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The Crystal Structure of μ-Oxo-bis{pentamminechromium(III)} Chloride Monohydrate, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]Cl_4 \cdot H_2O$[1]

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The crystal structure of μ-oxo-bis{pentamminechromium(III)} chloride (basic rhodochromic chloride) monohydrate, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]Cl_4 \cdot H_2O$, has been determined from the three-dimensional X-ray data. The crystals are orthorhombic. The cell dimensions are: $a=11.94\pm0.01$, $b=11.71\pm0.01$, and $c=13.40\pm0.02$ Å. The space group is *Pbca*, with four formula units in a unit cell. The structure was refined by the least-squares method, with anisotropic temperature factors, to $R=0.14$. A bridging oxygen atom of the basic rhodochromic complex ion is situated on the inversion center. Therefore, the complex has a center of symmetry and, accordingly, a linear Cr–O–Cr system. The N–Cr–O angles are nearly 90° or 180°, and the Cr–N bond distances are in the range from 2.09 to 2.14 Å (average 2.11 Å). The complex ion has approximately a D_{4h} symmetry. The Cr–O distance is 1.80 Å, which is quite short compared with that found in the other Cr(III) complexes. The linear Cr–O–Cr system and its short bond distance suggest the presence of an extensive π-bonding in this system. The single-crystal polarized absorption spectra in the visible and ultraviolet regions were also measured. It was found that the characteristic sharp absorption bands of the basic rhodochromic complex ion are all polarized along the four-fold rotation axis of the complex.

Since the rhodochromic (μ-hydroxo-bis{pentamminechromium(III)} ion: rhodochromic ion, μ-oxo-bis{pentamminechromium(III)} ion: basic rhodochromic ion) and erythrochromic (μ-hydroxo-aquotetramminechromium(III) pentamminechromium(III) ion: erythrochromic ion, μ-hydroxo-hydroxotetramminechromium(III) pentamminechromium(III) ion: basic erythrochromic ion) series of compounds were first prepared by Jørgensen[2] in 1882, their correct constitutions and their interesting transformation relationships have been discussed in several studies.[3,4] Wilmarth *et al.*,[5] in 1955, on the basis of their careful analyses, determination of pK values, and cleavage-reaction studies of these compounds, proposed the following formulae and relationships for these binuclear complexes of chromium(III):

$$\underset{\text{rhodochromic ion}}{[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]^{5+}} \underset{H^+}{\overset{OH^-}{\rightleftarrows}} \underset{\text{basic rhodochromic ion}}{[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}}$$

$$\underset{\text{erythrochromic ion}}{[(NH_3)_5Cr\text{-}OH\text{-}Cr(H_2O)(NH_3)_4]^{5+}} \underset{OH^-}{\overset{H^+}{\rightleftarrows}} \underset{\text{basic erythrochromic ion.}}{[(NH_3)_5Cr\text{-}OH\text{-}Cr(OH)(NH_3)_4]^{4+}}$$

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[1] A short communication including the present X-ray work has been reported: a) A. Urushiyama, T. Nomura, and M. Nakahara, This Bulletin, **43**, 3971 (1970). Subsequently, correspondence on the structures of the binuclear complexes of chromium(III), including the basic rhodochromic complex ion, has appeared: b) M. Yevitz and J. A. Stanko, *J. Amer. Chem. Soc.*, **93**, 1512 (1971). The results obtained by these arthors were essentially consistent with our X-ray studies. The polarized absorption spectra of the basic rhodochromic salt have also been reported in a short communication: c) A. Urushiyama, M. Nakahara, and Y. Kondo, This Bulletin, **44**, 2290 (1971).

[2] S. M. Jørgensen, *J. Prakt. Chem.*, **25**, 231 (1882).

[3] A. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 5 Aufl. (1923), p. 273.

[4] K. A. Jensen, *Z. Anorg. Chem.*, **232**, 257 (1937).

[5] W. K. Wilmarth, H. Graff, and S. T. Gustin, *J. Amer. Chem. Soc.*, **78**, 2683 (1956).

Subsequently, a variety of the μ-hydroxo-acidotetramminechromium(III)pentamminechromium(III) (acido-erythrochromic) complexes, $[(NH_3)_5Cr\text{-}OH\text{-}CrX(NH_3)_4]^{4+}$ ($X = F^-$, Cl^-, Br^-, I^-, NCS^-, and NO_2^-),[6,7] have been synthesized from the erythrochromic complex, and $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_4enH]^{6+}$ [8] from the thiocyanato-erythrochromic complex (en= ethylenediamine).

In these binuclear complexes of chromium(III), the chracteristic "blue" basic rhodochromic salts have been reported to have very different properties from the other compounds in the series. That is, the remarkably reduced magnetic susceptibilities of these salts and their variation with the temperature have been investigated by several workers.[9–12] Schwarzenbach and Magyar[13] investigated the hydrolysis reaction of the rhodo- and erythrochromic series of complexes in an aqueous solution, and reported that the basic rhodochromic complex ion in a basic aqueous solution is transformed very rapidly into the red basic etythrochromic complex with a half-lifetime of 44 sec at 25°C. The visible and ultraviolet absorption spectra of the basic rhodochromic salts show one broad band in the 16600 cm^{-1} region and several unfamiliar sharp bands in the near-ultraviolet region[9,14–16] which have never been found in the spectra of the ordinary chromium(III) complexes.

These unusual properties of the basic rhodochromic complex have been ascribed to the fact that the Cr–O–Cr system of the basic rhodochromic complex may be linear and, hence, may contain an extensive π-bond character, while the other red binuclear complexes in these series may have the bent Cr–OH–Cr bridging system.[1a]

Therefore, it is important to know the structural features of the basic rhodochromic complex, *i.e.*, the Cr–O–Cr angle, the Cr–O and Cr–N bond distances, *etc.* In the present work, in order to determine the structure of the basic rhodochromic complex, the relatively stable crystal of the basic rhodochromic chloride monohydrate, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]Cl_4 \cdot H_2O$, was subjected to three-dimensional X-ray analysis. The single-crystal polarized absorption spectra of the basic rhodochromic perchlorate monohydrate, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5](ClO_4)_4 \cdot H_2O$, were also measured and found to be related to the orientation of the complex.

