	16	21	24
7	16	31	27
k = 4			
4	0	48	52
6	0	18	12
8	0	13	4
10	0	36	36
12	0	35	30
-4	1	36	40
4	1	70	75
6	1	28	30
-6	1	48	52
-8	1	25	32
8	1	23	26
-10	1	25	32
10	1	68	57
12	1	46	46
-12	1	42	43
-14	1	26	28
2	2	106	103
4	2	85	89
-4	2	114	148
-6	2	57	56
6	2	0	2
8	2	0	12
-8	2	0	9
-10	2	21	27
10	2	42	36
12	2	26	25
-12	2	40	40
-14	2	26	10
2	3	99	105
-2	3	94	86
4	3	105	105
-4	3	144	160
6	3	30	27
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8	3	0	10
-8	3	23	22
10	3	44	37
-10	3	42	37
-12	3	47	56
12	3	25	23
-14	3	22	29
0	4	18	16
2	4	64	66
-2	4	66	54
4	4	40	36
-4	4	13	0
-6	4	47	42
6	4	12	6
-8	4	24	28
8	4	0	10
-10	4	31	31
10	4	48	43
12	4	22	16
-14	4	23	17
0	5	67	65
-2	5	61	55
2	5	105	98
-4	5	65	71
4	5	60	58
-6	5	77	75
6	5	0	11
-8	5	51	63
8	5	45	39
10	5	58	54
-10	5	41	45
12	5	23	23
-12	5	29	37
-14	5	21	28
0	6	39	35
-2	6	14	7
2	6	64	61
4	6	16	9
4	6	30	33
-6	6	59	59
6	6	0	5
8	6	41	41
-8	6	39	33
10	6	30	31
-10	6	0	16
-12	6	24	25
0	7	79	72
2	7	87	89
-2	7	19	16
4	7	46	50
-4	7	44	42
-6	7	47	63
6	7	51	55
8	7	76	70
-10	7	0	1
10	7	39	44
-14	7	27	26
0	8	18	20
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2	8	31	19
-4	8	25	13
-6	8	48	52
6	8	21	19
8	8	0	4
-8	8	27	29
-10	8	0	10
10	8	25	17
-12	8	0	13
-14	8	27	25
0	9	66	68
2	9	75	74
-2	9	21	19
4	9	21	21
-6	9	56	60
6	9	29	12
8	9	42	40
-8	9	41	39
10	9	33	32
0	10	75	68
-2	10	19	8
2	10	80	68
4	10	0	8
-4	10	0	11
6	10	0	17
-6	10	64	34
8	10	40	43
-8	10	33	30
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2	11	0	7
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4	11	0	6
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-6	11	35	34
6	11	33	27
-8	11	44	43
8	11	27	25
0	12	28	25
2	12	0	0
-2	12	21	16
4	12	0	6
-4	12	0	11
6	12	24	17
-6	12	22	5
8	12	28	25
-8	12	19	23
0	13	47	46
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2	13	27	23
4	13	0	14
-4	13	18	14
-6	13	0	18
6	13	31	30
8	13	30	29
-8	13	26	35
0	14	42	33
2	14	0	7
-2	14	23	15
4	14	0	2
-4	14	0	2
6	14	26	19
-6	14	24	21
-8	14	27	25
0	15	35	35
2	15	27	23
-2	15	32	32
-6	15	33	30
-2	17	26	23
k = 5			
3	0	17	19
5	0	22	4
7	0	45	44
9	0	47	39
15	0	28	20
3	1	110	129
-3	1	91	101
-5	1	70	82
5	1	34	38
7	1	0	10
-7	1	19	24
9	1	33	27
-9	1	28	26
