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The Solid State Structure of Dioxodichlorobis(N,N-dimethylformamido)molybdenum(VI)

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The solid-state structure of dioxodichlorobis(N,N-dimethylformamido)molybdenum(VI) has been determined from single-crystal X-ray diffraction data collected by standard film techniques. The structure has been refined isotropically by least-squares methods to a conventional R factor of 9.9% for 1438 nonzero reflections. $Mo[(CH_3)_2NCHO]_2O_2Cl_2$ crystallizes in the monoclinic space group C2/c with a = 20.90 Å, b = 7.717 Å, c = 11.99 Å, and β = 139° 52′. An experimental density of 1.81 g/cc agrees well with the calculated density of 1.78 g/cc based on four molecules per unit cell (Z = 4). The discrete monomeric molecules possess crystallographically required C_2 symmetry. The molybdenum to terminal oxygen bond length ($Mo-O_t$) is 1.68 (1) Å while the molybdenum to dimethylformamido oxygen bond length ($Mo-O_l$) is 2.20 (1) Å; the Mo–Cl distance is 2.341 (7) Å. Both the oxo ligands and the dimethylformamido ligands are *cis* to one another; the chloro ligands are *trans* to one another. Distortions are observed in the idealized octahedral coordination of the molybdenum atom: O_t-Mo-O_t, 102.2 (7)°; O_l-Mo-O_l, 76.2 (5)°; and Cl–Mo–Cl, 161.3 (2)°.

Introduction

The solid-state structures of only a few mixed-ligand molybdenum(VI) structures have been reported. $NaNH_4[MoO_3(C_2O_4)]\cdot 2H_2O$ has an infinite chain structure with approximate octahedral coordination of molybdenum atoms unsymmetrically bridged by oxo ligands;[3] $K_2[MoO_2(C_2O_4)(H_2O)]_2O$ has a dinuclear structure with a symmetrically bridging oxo ligand;[4] $MoO_3(H_2NCH_2CH_2NHCH_2CH_2NH_2)$ is a discrete molecular complex with the tridentate amine occupying three coordination sites on the distorted octahedrally coordinated molybdenum atom.[5] A variety of mixed-ligand molybdenum(VI) and tungsten(VI) complexes that contain unidentate ligands only have been prepared and characterized.[6-8] This study reports the first solid-state structure determination of the latter class of molybdenum(VI) coordination compounds.

Experimental Section

Crystals of $Mo[(CH_3)_2NCHO]_2O_2Cl_2$ were supplied by Dr. Till J. N. Peters of Dr. Mark Chamberlain's laboratory at Western Reserve University.

Single-Crystal Data.—Multiple-film equiinclination Weissenberg data were collected at room temperature for the reciprocal levels $h0l$ through $h8l$ with Zr-filtered Mo Kα radiation (λ 0.7107 Å). The intensities of 1438 independent reflections were estimated visually and were corrected for Lorentz-polarization effects. The crystal chosen for data collection was 1.7 mm in length and 0.40 × 0.52 mm in width and was mounted with the long dimension coincident with the rotation axis. The linear absorption coefficient for Mo Kα radiation is 15.4 cm^{-1}; μR varies from 0.32 to 0.40. No corrections were made for absorption errors. The maximum variation in intensity over the range of observed reflections is 15% for any reciprocal level of data. Separate scale factors for each reciprocal level of data were used in the refinement in order to minimize errors due to absorption. Mo Kα radiation was used to determine lattice constants from $0kl$ and $hk0$ precession photographs which were calibrated by superposition of a sodium chloride diffraction pattern (a = 5.627 Å). The angle β was determined from the $h0l$ Weissenberg photograph. The accuracy in measurement of spot positions on the photographs was used to estimate lattice constant errors.