Experimental

X-ray Studies. Crystals of basic rhodochromic chloride monohydrate, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]Cl_4 \cdot H_2O$, were prepared by Jørgensen's method.[2] When 7g of the rhodochromic chloride monohydrate, $[(NH_3)_5Cr\text{–}OH\text{–}Cr(NH_3)_5]Cl_5 \cdot H_2O$, were dissolved in 50 m*l* of an ice-cold 2 N NH_3 aqueous solution, almost black crystals of basic rhodochormic chloride monohydrate were soon produced. Because the hydrolysis reaction of the complex takes place immediately in an aqueous solution, the crystallization has to be hastened, and so it is difficult to obtain large crystals. However, a few crystals with dimensions as large as about 0.15 × 0.15 × 0.10 mm were found upon a carefull examination under a microscope of the crystals produced. The crystals exhibited some dichroism (blue—greenish blue)and were unstable to even ordinary levels of humidity, turning to red after a few days in the atmosphere of the laboratory. Therefore, the crystals were sealed in a Lindemann glass capillary and mounted on a goniometer. The changes in their color could not be observed for at least a week under these conditions. The oscillation and Weissenberg photographs indicated the crystals are orthorhombic, with unit cell dimensions of $a = 11.94 \pm 0.01$, $b = 11.71 \pm 0.01$, and $c = 13.40 \pm 0.02$ Å, and that the Laue symmetry is mmm. The systematic absences—$0kl$ for $k = 2n+1$, $h0l$ for $l = 2n+1$, and $hk0$ for $h = 2n+1$—are compatible with the *Pbca* space group. The density of the crystals observed by the flotation method was 1.58 g cm^{-3}, and the calculated one was 1.59 g cm^{-3} for $z = 4$. The schematic drawing of the crystal related to its crystallographic axes is shown in Fig.1. For the intensity data collection, multiple-film equi-inclination Weissenberg photographs were taken around the *a* axis from zero through the 7th layer and around the *c* axis from zero through the 5th layer, changing the crystals, whose approximate dimensions were 0.15 × 0.15 × 0.10 mm, for each layer. Ni-filtered CuK_α radiation was used. The intensities were estimated visually with a standard film strip; 811 independent reflections were thus obtained. Lorentz and polarization corrections were applied.

Spectroscopic Studies. For the measurement of the visible and ultraviolet absorption spectra of single crystals of a microscopic size, an apparatus was used constructed of a Hitachi EPS-3T spectrophotometer and a Nippon Kogaku POH polarizing microscope, together with two Olympus M090 reflecting-type objectives (×90). The microscope part of the apparatus was sealed in a stainless steel box and was evacuated to 10^{-3} mmHg for the studies at low temperatures. A thin plate of a single-crystal of the basic rhodochromic perchlorate monohydrate, prepared by Linhard's method[6] and of the approximate dimensions of 0.5 × 0.6 mm, was

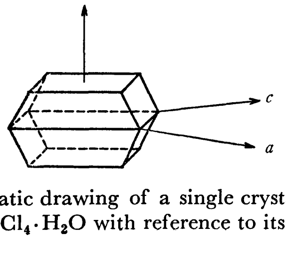

Fig. 1. Schematic drawing of a single crystal of $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]Cl_4 \cdot H_2O$ with reference to its crystallographic axes.

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Table 1. Observed and calculated structure factors