11	1	43	41
-11	1	43	44
-13	1	25	24
-3	2	49	50
3	2	17	13
-5	2	0	6
5	2	35	39
7	2	67	61
-7	2	17	21
-9	2	38	43
9	2	21	14
11	2	25	13
-11	2	0	10
13	2	21	20
15	2	30	23
1	3	33	36
-1	3	36	39
-3	3	12	19
3	3	48	61
-5	3	61	62
5	3	33	39
-7	3	18	14
7	3	49	44
-9	3	0	2
9	3	65	59
-11	3	33	35
11	3	51	51
-13	3	31	36
13	3	28	31
17	3	25	21
1	4	62	59
-1	4	104	100
3	4	16	7
-3	4	24	28
-5	4	17	26
7	4	39	38
-7	4	63	68
9	4	0	7
-9	4	43	48
1	5	83	76
-1	5	22	22
3	5	66	65
-3	5	24	19
5	5	14	5
-5	5	67	67
7	5	0	5
-7	5	40	56
-9	5	0	10
9	5	46	40
11	5	21	29
-11	5	21	16
-13	5	27	32
-1	6	44	44
1	6	12	10
3	6	22	17
-3	6	52	48
-5	6	0	1
5	6	45	50
-7	6	0	3
7	6	51	43
9	6	0	7
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13	6	30	27
1	7	66	54
-1	7	37	31
-3	7	29	30
3	7	43	44
-5	7	59	61
-7	7	47	49
7	7	72	20
9	7	29	26
-9	7	0	13
-13	7	30	32
-1	8	57	49
1	8	0	12
-3	8	77	67
3	8	33	35
5	8	74	72
-5	8	0	5
7	8	23	20
-7	8	0	7
9	8	0	1
-9	8	0	18
-11	8	24	20
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1	9	56	51
-3	9	0	12
3	9	24	27
5	9	0	5
-5	9	23	27
-7	9	43	51
7	9	34	28
9	9	40	39
-9	9	36	38
-11	9	26	19
-13	9	28	26
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-1	11	55	50
3	11	26	28
-3	11	26	22
5	11	23	19
-5	11	37	36
7	11	41	35
-7	11	34	45
9	11	30	26
1	12	0	3
-1	12	0	2
-3	12	30	33
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5	12	23	22
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7	13	34	26
1	14	23	21
3	14	33	28
-5	14	32	33
5	15	24	21
7	15	25	23
k = 6			
2	0	44	65
4	0	26	27
6	0	46	52
8	0	65	62
10	0	33	25
2	1	0	11
-4	1	30	37
4	1	24	22
-8	1	29	30
8	1	32	28
-10	1	0	0
10	1	0	0
0	2	54	41
2	2	45	53
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-4	2	40	44
4	2	37	43
6	2	59	58
-6	2	68	73
8	2	53	44
-8	2	68	70
10	2	33	29
-10	2	29	29
12	2	28	28
14	2	32	29
16	2	31	24
0	3	25	30
-2	3	17	15
2	3	0	5
4	3	13	14
-4	3	0	2
6	3	38	28
8	3	0	10
-8	3	0	9
10	3	29	21
-10	3	0	9
0	4	31	36
-2	4	48	61
2	4	0	13
4	4	38	42
-4	4	0	8
6	4	70	66
-6	4	37	30
8	4	52	47
-8	4	0	13
10	4	24	21
-10	4	33	31
12	4	27	21
14	4	30	25
0	5	16	17
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4	5	0	2
6	5	30	25
-6	5	24	22
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8	5	0	4
0	6	49	47