Unit Cell and Space Group.—Crystals of $Mo[(CH_3)_2NCHO]_2O_2Cl_2$ are monoclinic with lattice parameters a = 14.05 ± 0.02 Å, b = 7.717 ± 0.02 Å, c = 11.99 ± 0.02 Å, and β = 106° 29′ ± 15′. Systematic absences of hkl reflections for $h + k + l$ odd and $h0l$ reflections with h odd indicate the probable space groups Ia or I2/a. Before solution of the structure, indices were transformed to conform with the standard choice of space group Cc (C_s^4) or C2/c (C_{2h}^6).[9] Lattice parameters for the new unit cell are a = 20.90 ± 0.04 Å, b = 7.717 ± 0.02 Å, c = 11.99 ± 0.02 Å, and β = 139° 52′ ± 20′. The volume of the unit cell is 1247 Å^3. An experimental density of 1.81 ± 0.06 g/cc determined by the flotation method agrees well with the calculated density of 1.78 g/cc based on four molecules per unit cell. The space group C2/c was confirmed by solution of the structure. The molybdenum atoms are located on twofold axes corresponding to sets of fourfold positions (4e), and the remaining atoms occupy general eightfold positions (8f). The positions are: 4e $(0, 0, 0;\ ^1/_2, ^1/_2, 0) \pm (0, y, ^1/_4)$ and 8f $(0, 0, 0;\ ^1/_2, ^1/_2, 0) \pm [x, y, z;\ x, -y, ^1/_2 - z)$. The total number of electrons per unit cell, $F(000)$, is 688.

Determination of the Structure.—A three-dimensional Patterson function[10] provided a trial coordinate for the molybdenum atom. The intensity coefficients in the Patterson calculation were scaled approximately on the basis of exposure times for the different reciprocal levels of data. A structure factor calculation with only the molybdenum atom placed resulted in an unweighted discrepancy factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, of 29%. The phases from this structure factor calculation were used to calculate a three-dimensional electron density map.[11] All atoms (except hydrogens) were located from the peaks in this synthesis. Addition of these atoms to the structure factor calculation lowered the discrepancy index, R_1, to 22.5%. Six cycles of full-matrix isotropic least-squares refinement[12] of the eight nonhydrogen atoms in the asymmetric unit minimizing $\Sigma w(F_o - F_c)^2$

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TABLE I

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	x	y	z	B, Å^2
Mo	0.5000 (−)	0.4586 (2)	0.2500 (−)	1.43 (3)
Cl	0.3678 (2)	0.4094 (4)	0.1963 (4)	2.69 (5)
O_1	0.4395 (6)	0.5951 (13)	0.0843 (11)	2.7 (1)
O_2	0.4361 (5)	0.2341 (11)	0.0773 (9)	2.0 (1)
C_1	0.4275 (7)	0.2193 (14)	−0.0409 (13)	2.0 (2)
C_2	0.3730 (10)	0.0853 (21)	−0.2808 (18)	3.4 (2)
C_3	0.3172 (11)	−0.0210 (23)	−0.1671 (20)	3.9 (3)
N	0.3760 (6)	0.1004 (12)	−0.1559 (11)	2.0 (1)

[a] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits; (−) indicates a fixed parameter.