L	Fo	Fc
H, K = 0, 0		
2	111	110
4	486	-503
6	85	-81
8	163	161
10	134	138
12	56	44
H, K = 0, 2		
0	189	174
1	260	-238
2	56	77
3	247	-257
4	140	-127
5	12	-11
6	165	-155
7	246	218
8	77	63
9	145	152
10	107	97
11	34	-34
12	27	-32
13	85	-96
H, K = 0, 4		
0	420	390
1	126	122
2	115	-130
3	82	-81
4	71	-60
5	103	-96
6	295	270
7	101	95
8	121	109
9	87	88
10	118	-114
11	39	-47
12	92	-77
13	81	-97
14	71	85
15	0	3
16	28	41
H, K = 0, 6		
0	62	-71
1	0	-13
2	36	-48
3	92	92
4	120	118
5	62	44
6	88	81
7	37	-29
8	68	55
12	83	-87
H, K = 0, 8		
0	102	110
1	178	213
2	41	-52
3	154	186
4	85	-94
5	68	-81
6	49	50
7	91	-95
8	41	56
H, K = 1, 0		
2	93	-75
4	10	10
6	12	-25
8	67	76
10	61	56
12	25	-19
14	52	-47
H, K = 1, 1		
1	271	260
2	114	-91
3	37	-20
4	164	-182
5	58	-80
6	21	-24
7	127	-130
8	206	241
9	153	153
10	42	40
11	124	142
12	77	-86
H, K = 1, 2		
1	129	-137
2	177	219
3	76	74
4	236	-238
5	33	29
6	86	-99
7	0	-20
8	120	135
9	33	-37
10	56	60
11	0	-11
12	85	-96
H, K = 1, 3		
1	102	-87
2	359	-384
3	21	-17
4	176	-159
5	140	132
6	130	148
7	52	43
8	71	65
14	73	-83
H, K = 1, 4		
1	21	-41
2	31	35
3	43	51
4	61	57
5	128	146
6	57	-37
7	33	25
8	26	-32
H, K = 1, 5		
1	83	-85
2	36	34
3	120	133
4	79	-79
5	273	278
6	30	-37
7	18	-5
8	75	60
9	0	-13
10	0	6
11	65	-51
12	45	-25
15	56	54
H, K = 1, 6		
1	54	-76
2	177	183
3	75	79
4	39	-8
5	57	-54
6	81	-77
7	87	-96
H, K = 1, 7		
1	32	-40
2	46	62
3	24	-24
4	96	107
5	72	90
6	0	-8
7	61	54
8	98	-119
H, K = 1, 8		
1	35	52
2	51	43
H, K = 1, 9		
1	67	87
2	148	149
3	38	40
4	58	61
5	36	-32
6	40	-39
7	76	-88
8	75	-90
9	67	69
10	51	-37
11	67	72
H, K = 1, 10		
1	49	-66
H, K = 2, 0		
2	86	107
4	108	100
6	164	-166
8	90	-90
10	148	157
12	95	89
14	0	-24
H, K = 2, 1		
1	167	-164
2	83	-93
3	168	-179
4	248	-232
5	49	58
6	94	103
7	146	147
8	21	29
9	50	36
10	128	-136
H, K = 2, 2		
0	54	-60
1	168	-155
2	34	50
3	200	-204
4	227	230
5	36	18
6	44	-49
7	149	151
8	90	-85
9	78	81
10	87	81
H, K = 2, 3		
0	311	-296
1	109	-108
2	37	-32
3	223	-181
4	306	287
5	111	107
6	94	85
7	52	33
8	0	-76
H, K = 2, 4		
0	211	-210
1	58	-68
2	89	-79
3	97	-103
4	284	286
5	30	32
6	137	140
7	88	89
8	66	-69
9	31	24
10	42	-43
H, K = 2, 5		
0	85	67
1	87	81
2	75	-64
3	185	177
4	96	-84
5	0	11
6	108	94
7	50	-53
8	35	40
9	33	-50
10	93	-86
11	0	-11
12	0	0
13	85	77
14	0	32
15	63	43
H, K = 2, 6		
0	246	-225
1	10	6
2	81	-72
3	72	61
4	228	233
5	72	61
6	122	127
7	29	-33
8	40	-44
9	76	-66
H, K = 2, 7		
0	69	58
1	62	-56
2	55	59
3	65	-67
4	82	-70
5	91	82
6	108	-131
7	37	-15
8	0	-5
9	95	-91
10	93	88
H, K = 2, 8		
0	0	-33
1	90	72
2	0	-23
3	105	119
4	51	73
5	43	37
6	0	30
7	94	-84
8	0	-18
9	76	-98
H, K = 2, 9		
0	118	125
1	64	-15
H, K = 2, 10		
0	94	93
H, K = 3, 0		
2	419	-437
4	63	46
6	183	165
H, K = 3, 1		
1	190	192
2	155	-159
3	142	-146
4	44	-39
5	50	-41
6	90	73
7	16	39
8	24	-23
9	82	80
H, K = 3, 2		
1	167	-155
2	45	-34
3	42	46
4	194	-200
5	108	96
6	62	50
7	63	55
8	79	66
9	95	-76
10	0	0
11	85	-80
H, K = 3, 3		
1	117	-95
2	36	-40
3	22	-21
4	177	-156
5	133	123
8	179	161
H, K = 3, 4		
1	43	-24
2	0	-7
3	25	-28
4	206	195
5	202	181
6	34	35
7	125	116
8	188	-180
9	62	-55
10	56	-45
11	113	-113
12	112	107
H, K = 3, 5		
1	81	-61
2	60	-45
3	64	-63
4	29	-18
5	136	128
6	0	7
7	113	109
8	21	-10
9	39	-54
10	0	15
11	116	-106
15	59	60
H, K = 3, 6		
1	78	61
2	275	234
3	38	-8
4	80	95
5	139	-151
6	62	-49
7	50	-55
8	117	-94
H, K = 3, 7		
1	0	12
2	182	173
3	0	42
4	0	19
5	110	103
6	104	-75
H, K = 3, 8		
1	196	192
2	67	-75
3	112	-105
4	0	-3
5	117	-113
H, K = 3, 9		
1	95	84
H, K = 4, 0		
0	78	-59
2	31	47
4	0	4
6	120	-110
8	0	5
10	68	74
H, K = 4, 1		
0	119	-119
1	95	87
2	39	-41
3	37	-34
4	53	43
5	119	-109
6	107	97
7	73	76
8	0	11
9	133	141
10	77	-72
11	0	1
12	0	-18
13	92	-98
H, K = 4, 2		
0	558	574
1	77	66
2	15	-15
3	26	-25
4	106	-106
5	30	-36
6	84	98
7	32	27
8	76	75
9	50	24
H, K = 4, 3		
0	331	-337
1	180	169
2	104	-106
3	118	115
4	220	213
5	52	-67
6	142	152
7	75	-71
8	41	-20
9	0	13
10	91	-83
11	51	40
12	53	-64
H, K = 4, 4		
0	80	-68
1	104	-100
2	0	5
3	48	-42
4	97	85
5	22	25
6	0	-23
7	68	62
8	0	9
9	45	38
H, K = 4, 5		
0	82	-74
1	239	243
2	0	-17
3	300	302
4	33	28
5	53	-45
6	0	21
7	187	-185
8	0	2
9	75	-64
10	0	-10
11	43	54
12	0	1
13	70	69
14	0	0
H, K = 4, 6		
0	81	88
1	130	136
2	66	-63
3	68	57
4	0	-16
5	74	-68
6	116	120
7	0	-16
8	37	37
9	0	3
10	53	-49