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2	6	75	27
4	6	60	50
-4	6	49	47
6	6	57	49
-6	6	47	43
-8	6	47	54
8	6	23	20
10	6	0	15
-10	6	42	45
-12	6	26	24
0	7	0	1
2	7	34	30
-2	7	35	32
-4	7	0	3
4	7	19	13
6	7	40	34
-6	7	20	20
-8	7	0	1
0	8	30	28
-2	8	51	47
2	8	15	10
4	8	0	6
-4	8	44	46
6	8	25	18
-6	8	26	28
-8	8	31	33
-10	8	37	45
0	9	21	21
2	9	0	1
-2	9	17	20
-4	9	21	24
4	9	30	26
0	10	39	35
2	10	52	47
-2	10	59	56
-4	10	47	51
4	10	79	71
6	10	59	46
-6	10	29	24
0	11	0	14
2	11	0	6
-2	11	0	6
0	12	21	15
-2	12	33	28
2	12	27	22
4	12	35	30
-4	12	36	45
6	12	30	21
0	13	0	17
0	14	0	13
4	14	29	20
-4	14	28	24
k = 7			
5	0	0	0
7	0	19	18
9	0	25	18
11	0	0	3
3	1	27	34
-3	1	23	29
5	1	39	38
-5	1	34	33
-7	1	54	57
7	1	59	51
-9	1	41	42
9	1	0	17
11	1	0	5
-11	1	0	8
13	1	27	18
-1	2	18	30
1	2	14	23
-3	2	0	15
3	2	0	4
-5	2	15	12
5	2	0	13
7	2	25	23
-7	2	15	22
-9	2	21	19
9	2	0	8
-1	3	56	68
1	3	0	8
3	3	14	10
-3	3	18	20
5	3	46	45
-5	3	33	28
-7	3	27	28
7	3	74	66
9	3	46	38
-9	3	48	49
11	3	25	17
13	3	41	27
15	3	34	31
-1	4	29	34
1	4	21	18
-3	4	25	20
3	4	0	2
5	4	19	16
-5	4	14	6
7	4	26	21
-7	4	0	15
-9	4	20	21
1	5	33	29
-1	5	51	50
-3	5	49	44
3	5	21	19
-5	5	21	21
5	5	47	39
7	5	35	41
-7	5	15	17
-9	5	32	34
-11	5	26	24
1	6	0	8
-1	6	31	30
3	6	18	9
-3	6	22	22
-5	6	0	3
5	6	25	28
7	6	30	19
-7	6	21	11
-9	6	25	19
1	7	0	7
-1	7	34	36
3	7	42	29
-3	7	66	60
-5	7	30	25
5	7	50	38
7	7	20	16
-7	7	0	15
-9	7	34	37
-11	7	26	27
1	8	0	1
-1	8	27	15
3	8	0	12
-3	8	19	23
-5	8	0	5
5	8	28	21
7	8	0	9
-7	8	0	1
1	9	0	6
-1	9	47	36
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-3	9	35	36
-5	9	0	14
5	9	50	39
-7	9	0	10
7	9	33	26
-9	9	38	125
-11	9	35	39
1	10	0	1
-1	10	0	6
-3	10	24	18
3	10	23	15
-5	10	0	10
5	10	25	14
-1	11	20	18
1	11	23	19
3	11	56	46
-3	11	53	48
5	11	41	35
-5	11	39	39
1	12	0	2
3	12	0	9
1	13	22	13
3	13	37	25
3	15	30	21
k = 8			
4	0	18	24
6	1	26	28
8	1	38	36
-8	1	33	39
2	2	24	34
-4	2	31	37
4	2	29	26
-6	2	37	42
-8	2	24	17
0	3	35	46
-2	3	33	42
-4	3	22	26
6	3	38	40
8	3	28	24
-8	3	23	30
4	4	23	20
0	5	38	42
-2	5	47	53
4	5	23	17
6	5	35	34
-8	5	41	42
0	6	23	23
2	6	27	27
4	6	29	20
-4	6	23	17
-6	6	34	33
-8	6	28	24
-2	7	40	45
4	7	34	36
-4	7	26	22
6	7	50	47
-2	9	30	29
4	9	42	32
2	10	34	26
4	10	36	26