TABLE II

H	L	FO	FC
	K = 0		
0	2	253	211
0	4	101	93
0	6	77	77
0	10	34	29
0	12	31	26
2	2	19	10
2	4	72	67
2	6	55	56
2	10	39	39
4	2	34	17
4	4	94	97
4	6	83	88
4	8	45	46
4	10	36	40
6	2	138	138
6	4	107	119
6	6	60	61
6	8	36	40
8	2	131	131
8	4	54	60
10	2	55	58
12	2	42	49
12	4	39	41
12	6	26	33
14	2	45	52
14	4	31	33
16	2	33	34
-2	4	127	139
-2	6	175	191
-2	8	105	115
-2	10	34	39
-2	12	32	25
-4	0	83	47
-4	4	63	66
-4	6	115	124
-4	8	123	136
-4	10	43	47
-4	12	47	49
-4	14	34	33
-6	0	89	85
-6	2	251	241
-6	6	68	45
-6	8	64	74
-6	10	34	37
-6	12	55	56
-6	14	46	45
-8	0	109	112
-8	2	304	286
-8	4	227	191
-8	6	41	52
-8	8	88	89
-8	10	50	44
-8	12	29	20
-8	14	29	26
-10	0	38	39
-10	2	114	115
-10	4	278	219
-10	6	191	165
-10	8	143	136
-10	10	109	119
-10	12	34	26
-10	14	29	19
-10	16	27	25
-12	0	23	26
-12	2	37	23
-12	4	91	91
-12	6	110	111
-12	8	65	77
-12	10	146	148
-12	12	70	71
-12	14	54	46
-12	16	43	39
-14	0	79	90
-14	2	44	42
-14	4	85	91
-14	6	57	61
-14	8	41	27
-14	10	67	61
-14	12	67	66
-14	14	57	56
-14	16	48	45
-14	18	30	26
-16	0	76	92
-16	2	80	85
-16	4	101	100
-16	6	101	100
-16	8	36	41
-16	10	35	40
-16	12	57	56
-16	14	29	25
-16	16	28	20
-16	18	34	32
-18	2	32	38
-18	4	55	53
-18	6	124	126
-18	8	153	150
-18	10	81	74
-18	12	75	75
-18	14	30	25
-18	16	35	30
-20	2	21	31
-20	6	48	54
-20	8	90	91
-20	10	55	43
-20	12	94	89
-20	14	72	76
-20	16	45	41
-20	18	38	30
-22	2	41	50
-22	4	18	27
-22	12	70	52
-22	14	71	70
-22	16	50	48
-22	18	34	27
-22	20	34	26
-24	2	32	38
-24	4	38	42
-24	6	39	42
-24	8	45	51
-24	14	23	26
-24	16	31	28
-24	20	34	33
-26	6	36	39
-26	8	52	54
-26	10	71	76
-26	12	34	31
-26	14	35	34
-26	16	26	33
-28	10	48	51
-28	12	48	42
-28	14	56	49
-28	16	47	49
-28	18	25	27
-30	14	32	31
-30	16	45	38
-30	18	40	37
	K = 1		
1	2	43	46
1	3	22	17
1	4	63	56
1	6	71	64
1	8	43	40
1	10	29	28
1	12	18	24
3	1	65	45
3	2	46	44
3	4	58	56
3	6	52	54
3	8	46	51
3	10	33	41
5	2	116	107
5	3	58	47
5	4	113	112
5	5	30	30
5	6	56	65
5	8	33	39
5	10	24	26
7	1	53	44
7	2	111	106
7	3	41	40
7	4	74	81
7	6	31	37
7	8	20	20
9	1	23	22
9	2	56	60
9	4	27	36
9	6	23	24
11	1	17	17
11	2	31	39
11	4	21	29
11	6	23	29
13	1	28	28
13	2	44	43
13	4	29	36
15	2	38	49
-1	3	82	73
-1	4	178	167
-1	5	51	42
-1	6	126	111
-1	7	30	27
-1	8	41	39
-1	10	19	16
-1	12	20	21
-3	3	32	29
-3	4	107	101
-3	6	125	112
-3	7	49	48
-3	8	86	89
-3	10	53	57
-3	12	34	37
-3	14	22	19
-5	0	88	91
-5	1	81	55
-5	3	63	49
-5	4	30	24
-5	6	98	86
-5	7	37	26
-5	8	117	110
-5	9	31	32
-5	10	76	78
-5	12	41	47
-5	14	25	29
-7	0	129	117
-7	1	48	33
-7	2	199	161
-7	4	167	127
-7	5	27	24
-7	6	78	60
-7	8	73	59
-7	9	28	18
-7	10	44	40
-7	12	32	33
-7	14	36	37
-7	16	19	26
-9	0	81	80
-9	1	21	14
-9	2	173	146
-9	3	132	95
-9	4	223	189
-9	5	97	75
-9	6	119	103