H, K = 4, 7		
0	123	125
1	83	97
2	78	72
3	77	91
4	87	-80
5	26	-26
6	133	-149
7	78	-88
8	0	-6
9	21	-33
10	98	115
11	44	44
12	57	53
H, K = 4, 8		
0	38	56
1	0	-17
2	0	25
3	39	35
4	53	40
5	41	41
6	29	-32
10	60	61
H, K = 4, 9		
0	86	82
1	0	-3
2	50	42
3	50	-48
4	41	-43
5	43	-49
6	93	-82
7	34	33
8	0	-6
9	66	64
10	61	58
H, K = 5, 0		
2	136	-139
4	240	-267
6	50	53
8	176	186
10	29	54
12	104	-105
H, K = 5, 1		
1	14	-45
2	52	-70
3	67	74
4	61	51
5	86	85
6	76	71
7	57	-50
8	124	-135
9	18	19
10	19	-21
11	67	46
12	74	48
H, K = 5, 2		
1	148	-149
2	134	-128
3	81	66
4	72	-53
5	203	207
6	43	56
7	75	77
8	42	38
9	80	-80
10	33	21
11	110	-102
12	0	-3
13	0	0
14	32	-29
15	59	56
H, K = 5, 3		
1	53	53
2	52	36
3	114	103
4	42	-35
5	66	65
6	23	-34
7	131	-118
8	82	75
9	60	67
10	42	-1
11	105	80
H, K = 5, 4		
1	176	-161
2	236	224
3	74	69
4	61	52
5	101	99
6	64	-63
7	0	9
8	86	-78
9	73	-71
10	0	-20
11	81	-61
12	28	33
13	0	-15
14	57	50
15	39	32
H, K = 5, 5		
1	0	-21
2	148	-134
3	0	0
4	35	18
5	37	26
6	81	81
7	0	0
8	60	-52
9	10	-14
10	0	-15
11	0	14
12	33	42
H, K = 5, 6		
1	111	105
2	126	139
3	0	-4
4	111	117
5	60	-48
6	0	-20
7	32	-22
8	133	-137
9	33	34
10	22	-26
11	44	38
12	58	65
13	0	15
14	40	42
H, K = 5, 7		
1	21	22
2	0	18
3	93	81
4	0	-19
5	64	46
6	0	3
7	95	-88
8	0	0
9	39	50
10	17	-18
11	61	56
H, K = 5, 8		
1	81	74
2	0	17
3	0	0
4	0	-9
5	138	-132
6	0	16
7	80	-91
8	0	27
9	68	58
10	0	0
11	76	83
H, K = 5, 9		
1	38	37
2	92	-87
3	47	-33
4	0	6
5	0	-4
H, K = 5, 10		
1	34	28
2	114	-109
3	0	-14
4	75	-67
5	0	-20
6	57	57
7	0	2
8	57	62
9	0	9
10	32	20
H, K = 6, 0		
0	109	-110
2	0	-12
4	128	130
6	61	66
8	0	14
10	21	-10
12	32	-29
14	0	13
16	27	37
H, K = 6, 1		
0	186	-196
1	178	-191
2	0	-22
3	245	-285
4	207	223
5	95	98
6	66	64
7	175	181
H, K = 6, 2		
0	165	163
1	77	73
2	0	-18
3	93	89
4	0	1
5	0	9
6	16	32
7	71	-57
8	0	16
9	70	-52
H, K = 6, 3		
0	125	-132
1	19	-25
2	138	-124
3	0	8
4	35	-3
5	77	66
6	204	196
7	47	35
8	22	31
9	39	-49
10	182	-168
11	28	-13
12	53	-41
13	54	43
14	59	56
H, K = 6, 4		
0	66	81
1	16	-20
2	44	40
3	0	14
4	0	5
5	14	26
6	54	-50
7	0	-5
8	0	15
9	0	-18
10	39	61
H, K = 6, 5		
0	69	-75
1	0	8
2	0	-1
3	24	16
4	49	44
5	129	108
6	0	-3
7	79	-68
8	0	9
9	161	-151
10	21	18
11	40	34
12	21	-19
13	87	73
H, K = 6, 6		
0	111	120
1	34	21
2	0	4
3	0	-10
4	53	-28
H, K = 6, 7		
0	197	196
1	31	33
2	18	17
3	47	38
4	119	-122
8	48	43
12	35	30
13	35	39
H, K = 6, 8		
0	63	47
1	43	-52
2	0	9
3	26	-52
4	0	6
5	0	13
H, K = 6, 9		
0	84	75
1	98	-96
2	51	37
3	131	-128
4	93	-82
5	51	44
6	91	-92
7	74	65
H, K = 6, 10		
6	60	52
H, K = 6, 11		
0	0	14
1	0	-34
2	0	-5
3	85	-104
4	0	20
5	43	-38
6	47	49
7	69	87
8	33	10
9	52	69
H, K = 7, 0		
2	40	-56
4	282	-262
6	25	21
8	162	163
10	62	60
12	104	-104
14	61	-58
H, K = 7, 1		
1	0	-19
2	123	132
3	0	-18
4	43	37
5	119	132
6	62	-54
7	91	97
11	72	-85
15	36	56
H, K = 7, 2		
1	75	-97
2	108	-103
3	0	24
4	29	22
5	146	157
6	58	41
7	61	66
8	0	-6
9	64	-63
10	0	24
11	82	-89
H, K = 7, 3		
1	88	82
2	100	104
3	62	-70
4	80	79
5	0	-21
6	0	-37
7	67	37
8	104	-88
H, K = 7, 4		
1	95	-83
2	186	200
3	67	57
4	0	-16
5	18	21
6	73	-65
H, K = 7, 5		
1	140	123
2	86	80
3	29	-20
4	0	-19
5	30	-39
6	31	-37
7	32	-7
8	31	18
9	79	67
H, K = 7, 6		
1	83	80
2	66	57
3	55	-39
4	79	73
5	0	-6
6	0	-3
7	0	16
8	105	-92
H, K = 7, 7		
1	74	59
H, K = 7, 8		
1	0	35
2	60	70
5	105	-102
7	83	-71
11	71	64
H, K = 7, 9		
2	0	-9
3	60	27
4	84	-60
5	72	65
6	0	-6
7	16	21
8	34	53
H, K = 8, 0		
0	57	-45
2	72	-74
4	144	156
6	167	187
8	0	-2
10	66	-88
H, K = 8, 1		
0	121	-127
1	36	39
2	29	-35
3	40	-38
4	96	103
5	57	-45
H, K = 8, 2		
0	195	-215
1	55	47
2	0	-7
3	127	125
4	137	153
5	38	31
6	0	0
7	89	-85
H, K = 8, 3		
0	83	-90
1	133	109
2	34	-30
3	123	100
H, K = 8, 4		
0	173	160
1	96	94
2	0	24
3	81	83
7	61	-66
8	0	-2
9	74	-53
12	67	50
H, K = 8, 5		
0	85	-66
1	105	76
2	0	0
3	76	51
4	42	46
5	80	-13
H, K = 9, 0		
2	82	-101
4	0	-31
6	55	74
8	0	1
10	0	-6
H, K = 9, 1		
1	80	-90
2	101	119
3	76	74
4	0	29
5	141	139
6	61	-64
7	0	10
8	0	18
H, K = 9, 3		
8	177	-164
H, K = 9, 5		
1	151	123
2	45	45
3	27	21
4	0	1
5	92	-84
6	0	-11
7	111	-101
8	0	10
9	102	95
10	0	-11
11	95	101
H, K = 10, 0		
0	0	30
2	67	-62
4	0	11
6	103	120
8	46	45
10	58	-73
12	42	-52
H, K = 10, 1		
4	52	-67
H, K = 10, 2		
0	44	-35
3	109	101
H, K = 10, 4		
0	228	216
1	87	89
2	35	26
3	98	98
4	116	-118