from an *h0l* Weissenberg photograph and a *b*-axis layer line photograph, both calibrated with superimposed NaCl powder lines, a = 5.6402 Å. The cell dimensions are a = 14.167 (8), b = 8.419 (5), c = 14.625 (8) Å and β = 96° 16 (5)′. The errors are standard deviations obtained from manual calculations of the cell edges from a number of reflections. The density of 1.50 (3) g/cm^3, determined by the flotation method using a mixture of acetone and carbon tetrachloride, indicated the presence of four molecules per unit cell (d_c = 1.47 g/cm^3). The systematic extinctions (*hkl* absent for $h + k$ odd and *h0l* absent for l odd) were consistent with either space group C2/c or Cc, although a careful examination of the crystal habit indicated the centric space group.

Three-dimensional intensity data were collected at room temperature around the *b* axis for levels 0 through 8 using the multiple-film (three films) equiinclination Weissenberg technique. Zirconium-filtered molybdenum radiation (Mo Kα = 0.71069 Å) was used to collect 991 observed and 234 unobserved reflections. The intensities were estimated by visual comparison with a calibration strip, and Lorentz-polarization corrections were applied to the data. No corrections to the observed intensities were made for extinction. The data were corrected for absorption using Bond's[11] values for a cylinder, with μ = 17.8 cm^{-1} and μR = 0.18. The corrections are only approximate since the cross section of the crystals is rectangular. Calculations of the maximum and minimum absorption showed that the maximum error in any structure factor due to the cylindrical approximation is 3%.