-9	8	91	79
-9	9	26	21
-9	10	53	51
-9	11	21	13
-9	12	32	26
-9	14	33	27
-9	16	21	22
-11	0	34	40
-11	2	67	72
-11	3	53	46
-11	4	180	141
-11	6	142	119
-11	7	25	24
-11	8	131	113
-11	9	54	50
-11	10	109	100
-11	11	22	23
-11	12	55	57
-11	14	31	30
-11	16	19	18
-13	0	62	68
-13	2	42	51
-13	4	44	54
-13	5	25	10
-13	6	51	54
-13	8	74	70
-13	9	36	30
-13	10	109	102
-13	11	43	39
-13	12	85	85
-13	13	18	21
-13	14	47	49
-13	16	32	33
-15	0	57	65
-15	2	60	61
-15	4	55	68
-15	5	23	20
-15	6	90	87
-15	7	24	25
-15	8	54	55
-15	9	23	16
-15	10	43	48
-15	12	58	49
-15	14	40	39
-15	16	39	41
-15	18	27	31
-17	0	29	36
-17	2	56	63
-17	4	99	93
-17	5	52	41
-17	6	143	117
-17	7	48	39
-17	8	87	68
-17	10	41	35
-17	11	16	14
-17	12	40	38
-17	14	37	31
-17	16	33	29
-17	18	29	24
-19	2	23	38
-19	4	31	40
-19	6	62	62
-19	7	33	23
-19	8	93	78
-19	9	39	28
-19	10	96	84
-19	11	37	33
-19	12	82	81
-19	13	22	19
-19	14	52	51
-19	16	27	20
-19	18	21	14
-21	2	19	28
-21	6	19	33
-21	8	51	61
-21	9	25	26
-21	10	70	67
-21	12	68	64
-21	13	30	26
-21	14	59	59
-21	16	37	38
-21	18	27	29
-23	2	26	32
-23	4	31	41
-23	6	31	40
-23	8	28	42
-23	14	45	45
-23	16	42	45
-23	18	36	37
-23	20	25	25
-25	4	26	36
-25	6	34	40
-25	8	46	47
-25	10	37	42
-25	12	30	32
-25	14	26	31
-25	16	25	27
-25	20	20	19
-27	8	31	37
-27	10	51	50
-27	11	27	22
-27	12	50	49
-27	13	20	16
-27	14	35	38
-27	16	27	28
-29	10	24	33
-29	12	34	39
-29	14	38	36
-29	16	37	39
-29	18	25	29
-31	16	26	30
-31	18	25	31
	K = 2		
0	2	165	212
0	3	129	138
0	4	83	84
0	5	23	23
0	6	47	38
0	9	18	16
0	10	26	25
2	1	57	68
2	2	109	116
2	3	32	27
2	4	62	64
2	5	19	18
2	6	36	34
2	8	43	43
4	2	53	51
4	3	28	24
4	4	56	59
4	5	40	38
4	6	48	53
4	7	46	49
4	8	44	48
6	1	95	96
6	2	84	87
6	3	55	53
6	4	69	71
6	5	44	48
6	6	47	50
6	7	35	41
6	8	28	28
8	1	95	105
8	2	59	62
8	3	27	29
8	4	44	47
8	6	32	35
10	2	37	35
10	4	25	27
12	2	38	43
12	4	28	35
12	5	24	28
14	1	32	31
14	2	36	44
14	3	23	28
14	4	24	30
16	1	23	30
16	2	21	33
-2	3	128	146
-2	4	111	121
-2	5	107	118
-2	6	108	105
-2	7	61	61
-2	8	73	71
-2	9	52	50
-2	10	48	44
-4	0	53	56
-4	4	101	117
-4	5	86	87
-4	6	97	103
-4	7	58	54
-4	8	57	54
-4	9	53	55
-4	10	60	61
-4	11	37	36
-4	12	31	31
-6	0	136	152
-6	1	51	47
-6	2	59	58
-6	4	61	68
-6	6	60	57
-6	7	28	22
-6	8	29	28
-6	10	62	62
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-8	6	106	110
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-8	11	20	18
-8	12	37	30
-8	14	26	24
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-10	1	45	65
-10	2	94	94
-10	3	28	33
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-10	5	109	109
-10	6	117	115
-10	7	147	152
-10	8	103	101
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-10	10	60	53