mounted on a fused quartz slide. This slide was placed on a copper stage and cooled to near the temperature of liquid nitrogen, and the absorption spectra were measured through the crystal on the aperture of the copper stage. By using a small amount of grease on the slide, the crystal was fixed with its faces upright; its thickness was estimated with a micrometer eyepiece to be about 2μ. A thermocouple indicated that the crystal was cooled to 90°K in the low-temperature studies.

Structure Determination

As there are four formula units, $[(NH_3)_5Cr\text{–}O\text{–}Cr(NH_3)_5]Cl_4\cdot H_2O$, in a unit cell, the space group symmetry (*Pbca*) requires the bridging oxygen atom of the complex to lie on a special position with inversion symmetry. Therefore, the binuclear basic rhodochromic complex should have a center of symmetry, and the Cr–O–Cr group should be strictly linear. The position of the chromium atom was deduced from a three-dimensional Patterson map. The chloride ions and the nitrogen atoms were easily located by a series of three-dimensional Fourier syntheses. After these atomic positions were refined by several cycles of block-diagonal-matrix least-squares refinement, the discrepancy factor, R, defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o||$ was reduced to 0.21. At this stage, a difference Fourier synthesis was calculated to search for the position of the water molecule of crystallization, whose presence was also confirmed by infrared spectroscopy. A relatively low electron density peak was found at the general position of $x=0.04$, $y=0.44$, and $z=0.06$. Thus, the oxygen atom of the water molecule with a multiplicity of 0.5 was placed at this position, and after several cycles of the block-diagonal-matrix least-squares refinement with isotropic temperature factors, R was reduced to 0.15. Finally, a refinement using the anisotropic temperature factors for all atoms led to $R=0.14$ (0.11 for non-zero reflections). In the final least-squares refinement, the weights were assumed to be $w=1$ for $F_o \geqq 3.6$ and $w=0.5$ for $F_o<3.6$. The final atomic coordinates and the temperature factors are given in Table 2, and their standard deviations are in Table 3. The observed and calculated structure factors are listed in Table 1. The atomic scattering factors used in the calculations were taken from the International Tables for X-ray Crystallography.[17] All the computations were done on a HITAC 5020E computer at the Computer Center of the University of Tokyo, using the library program system UNICS.

Results and Discussion

Crystal Structure. A perspective drawing of the basic rhodochromic ion is shown in Fig. 2. The bond distances and angles, with their standard deviations, are listed in Tables 4 and 5. The basic rhodochromic ion has the center of symmetry as already described;

TABLE 2. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

Anisotropic temperature factors are expressed in the form $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.0514	0.0956	0.0950	0.00286	0.00297	0.00296	0.00044	−0.00043	0.00018
Cl(1)	0.2938	0.4841	0.3661	0.00789	0.01125	0.00607	0.00635	0.00233	0.00421
Cl(2)	0.3844	0.2312	0.1487	0.00604	0.00615	0.00515	−0.00045	−0.00030	0.00139
N(1)	0.2031	0.0083	0.1063	0.00664	0.00180	0.00523	0.00216	0.00265	0.00037
N(2)	−0.0174	−0.0055	0.2078	0.00629	0.00688	0.00573	−0.00027	0.00454	0.00653
N(3)	−0.0992	0.1899	0.0926	0.00247	0.00229	0.00488	0.00185	0.00141	−0.00132
N(4)	0.1227	0.2052	−0.0131	0.00800	0.00426	0.00695	0.00051	0.00643	0.00256
N(5)	0.1112	0.2086	0.2092	0.00624	0.01278	0.00528	−0.00620	0.00353	−0.00787
H_2O	0.0376	0.4355	0.0598	0.00683	0.00510	0.00851	−0.00539	−0.00385	0.00200
O	0.0000	0.0000	0.0000	0.00463	0.00700	0.00385	0.00089	−0.00484	−0.00179

TABLE 3. ESTIMATED STANDARD DEVIATIONS

$\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ in Å, (B) in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Cr	0.0034	0.0030	0.0029	0.00024	0.00024	0.00015	0.00047	0.00041	0.00037
Cl(1)	0.0067	0.0072	0.0064	0.00064	0.00073	0.00041	0.00117	0.00086	0.00098
Cl(2)	0.0059	0.0059	0.0058	0.00052	0.00054	0.00037	0.00090	0.00076	0.00073
N(1)	0.0167	0.0151	0.0161	0.00168	0.00135	0.00112	0.00250	0.00227	0.00213
N(2)	0.0184	0.0192	0.0171	0.00183	0.00174	0.00126	0.00280	0.00239	0.00250
N(3)	0.0131	0.0144	0.0162	0.00128	0.00131	0.00102	0.00209	0.00200	0.00204
N(4)	0.0194	0.0159	0.0189	0.00194	0.00166	0.00138	0.00275	0.00267	0.00246
N(5)	0.0194	0.0205	0.0179	0.00177	0.00239	0.00132	0.00344	0.00259	0.00288
H_2O	0.0312	0.0270	0.0309	0.00297	0.00270	0.00241	0.00482	0.00436	0.00401
O	0.0000	0.0000	0.0000	0.00175	0.00199	0.00124	0.00304	0.00241	0.00275

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17) International Table for X-ray Crystallography Vol. III, Kynoch Press, Birmingham (1952).