The computer programs given in ref 12 were used.

Structure Determination

A three-dimensional Patterson map showed large peaks at (0, $^1/_3$, $^1/_2$) and ($^1/_2$, $^1/_6$, $^1/_2$) which were assumed to be Zn–Zn vectors. The *y* coordinate of the zinc atoms could be determined from these peaks. If C2/c is the correct space group, the zinc atoms must occupy special positions along a twofold rotation axis and the *x* and *z* coordinates are fixed by the space group. If Cc is the correct space group, the *x* and *z* coordinates may be chosen arbitrarily.

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(11) "International Tables for X-ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

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TABLE II

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	*X*	*Y*	*Z*	*B*, Å²
Zn	0.5000	0.3308 (3)	0.2500	2.42 (6)
Cl	0.3690 (3)	0.4746 (5)	0.2076 (2)	3.64 (8)
O	0.5221 (7)	0.169 (1)	0.1537 (6)	3.6 (2)
N	0.4679 (7)	0.175 (1)	0.0721 (7)	2.8 (2)
C_2	0.382 (1)	0.105 (2)	0.060 (1)	3.4 (3)
C_3	0.331 (1)	0.111 (2)	−0.029 (1)	3.9 (3)
C_4	0.369 (1)	0.181 (2)	−0.100 (1)	4.4 (3)
C_5	0.458 (1)	0.253 (2)	−0.087 (1)	3.7 (3)
C_6	0.510 (1)	0.255 (2)	0.001 (1)	3.1 (3)
C_7	0.348 (1)	0.024 (2)	0.143 (1)	4.8 (4)
C_8	0.603 (1)	0.327 (2)	0.025 (1)	4.5 (3)

[a] Standard deviations of last significant figures are given in parentheses.

The positions of the chlorine, oxygen, and nitrogen atoms and one pair of carbon atoms were obtained from the Patterson map. The chlorine and oxygen atoms were tetrahedrally arranged around the zinc atom with a twofold axis parallel to the crystallographic *b* axis. Although this pointed to C2/c as the correct space group, we decided to use Cc until the structure became more obvious. Structure factors were calculated using the coordinates of the zinc, chlorines, oxygens, nitrogens, and one carbon atom. All observed reflections were used, and a temperature factor of 3.0 was assumed for all atoms. A value of $R = 0.32$ was obtained, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

TABLE III

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG)[a]