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-10	12	54	46
-10	14	32	28
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-12	7	89	84
-12	8	105	113
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-12	10	68	61
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-12	12	69	66
-12	13	47	43
-12	14	45	39
-12	15	28	25
-12	16	26	20
-14	0	35	37
-14	1	51	49
-14	2	69	78
-14	3	43	41
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-14	6	56	51
-14	7	36	19
-14	8	66	64
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-14	12	52	52
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-14	14	43	43
-14	15	36	36
-14	16	32	31
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-16	2	69	78
-16	3	69	76
-16	4	68	69
-16	5	49	42
-16	6	64	60
-16	7	32	23
-16	8	57	55
-16	9	40	40
-16	10	52	52
-16	12	39	40
-16	14	37	33
-16	16	30	29
-18	2	31	33
-18	3	30	34
-18	4	53	54
-18	5	54	53
-18	6	77	77
-18	7	76	66
-18	8	83	77
-18	9	86	86
-18	10	88	88
-18	11	41	39
-18	12	45	38
-18	14	36	30
-18	16	33	28
-20	4	34	42
-20	6	45	49
-20	7	23	22
-20	8	48	41
-20	9	52	41
-20	10	73	69
-20	11	60	54
-20	12	49	46
-20	13	45	38
-20	14	54	50
-20	15	36	34
-20	16	45	39
-20	17	25	23
-20	18	26	20
-22	3	19	18
-22	4	26	35
-22	6	20	28
-22	9	23	13
-22	10	43	43
-22	11	20	23
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-22	14	46	44
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-22	17	32	29
-22	18	28	27
-24	4	28	32
-24	5	24	28
-24	7	24	24
-24	8	39	42
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-24	12	30	35
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-24	18	29	30
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-26	7	32	36
-26	8	35	44
-26	9	37	36
-26	10	30	32
-26	11	36	32
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-26	14	27	29
-26	16	23	22
-26	18	23	25
-28	8	27	29
-28	10	26	26
-28	11	28	17
-28	12	42	41
-28	13	38	34
-28	14	36	34
-28	15	31	30
-28	16	29	29
-28	17	18	18
-28	18	22	23
-30	14	25	27
-30	15	21	22
-30	16	25	29
-30	17	22	15
	K = 3		
1	2	61	61
1	3	77	79
1	4	66	63
1	6	54	54
1	7	22	17
1	8	35	34
1	9	35	29
1	10	27	28
3	1	80	81
3	2	83	92
3	4	61	59
3	6	41	42
3	7	51	53
3	8	20	21
3	9	33	38
5	1	120	143
5	2	58	63
5	3	61	65
5	4	42	46
5	5	45	44
5	6	40	38
5	7	47	52
5	8	24	22
7	1	115	121
7	2	49	47
7	3	61	62
7	4	31	29
7	5	38	41
7	6	27	28
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-12	9	28	24
-12	11	30	22
-14	3	36	32
-14	5	55	56
-14	7	60	63
-14	8	26	23
-14	9	44	44
-14	11	46	43
-16	4	26	23
-16	5	34	32
-16	7	50	47
-16	9	34	28
-16	11	47	47
-16	13	36	31
-18	5	24	21
-18	10	25	21
-18	11	30	27
-18	13	38	33
-20	7	28	30
-20	9	28	26
-20	10	26	23
-20	13	22	19
-22	7	39	37
-22	9	43	47
-22	13	24	22
-24	9	28	30
-24	11	22	21
-24	13	31	31