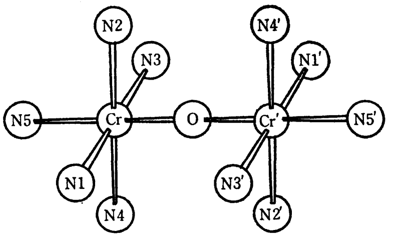

Fig. 2. Perspective drawing of the basic rhodochromic complex ion, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}$.

Table 4. Interatomic distances in the complex cation, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}$
(e.s.d.'s are given in parentheses)

Cr-O	1.803(3) Å	N(1)-N(2)	2.97(2)
Cr-Cr	3.607(4)	N(1)-N(3)	4.19(2)
Cr-N(1)	2.09(2)	N(1)-N(4)	2,97(2)
Cr-N(2)	2.09(2)	N(1)-N(5)	2.93(3)
Cr-N(3)	2.11(2)	N(1)-N(3)'	3.75(3)
Cr-N(4)	2.11(2)	N(2)-N(3)	2.93(2)
Cr-N(5)	2.14(2)	N(2)-N(4)	4.20(3)
Cr-N(1)'	4.24(2)	N(2)-N(5)	2.94(3)
Cr-N(2)'	4.23(2)	N(2)-N(4)'	3.72(3)
Cr-N(3)'	4.22(2)	N(3)-N(4)	3.01(2)
Cr-N(4)'	4.24(2)	N(3)-N(5)	2.97(2)
Cr-N(5)'	5.75(2)	N(3)-N(1)'	3.75(3)
O-N(1)	2.81(2)	N(4)-N(5)	2.98(3)
O-N(2)	2.79(2)	N(4)-N(2)'	3.72(3)
O-N(3)	2.81(2)		
O-N(4)	2.82(2)		
O-N(5)	3.95(2)		

Table 5. Bond angles in the complex cation, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}$
(e.s.d.'s are given in parentheses)

O-Cr-N(1)	92.4(4)°	N(2)-Cr-N(3)	88.5(7)
O-Cr-N(2)	91.4(5)	N(2)-Cr-N(4)	176.8(7)
O-Cr-N(3)	91.4(4)	N(2)-Cr-N(5)	88.0(7)
O-Cr-N(4)	91.7(5)	N(3)-Cr-N(4)	90.8(7)
O-Cr-N(5)	179.4(5)	N(3)-Cr-N(5)	88.4(7)
N(1)-Cr-N(2)	90.6(7)	N(4)-Cr-N(5)	88.9(7)
N(1)-Cr-N(3)	176.1(6)		
N(1)-Cr-N(4)	89.9(7)		
N(1)-Cr-N(5)	87.8(7)		

therefore, the Cr–O–Cr oxygen bridging system is linear. Each N_1–Cr–N_2, N_2–Cr–N_3, N_3–Cr–N_4, and N_4–Cr–N_1 angle is nearly 90°, and the N_5–Cr–O angle is approximately 180°, as is shown in Table 5, the complex roughly has a four-fold rotation axis passing through a sequence of the N_5–Cr–O–Cr′–N'_5 atoms. Hence, the basic rhodochromic complex ion must have an approximately D_{4h} symmetry. Hewkin and Griffith[18] have reported, in their infrared spectroscopic studies of the binuclear transition metal complexes, that the basic rhodochromic complex chloride shows the absorption band assigned to the asymmetric stretching vibration of the Cr–O–Cr group at almost the same position as in the similar oxo-bridged binuclear complexes, $K_4[Cl_5Ru\text{–}O\text{–}RuCl_5]$[19] and $K_4[Cl_5Re\text{–}O\text{–}ReCl_5]$,[20] both of which have been confirmed to be of the D_{4h} symmetry by the X-ray method (Table 6). They also suggested that, in the case of the linearly oxygen-bridged transition metal binuclear complexes, the asymmetric stretching vibrations of the bridge atoms are almost independent of the mass of the metal atoms involved, assuming that the Cr–O–Cr group in the basic rhodochromic complex is linear. The results of the present X-ray work are consistent with these findings.

Table 6. Infra-red absorption data[a)]

Complex	M-O-M asym. str.	M-O-M sym. str.
$K_4[Cl_5Ru\text{-}O\text{-}RuCl_5]\cdot H_2O$	866 cm^{-1}	226 cm^{-1}
$K_4[Cl_5Re\text{-}O\text{-}ReCl_5]\cdot H_2O$	885	230
$[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]Cl\cdot H_2O$	873	215

a) Date from ref. 18.

The Cr–O distance is 1.80 Å, which is quite short compared with the values found in the rhodochromic complex ion, $[(NH_3)_5Cr\text{–}OH\text{–}Cr(NH_3)_5]^{5+}$, (Cr–O 2.00 Å);[1a)] it is comparable to that in $K_4[Cl_5Ru\text{–}O\text{–}RuCl_5]$ (Ru–O 1.80 Å) and in $K_4[Cl_5Re\text{–}O\text{–}ReCl_5]$ (Re–O 1.86 Å). Dunitz and Orgel[21], to explain the diamagnetic properties of $[Cl_5Ru\text{–}O\text{–}RuCl_5]^{4+}$, elucidated its electronic structure by means of a molecular orbital model, which allowed the unpaired electrons of ruthenium(IV) to couple through the bridging oxygen. The linear Cr–O–Cr system and its short bond distance certainly suggest the presence of an extensive π-bonding in this system, as in the ruthenium complex. The remarkably reduced magnetic susceptibilities and the unusual electronic spectra of the basic rhodochromic complex are certainly due to this π-bonding.