Bond distances	
Zn–Cl	2.246 (4)
Zn–O	2.01 (1)
O–N	1.35 (3)
N–C_2	1.35 (2)
N–C_6	1.42 (2)
C_2–C_3	1.41 (4)
C_3–C_4	1.36 (2)
C_4–C_5	1.39 (2)
C_5–C_6	1.41 (5)
C_2–C_7	1.52 (2)
C_6–C_8	1.46 (2)

Nonbonding distances	
Cl–C_7	3.91 (2)
Cl–Cl	3.783 (4)
Cl–O	3.508 (7)
O–O′	2.952 (9)
Cl–O′	3.524 (7)
Cl–C_3''	3.72 (1)
Cl–C_4''	3.80 (1)
Cl–C_5'	3.91 (1)
Cl–C_5'''	3.87 (1)

Nonbonding distances	
Cl–C_7'''	3.97 (2)
Cl–C_8'	3.85 (2)
O–C_3'	3.75 (2)
O–C_4'	3.45 (2)
O–C_5'	3.71 (2)
N–N′	3.79 (1)
N–C_2'	3.83 (2)
N–C_3'	3.83 (2)
N–C_4'	3.78 (3)
N–C_5'	3.76 (2)
N–C_6'	3.80 (2)
C_2–C_3''	3.84 (2)
C_2–C_5'	3.77 (2)
C_2–C_6'	3.55 (3)
C_3–C_3''	3.45 (2)
C_3–C_6'	3.81 (2)
C_3–C_8'	3.80 (3)
C_5–C_7	3.77 (4)
C_3–C_8'	3.77 (5)
C_5–C_8'	3.86 (5)

Bond angles	
Cl–Zn–Cl	114.8 (2)
O–Zn–O′	94.7 (4)
O–Zn–Cl	111.0 (3)
O–Zn–Cl′	111.8 (3)
Zn–O–N	118.6 (7)
O–N–C_2	121 (1)
O–N–C_6	123 (1)
C_2–N–C_6	115 (1)
N–C_2–C_3	118 (1)
N–C_2–C_7	117 (1)
C_3–C_2–C_7	125 (1)
C_2–C_3–C_4	121 (1)
C_3–C_4–C_5	121 (1)
C_4–C_5–C_6	120 (1)
C_5–C_6–N	117 (1)
N–C_6–C_8	117 (1)
C_5–C_6–C_8	126 (1)

[a] Standard deviations of last significant figures are given in parentheses. Lattice errors have not been taken into account in the calculations of the esd's.

A three-dimensional Fourier map assuming space group Cc was calculated using the phases determined by the structure factor calculations, and the remaining carbon atoms were located. Reflections having $F_o > 2F_c$ were omitted in the calculations. At this point it was seen that all atoms of one ligand were related to the corresponding atoms of the second ligand by a twofold rotation axis, and C2/c was chosen as the correct space group. This choice appears justified by the successful refinement of the structure. Structure factors were calculated using the coordinates of all atoms, and the *R* factor was lowered to 0.26. A second three-dimensional Fourier map was calculated, and a refined set of atomic parameters was obtained. The data for the nine levels were rescaled using plots of ln (F_o/F_c) *vs.* $\sin^2 \theta$. An *R* factor of 0.197 was obtained.

Three cycles of a full-matrix least-squares refinement using Busing and Levy's program were carried out on scale, positional, and isotropic thermal parameters. The contributions of the hydrogen atoms have been ignored. The quantity minimized was $\Sigma w(F_o - F_c)^2$. A modified Hughes[13] weighting scheme was used where $w = 1.0$ for $F_o < 4F_{\min}$, $w = 4F_{\min}/F_o$ for $F_o > 4F_{\min}$, and $w = 0.0$ for unobserved reflections. Atomic scattering factors were taken from the tables of Cromer and Waber.[14] Those for Zn and Cl^- were corrected for the real part of anomalous dispersion using Cromer's values.[15] Three additional least-squares refinement cycles were calculated on the IBM 360 Model 50 with Okaya's program for positional and thermal parameters. The weighting scheme used was $w = 0.0$ for unobserved reflections, $w = (1/7)(F_o)^{1/2}$ for $F_o < 4F_{\min}$, and $w = 4F_{\min}/F_o$ for $F_o > 4F_{\min}$ where $F_{\min} = 12.25$. The final *R* value is 0.116. The least-squares program does not give a weighted *R* value.