yielded an unweighted discrepancy index, R_1, of 9.9% and a weighted discrepancy index, $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$, of 13.2%. Variable weights were assigned as follows: $\sqrt{w} = 20/F_o$ if $I_o > \sqrt{20}I_{\min}$; $\sqrt{w} = I_o^2/F_oI_{\min}^2$ if $I_o \leq \sqrt{20}I_{\min}$. The standard deviation of an observation of unit weight was 2.4. Scattering factors for molybdenum were from Thomas and Umeda,[13] for chlorine from Dawson,[14] for nitrogen from Hoerni and Ibers,[15] and for carbon and oxygen from Berghuis, *et al.*[16] No corrections were applied for anomalous dispersion. Final positional and thermal parameters with estimated standard deviations are listed in Table I. Structure factors from the final least-squares cycle were used to calculate a three-dimensional electron density difference map. The maximum peak height in the difference map corresponded to 25% of the height of a carbon atom. Hydrogen atoms could not be located. Table II lists the observed and calculated structure factors scaled to $F(000)$. Unobserved data were not included in the refinement. Extinction errors in the data were unimportant.

Results and Discussion

Dioxodichlorobis(N,N-dimethylformamido)molybdenum(VI) exists as discrete monomers (Figure 1) with crystallographically required point group symmetry 2(C_2). The molybdenum atom exhibits distorted octahedral coordination. Both the oxo ligands and

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[14] B. Dawson, *Acta Cryst.*, **13**, 403 (1960).

[15] J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

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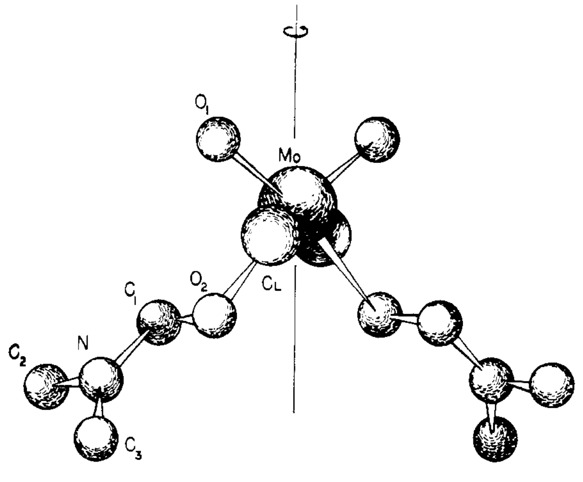

Figure 1.—The molecular configuration of $Mo[(CH_3)_2NCHO]_2O_2Cl_2$.

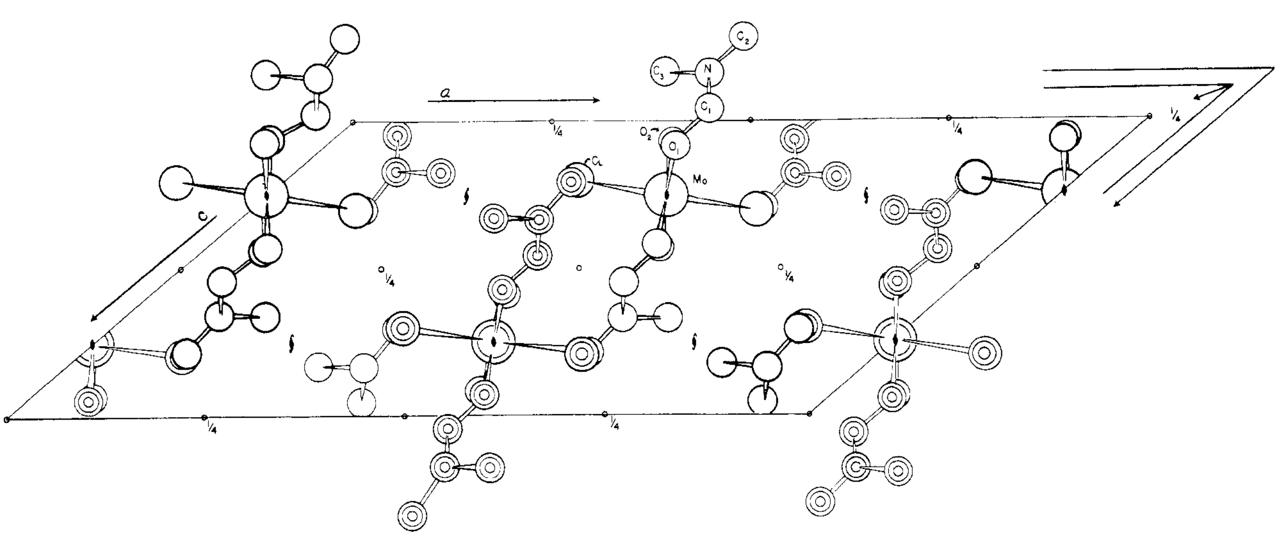

Figure 2.—[010] projection of the unit cell.