The basic aqueous solutions of the acido-erythrochromic complex salts show a characteristic blue color, although it fades out rapidly. The absorption spectra of these blue solutions,[13] similar to those of the basic rhodochromic complex ion, are characterized by one broad band in the visible region and several sharp bands in the near-ultraviolet region, indicating that these blue chemical species also contain the linear Cr–O–Cr system.

Several other binuclear transition metal complexes have been known to have a linear M–O–M group, as confirmed by the X-ray method. They are listed in Table 7, along with their M–O distances and M–O–M angles. All of them show the distinctive feature of the short M–O distance, strongly indicating the presence of the π-bonding character in these systems.

Some Cr–N bond distances of the basic rhodochro-

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[18] D. J. Hewkin and W. P. Griffith, *J. Chem. Soc.*, **1966**, 472.

[19] A. G. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Crystallogr.*, **5**, 185 (1952).

[20] L. C. Morrow, *ibid.*, **15**, 851 (1962).

[21] J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, **1953**, 2594.

TABLE 7. BINUCLEAR COMPLEXES CONTAINING LINEAR M-O-M

Complex	M-O distance	M-O-M angle	Ref.
$K_4[Cl_5Ru\text{-}O\text{-}RuCl_5]\cdot H_2O$	1.80Å	180°	19
$K_4[Cl_5Re\text{-}O\text{-}ReCl_5]\cdot H_2O$	1.86	180	20
$[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]Cl_4\cdot H_2O$	1.80	180	present work
$[(C_5H_5)Cl_2Ti\text{-}O\text{-}TiCl_2(C_5H_5)]$	1.78	180	22
[pyPcMn-O-MnPcpy][a]	1.71	178	23
$[Mo_2O(O)_2(C_2H_5OCS_2)_4]$	1.851, 1.872	178.03	24
$K_2[Mo_2O(O_2)_2(C_2O_4)_2(H_2O)_2]$	1.876	180	25
$K_2[Ti_2O_5(H_3NC_7O_4)_2]\cdot 5H_2O$	1.825	178.1	26
$[(H_2O)BFe\text{-}O\text{-}FeB(H_2O)](ClO_4)_4$[b]	1.8	180	28
$K_3[(H_2O)Cl_4Ru\text{-}N\text{-}RuCl_4(H_2O)]$	1.718 (M-N)	180	27

a) py: pyridine Pc: phthalocyanine

b) B: 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene

mic complex ion had been expected to be significantly longer than others, since a transformation reaction from the basic rhodochromic complex to the red basic erythrochromic complex takes place very rapidly in an aqueous solution, substituting an OH^- group for one of the ammonia molecules. Indeed, the $Cr\text{–}N_5$ distance (2.14 Å) was observed to be somewhat longer than the others. However, its difference from the other Cr–N distances (average value 2.10 Å) did not exceed three times the estimated standard deviation.

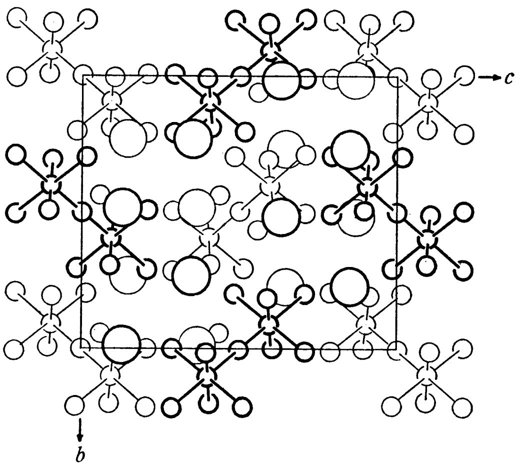

Fig. 3. Crystal structure viewed along the *a* axis.

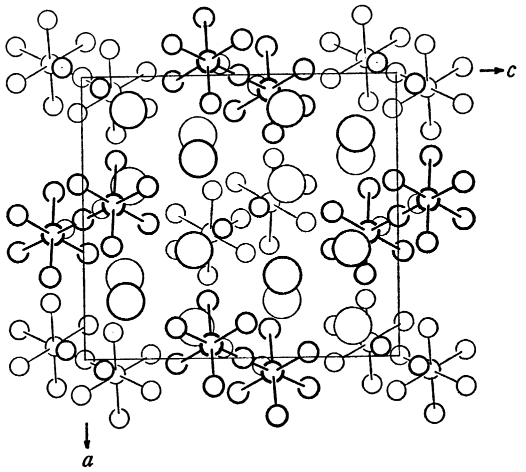

Fig. 4. Crystal structure viewed along the *b* axis.

The crystal structures viewed along the *a* and *b* axes are shown in Figs. 3 and 4 respectively. The complexes are arranged as shown in Fig. 4 by bold lines or fine lines, retaining the bridging oxygen atoms on the same planes, which are alternately piled up back to back, sliding along the *b* axis with a half unit for each layer. The chloride ions are packed into channels elongated along the *b* axis between these piles. The water of crystallization is located in the space surrounded by the six complex ions. The shortest $Cl^-\cdots N(NH_3)$ approach appears at a distance of 3.32 Å.

Visible and Ultraviolet Absorption Spectra. The visible and ultraviolet absorption spectra of the basic rhodochromic complex salts, which cannot be measured easily in an aqueous solution because of their rapid hydrolysis, have been studied by several methods, *e.g.*, the extrapolation of the aqueous solution spectrum,[14] the diffuse reflectance method,[9,15] the rapid-flow method,[13] and the microspectroscopic technique.[16,29]

As has already been stated, it has been found in these spectroscopic studies that the basic rhodochromic complex ion shows some unfamiliar sharp absorption bands in the near-ultraviolet region. Furthermore, Kondo[16] has pointed out that these sharp bands are strongly polarized, and recently Dubicki *et al.*[15] have found that some of these sharp bands disappear at the temperature of liquid nitrogen.

The crystal structure of the basic rhodochromic chloride monohydrate has been determined in the present X-ray studies; hence, it has become possible to relate the single-crystal polarized absorption spectra

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22) P. Corrakini and G. Allegra, *J. Amer. Chem. Soc.*, **81**, 5510 (1959).