After the last cycle, the largest shift was less than $^1/_{30}$ of the estimated standard deviation for that parameter. The observed and calculated structure factors are listed in Table I while Table II gives the final positional and thermal parameters and their estimated standard deviations.

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(14) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(15) D. T. Cromer, *ibid.*, **18**, 17 (1965).

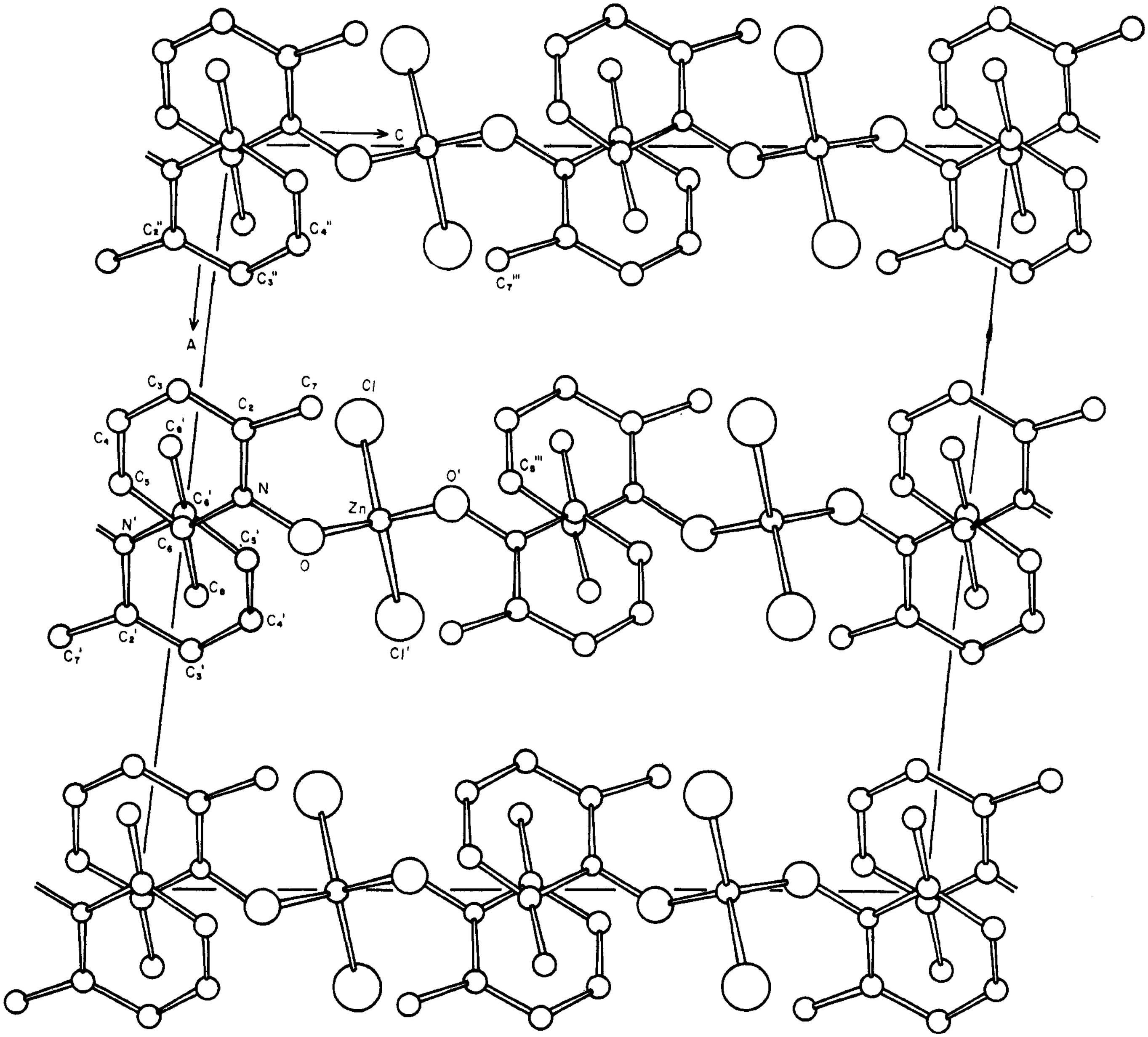

Figure 1.—A projection of $(C_6H_7NO)_2ZnCl_2$ on 010 showing the contents of one complete unit cell. The *b* axis is going into the plane of the paper.

A final three-dimensional difference Fourier showed no peaks higher than 0.8 $e^-/Å^3$, indicating the absence of solvent molecules. Of the peaks 0.4–0.8 $e^-/Å^3$ in magnitude several were located in areas where one would expect to find hydrogen atoms.

Discussion

The structure of dichlorobis(2,6-lutidine N-oxide)-zinc(II) is shown in Figure 1. Interatomic distances, bond angles, and their estimated standard deviations are listed in Table III. The structure consists of loosely packed discrete molecules separated by ordinary van der Waals distances. The shortest intermolecular distances are between two *meta* carbons (3.45 Å) and between an oxygen and a nearby *para* carbon (3.45 Å). The bulky 2,6-lutidine groups seem to be the main factor controlling the molecular packing. Each 2,6-lutidine group is surrounded by three other 2,6-lutidine groups and two chlorine atoms. Some selected short intermolecular distances, including all those less than 3.85 Å, are found in Table III.

The zinc(II) atom is tetrahedrally coordinated to two chlorine atoms and two oxygen atoms from the N-oxide ligands. The tetrahedron is distorted because of coordination to atoms of differing sizes. The Cl–Zn–Cl angle is expanded to 114.8°, the Cl–Zn–O angles are expanded to 111.8 and 111.0°, and the O–Zn–O angle is compressed to 94.7°.

The large Cl–Zn–Cl angle can be explained by the size and mutual repulsion of the chlorine atoms, but the small O–Zn–O angle cannot be easily explained. The plane of the chlorine and zinc atoms makes an angle of 89.4° to the plane of the zinc and oxygen atoms. In the yellow form of the dichlorobis(2,6-

lutidine N-oxide)copper(II) complex,[9] the plane of the chlorine and copper atoms makes an angle of 54.4° with the plane of the copper and oxygen atoms. The Zn–Cl bond length of 2.246 Å and the Zn–O bond length of 2.01 Å are comparable to those found in the copper complex where Cu–Cl = 2.221 and 2.247 Å and Cu–O = 1.93 and 1.97 Å. The oxygen–oxygen separation is 2.952 Å compared to 2.68 Å in the copper complex. A plane was least-squares-fitted to the six-ring atoms of the 2,6-lutidine molecule with all atoms weighted equally. The largest deviation was 0.018 Å which is less than the estimated standard deviations for the positions of the individual atoms. The N–O bond length of 1.35 Å compares with 1.36 and 1.31 Å found in the copper complex. The average C–N distance is 1.38 Å, and the average C–C distance around the ring is 1.39 Å.

The Zn–O–N angle, 118.6°, is slightly less than that found in the corresponding copper(II) complex where the angles are 118.6 and 121.6°. The N–O bond makes an angle of 3.1° with the 2,6-lutidine ring which leaves the oxygen atom 0.08 Å out of the plane of the ring. The two 2,6-lutidine rings make an angle of 61° relative to each other. This is greater than the angle of 53° found for the copper complex.