the dimethylformamido ligands are *cis* to one another while the chloro ligands are *trans* to one another.

Bond distances and angles with estimated standard deviations[17] including lattice constant errors are listed in Table III. The Mo–O_1 distance of 1.68 Å agrees within 2.5 standard deviations with the Mo–O distances in $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ (1.69 Å)[4] and $Ba\{[MoO(C_2O_4)(H_2O)]_2O_2\}\cdot 3H_2O$ (1.70 Å).[18] This bond distance is consistent with a Mo–O_1 bond order of 2.5[19] which is expected for a *cis* configuration of π-donor ligands.[4] The Mo–O_2 bond length of 2.20 Å is comparable to Mo–O in oxalate distances in previously studied complexes[4,18] and corresponds to a bond order of 1.[19] The Mo–Cl distance of 2.341 (7) Å is longer than the Mo^{VI}–Cl distance of 2.28 (3) Å found in the tetrahedrally coordinated MoO_2Cl_2 gas-phase structure.[20]

The O–Mo–O angles associated with similar types of oxygen ligands show the greatest distortions from 90° (O_1–Mo–O_1' = 102.2°; O_2–Mo–O_2' = 76.2°). The wider angle involves the oxygen atoms with the shorter metal–oxygen distances and probably results from oxygen–oxygen repulsion. The nonbonding $O_1\cdots O_1'$ distance is 2.61 Å, which is less than 2.8 Å, twice the van der Waals radius of oxygen.[21] The $O_2\cdots O_2'$ nonbonding distance, which involves the longer bond, is 2.72 Å. The O_1–Mo–O_2 angle is 90° within the errors assigned. Distortions of angles that involve the chlorine atom may be explained by the observation that the chlorine atom is positioned equidistant from all four oxygen atoms (Cl$\cdots O_1$, 3.03 Å; Cl$\cdots O_2$, 3.00 Å; Cl$\cdots O_1'$, 3.00 Å; Cl$\cdots O_2'$, 3.00 Å). The dihedral angle between the planar dimethylformamido ligand and the plane defined by the molybdenum and four oxygen atoms is approximately 54°.

Figure 2 shows the [010] projection of the unit cell.

Table III

Bond Distances and Angles in $Mo[(CH_3)_2NCHO]_2O_2Cl_2$ with Estimated Standard Deviations[a]

Bond	Distance, Å	Bond	Distance, Å
Mo–Cl	2.341 (7)	O_2–C_1	1.29 (1)
Mo–O_1	1.68 (1)	C_1–N	1.28 (1)
Mo–O_2	2.20 (1)	N–C_2	1.46 (2)
		N–C_3	1.47 (2)
Atoms	**Angle, deg**	**Atoms**	**Angle, deg**
O_1–Mo–O_1'	102.2 (7)	Cl–Mo–Cl′	161.3 (2)
O_2–Mo–O_2'	76.2 (5)	Mo–O_2–C_1	125.3 (7)
O_1–Mo–O_2	90.8 (5)	O_2–C_1–N	123.0 (10)
Cl–Mo–O_1	96.5 (5)	C_2–N–C_2	120.4 (10)
Cl–Mo–O_2	82.8 (3)	C_1–N–C_3	120.9 (10)
O_2–Mo–O_1'	167.1 (9)	C_2–N–C_3	118.7 (11)

[a] Primed atoms indicate twofold related atoms.

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[17] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964, Report No. ORNL-TM-306.