23) L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

24) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, **86**, 3024 (1964).

25) F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

26) D. Schwarzenbach, *Inorg. Chem.*, **9**, 2391 (1970).

27) M. Ciechanowicz and A. C. Skapski, *Chem. Commn.*, **1969**, 574.

28) E. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, **89**, 720 (1967).

29) M. Morita and S. Shionoya, *J. Phys. Soc. Jap.*, **28**, 134 (1970).

of the complex salt to the orientation of the dimeric unit. Unfortunately, single-crystals of basic rhodochromic chloride monohydrate, although they exhibit a dichroism (blue through light polarized parallel to the *a* axis, greenish-blue through light polarized parallel to the *c* axis), are unsuitable for study by means of the microspectroscopic technique because of their shape (Fig. 1). However, a similar dichroism can be observed more distinctly in thin plates of the crystals of the perchlorate, and they *are* suitable for microspectroscopic study. As the color of the chloride crystal has already been related to the orientation of the complex. it seems reasonable to say that the absorption parallel to the four-fold rotation axis of the complex contributes greatly to the polarized absorption spectrum along the extinction direction of the perchlorate crystal that shows greenish-blue with polarized light having a parallel electric vector.

The single-crystal polarized absorption spectra of the basic rhodochromic perchlorate monohydrate along two extinction directions are shown in Fig. 5.

The absorption spectra at room temperature consist of two broad bands in the 16600 and 22000 cm^{-1} regions, of three strong sharp bands at 25350, 26630, and 29830 cm^{-1}, and of at least four weak sharp bands at 14320, 23920, 28010, and 28320 cm^{-1}. These sharp bands were found to be all polarized along the four-fold rotation axis of the complex, while the broad band in the 16600 cm^{-1} region seems to be slightly reduced in intensity along the four-fold rotation axis. When the crystal was cooled to about 90°K, a new band was revealed at 32400 cm^{-1}; it was found also to be polarized along the four-fold rotation axis. The intensity of the strong sharp band at 26630 cm^{-1} was considerably sensitive to the temperature, as has already been pointed out by Dubicki *et al.* It had almost disappeared in the 90°K spectrum, implying that this band originated from the thermally-excitable electronic level above the ground state.

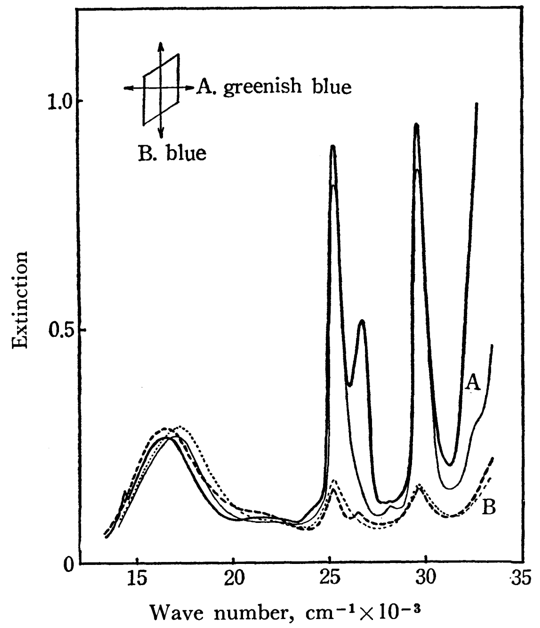

Fig. 5. Polarized absorption spectra of the basic rhodochromic perchlorate, $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5](ClO_4)_4\cdot H_2O$. —— and ----: at room temperature, —— and ······: at 90°K

The electronic spectra of the basic rhodochromic complex are very difficult to characteriz. Furthermore, no other polynuclear transition metal complexes have been found to show sharp absorption bands similar to those of the basic rhodochromic complex. If the electronic structure of the basic rhodochromic complex can be described in terms of the molecular orbital model,[15,21] the ordering of the molecular orbitals of the binuclear complex of D_{4h} symmetry can be expected to be;

$$e_u,\ (b_{2g},\ b_{1u},\ e_g),\ e_u{}^*.$$

These orbitals should be filled with ten electrons in the case of the basic rhodochromic complex. That the relative energies of the non-bonding b_{2g}, b_{1w}, and e_g orbitals are not known makes the problem very complicated. Recently, Schmidtke[30] has described the electronic structure of the basic rhodochromic complex in further detail, assuming the complex to have a D_{4h} or D_{4d} symmetry; he has pointed out that the $d_z{}^2$ orbitals of the metals should be coupled with the oxygen p_z orbital in either symmetry case to produce a higher-energy anti-bonding a_{2u} orbital than these molecular orbitals. He assigned the sharp band at 25350 cm^{-1} to the electronic transition from the metal-localized b_{2g} or b_{1u} orbital to the delocalized $a_{2u}{}^*$ orbital with some vibrational structures, and the band at 29830 cm^{-1} to that from the metal-localized e_g orbital to the delocalized $a_{2u}{}^*$ orbital.

However, that the intensity of the band at 26630 cm^{-1} is considerably sensitive to the temperature compared with that of the band at 25350 cm^{-1} leads to some confusion. If the same excited state is concerned, the "hot" band should appear on the lower-wave-number side of the band from the ground state. Thus, as Dubicki has suggested, it seems that some selection rule, perhaps the spin one,[31] has a strong influence upon the appearance of the absorption spectra in this region. These electronic transitions are possibly coupled with some vibrational modes of the complex. The results of the present polarized spectroscopy indicate that each direct product of the representations of the (vibronic) wavefunctions of the ground state and the excited state concerned with these sharp bands should contain not E_u but A_{2u}. Only such conditions can lead to the z polarization of the absorption bands of the complex in the D_{4h} symmetry.

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30) H. H. Schmidtke, *Theor. Chim. Acta*, **20**, 92 (1971).

31) B. Jezowska–Trzebiato ska and W. Wojciechoeski, "Theory and Structure of Complex Compounds," Wroclaw (1962), p. 375.