The zinc and copper complexes are not isostructural. Since the molecular packing imposes no restrictions on the chlorine atoms through strong nonbonding interactions, they are free to achieve the most stable configuration relative to the oxygen atoms. The copper complex should fit into the zinc lattice with a minimum of distortion of the N-oxide ligand. This slight rearrangement of the 2,6-lutidine N-oxide ligand should not be too energetically unfavorable. All zinc sites are equivalent in projection down the *b* axis. This need not be the case for the copper ion when substituted into the zinc lattice. Two nonequivalent sites would result if random statistical substitution occurred.

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The Structure of Tris(ethylenediamine)chromium(III) Pentacyanonickelate(II) Sesquihydrate, $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5]\cdot 1.5H_2O$

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The crystal and molecular structure of tris(ethylenediamine)chromium(III) pentacyanonickelate(II) sesquihydrate, $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5]\cdot 1.5H_2O$, has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined on F to a final conventional R factor of 9.4% and a weighted R factor of 6.9% for the 2758 observed reflections. The salt crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with eight formula units in a cell of dimensions $a = 14.883$ (4), $b = 15.748$ (4), $c = 16.464$ (5) Å, $\beta = 94.88$ (1)°. The calculated density of 1.55 g/cm³ agrees well with the observed density of 1.56 ± 0.02 g/cm³. The structure consists of discrete $Cr(C_2H_8N_2)_3^{3+}$ and $Ni(CN)_5^{3-}$ ions linked by intermolecular hydrogen bonds. The waters of crystallization participate in some of these bonds. There are two crystallographically independent $Ni(CN)_5^{3-}$ ions in the compound: one is a regular square pyramid and the other is a distorted trigonal bipyramid. The square pyramid has axial and average equatorial Ni–C bond lengths of 2.168 (14) and 1.862 (6) Å, respectively. The average C–Ni–C angle between the opposing basal carbon atoms is 159.5 (4)°, so that the nickel atom is 0.34 Å above the basal plane of carbon atoms. The distorted trigonal-bipyramidal $Ni(CN)_5^{3-}$ group has Ni–C axial bonds that are significantly shorter than the Ni–C equatorial bonds. The average axial Ni–C bond length is 1.837 (9) Å. The C–Ni–C angle between the axial carbon atoms is 172.8 (5)°. There are two equivalent equatorial Ni–C bonds of average length 1.907 (9) Å and one longer equatorial bond of 1.992 (14) Å. This longer bond and the large C–Ni–C angle, 141.2 (5)°, between the other two equatorial carbon atoms are the primary deviations from a regular trigonal-bipyramidal geometry. The observed C_2 geometry is apparently not due to crystal-packing interactions but is rather an energy minimum of the free ion. The isolation of both geometries in the same crystal demonstrates the very small energy difference between them. The conformations of the two tris(ethylenediamine)chromium cations are different. For the Λ configuration of each, one is Λλλ∂ and the other is Λ∂∂λ.

Introduction

It has long been known that pale yellow solutions of $Ni(CN)_4^{2-}$ form a cyanide adduct in concentrated aqueous cyanide solutions.[1] In a series of careful spectroscopic studies, Coleman, Peterson, and Penneman[1] showed that the complex formed in aqueous solution is $Ni(CN)_5^{3-}$. Repeated efforts to isolate this anion were unsuccessful, but recently stable salts of $Cr(NH_3)_6^{3+}$ and $Cr(en)_3^{3+}$ (en = $NH_2CH_2CH_2NH_2$) have been obtained.[2] Moreover, the unstable potassium salt has been isolated at low temperatures.[3]

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[1] J. S. Coleman, H. Peterson, Jr., and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965), and references therein.

[2] K. N. Raymond and F. Basolo, *ibid.*, **5**, 949 (1966).

[3] W. C. Anderson and R. H. Harris, *Inorg. Nucl. Chem. Letters*, **2**, 315 (1966).