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[21] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

The minimum intermolecular packing distance (excluding hydrogen atoms) is 3.54 Å between O_1 and C_3 in the molecule directly above the asymmetric portion of the unit cell.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA 95616,
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The Structure of Decaammine-μ-peroxo-dicobalt Disulfate Tetrahydrate[1]

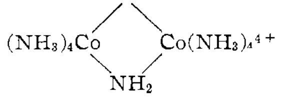
BY WILLIAM P. SCHAEFER[2]

Received August 7, 1967

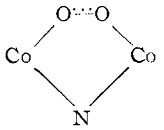
Decaammine-μ-peroxo-dicobalt disulfate tetrahydrate, $(NH_3)_5CoO_2Co(NH_3)_5(SO_4)_2\cdot 4H_2O$, a red-brown, diamagnetic salt, crystallizes in the monoclinic space group $P2_1/n$ with $a = 7.62$, $b = 29.72$, $c = 9.60$ Å, and $\beta = 96.97°$; there are four formula units in the cell. The measured density is 1.74 g/cm³, the calculated density is 1.80 g/cm³. The structure was solved by Patterson and Fourier techniques and refined by three-dimensional least-squares calculations, based on 2760 reflections collected on a Picker automatic diffractometer, to a final R index of 0.065. The coordinating ligands about the cobalt atoms form nearly regular octahedra with Co–N distances of 1.96 Å and Co–O distances of 1.88 Å. The bridging O–O group is a peroxide ion, with an O–O distance of 1.47 Å and a torsion angle of 146° about the O–O bond. The Co–O–O angles are 113°. The dimensions of the bridging group and the configuration of the cation are markedly different from those found for the paramagnetic, oxidized form of this compound.

Introduction

The structures of the peroxo-bridged dicobalt compounds have been speculated upon since their discovery and characterization by Werner[3] and others. Two series of these compounds are known, the one consisting of green, paramagnetic compounds and the other of red-brown diamagnetic compounds. The cobalt atoms may be joined by one, two, or three bridges, the bridging groups including, besides peroxo and superoxo ions, hydroxo, amido, nitrito, and sulfato groups. The questions of the molecular and electronic structures of these ions have been most recently reviewed by Goodman, Hecht, and Weil;[4] at the time of that review no reliable X-ray structure for any of these compounds was available. Since then, we have determined the structure of the paramagnetic peroxo-bridged ion shown in Figure 1.[5] We have made the point that the structural details of the cation can be well explained by Pauling's valence-bond theory, with the bridging group being considered a superoxide ion. This formulation was not original with us,[6] but it leads to some interesting predictions as to the structures of other compounds of this sort. For example, consider the paramagnetic ion



Because the single bond plus the three-electron bond joining the two oxygen atoms require the use of two orbitals, the entire



grouping is expected to be planar. Recently, the structure of this ion has been determined,[7] and the five central atoms are in fact nearly coplanar. As in the case of the singly bridged compound, the O–O bond distance, 1.31 Å, is typical of a superoxide group.

If the paramagnetic ions are considered to be derivatives of the superoxo ion,[8] then the addition of an electron to give the diamagnetic species should lead to a peroxo derivative. The two oxygen atoms are now joined by only a single bond, and this bond length should be near 1.48 Å; the O–O distance found in H_2O_2 is 1.47 Å,[9] and in BaO_2 it is 1.49 Å.[10] Furthermore, the Co–O–O–Co grouping should now not be planar; the torsion angle about the O–O bond in H_2O_2 is about 90°,[11] and a torsion angle is to be expected in the cobalt compound as well. This paper reports the structure of the compound decaammine-μ-peroxo-dicobalt disulfate tetrahydrate; the basic structure of the cation is as we have predicted. Our structure differs from the one reported by Vannerberg[12] for the μ-peroxo-dicobalt

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(1) Contribution No. 3548 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology. This work was supported in part by NSF Grant GP-5768.

(2) University of California, Davis, Calif. Work done at Davis.

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(7) G. G. Christoph, R. E. Marsh, and W. P. Schaefer, to be published.

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