

Studies on Peroxomolybdates

V. The Crystal Structure of Tetramminezinc(II) Tetraperoxomolybdate(VI), $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$

ROLF STOMBERG

Department of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

The crystal structure of the dark red compound $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ has been determined from Fourier calculations based on three-dimensional X-ray data, collected by the low temperature Weissenberg technique, and refined by the structure factor least squares method. The crystals are tetragonal, belonging to space group $I\bar{4}$, with $a=8.523 \pm 0.001$ Å, $c=7.024 \pm 0.001$ Å and $V=510.2$ Å³, and contain discrete tetramminezinc(II) and tetraperoxomolybdate(VI) ions.

Zinc is tetrahedrally coordinated by nitrogen whereas molybdenum is distorted dodecahedrally coordinated by eight oxygen atoms, the $[\text{Mo}(\text{O}_2)_4]^{2-}$ ion having, within the limits of experimental error, the symmetry $\bar{4}2m$.

The Mo—O₁ bond distance is 2.00 ± 0.02 Å, the Mo—O₂ bond distance 1.93 ± 0.03 Å, and the O₁—O₂ and Zn—N bond distances are 1.55 ± 0.05 Å and 2.05 ± 0.03 Å, respectively.

The chemistry of the peroxomolybdates is complex owing to the ability of molybdenum to form polyanions in aqueous solution. This is evident from a study, by Stomberg and Trysberg,¹ of the potassium peroxomolybdates crystallizing from aqueous solution in the pH range 4—8. It is only in moderately alkaline solutions that the mononuclear tetraperoxomolybdate ion is formed.

EXPERIMENTAL

Preparation of crystals. $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ was prepared according to Gleu.² 0.7 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 40 ml 10 M ammonia. To this solution 1.15 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 20 ml water and 6 ml H_2O_2 (30 %) were added at -10°C . Dark brown, octahedral crystals separated out within a few minutes.

Analysis. The peroxide content was determined by dissolving the compound in 3 M H_2SO_4 and titrating with a standardized KMnO_4 solution. Zinc was determined by titration with EDTA, molybdenum by reducing to the +3 state and then titrating with

KMnO₄, and ammonia by the Kjeldahl method (Found: Zn 18.1; NH₃ 18.9; Mo 26.8; O_{peroxide} 34.8. Calc. for [Zn(NH₃)₄][Mo(O₂)₄]: Zn 18.3; NH₃ 19.1; Mo 26.8; O_{peroxide} 35.8).

X-Ray methods. Approximate cell dimensions were obtained from rotation and Weissenberg photographs and more accurate dimensions from X-ray powder photographs taken in a Guinier focusing camera with CuK α radiation, using lead nitrate ($a=7.8566$ Å at 21°C)³ as an internal standard.

The compound decomposes completely within a few hours at room temperature, ammonia and oxygen being evolved. Greater stability is obtained at temperatures below 0°C. A low temperature camera was therefore used for the single crystal work. Multiple-film equi-inclination Weissenberg photographs were taken at -15°C for crystals with an approximate thickness of 0.05 mm, with rotation about [001] (layer lines 0-6) and [100] (layer line 0), using copper radiation. New crystals were mounted for each layer line. A total of 244 reflexions was registered, 153 of which were independent. The intensities of the reflexions were estimated visually and corrected for Lorentz and polarization effects but not for absorption and extinction.

Computing methods. The computational work was performed at Gothenburg Universities' Computing Centre using an IBM 360/50 computer and the following programmes: POWDER⁴ for indexing powder reflexions and refining cell parameters, DATAP2⁵ for calculation of $|F_o|$ from measured intensities, DRF⁶ for Fourier summations, LALS⁶ for structure factor least-squares refinement (full matrix) and DISTAN⁶ for calculation of interatomic distances and angles.

The atomic scattering factors used in the calculation of the structure factors were taken from Volume III of the *International Tables for X-ray Crystallography*, 1962.

SPACE GROUP AND UNIT CELL

The crystals, which are tetragonal with Laue symmetry 4/m, showed systematic absences only for $h+k+l=2n+1$. Possible space groups are thus $I4$ (No. 79), $I\bar{4}$ (No. 82), and $I\bar{4}/m$ (No. 87).

The unit cell dimensions at 21°C, obtained from the measured $\sin^2\theta$ values of the powder photograph by a least-squares procedure using 27 of the observed lines, are $a=8.523\pm 0.001$ Å, $c=7.024\pm 0.001$ Å, and $V=510.2$ Å³. Observed and calculated $\sin^2\theta$ values are given in Table 1.

The density of the crystals, as determined by weighing a sample in air and in benzene, is 2.30 g/cm³. The density calculated for a unit cell containing two formula units is 2.326 g/cm³.

STRUCTURE DETERMINATION

The Patterson function showed no large peaks other than at (0,0,0) and $(0, \frac{1}{2}, \frac{1}{4})$, and the latter peak was assumed to be a Mo-Zn vector. Since molybdenum and zinc cannot be situated at inversion centers, the most probable space group is, therefore, $I\bar{4}$ with molybdenum occupying the position $2a$, (0,0,0), and zinc the position $2c$, $(0, \frac{1}{2}, \frac{1}{4})$. A peak at (0.09, 0.22, 0) could be identified as a Mo-O vector of length 2.0 Å. One oxygen atom, O₁, ought thus to occupy the position $8g$ with $x=0.09$, $y=0.22$, and $z=0.00$.

A Fourier summation was undertaken using the signs of the contributions to the structure factors from Mo and Zn. Peaks, other than the Mo and Zn peaks, compatible with the Patterson function appeared at (0.10, 0.21, 0), (0.05, 0.14, -0.23), and (0.05, 0.32, 0.45). These were attributed to the atoms O₁, O₂, and N, respectively. When these atoms were included in the structure factor calculation an R value, $\sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.16 was obtained.

Table 1. Observed lines in the powder photograph of $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ at 21°C (Guinier focusing camera). $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$. Internal standard $\text{Pb}(\text{NO}_3)_2$ ($a = 7.8566 \text{ \AA}$ at 21°C). $d_{hkl} = d_{\bar{h}\bar{k}\bar{l}}$, $|F_{hkl}| \neq |F_{\bar{h}\bar{k}\bar{l}}|$.

$\begin{matrix} h & k & l \\ k & h & l \end{matrix}$	$10^5 \times \sin^2\theta_{\text{obs}}$	$10^5 \times \sin^2\theta_{\text{calc}}$	d_{calc}	I_{obs}	$ F_{hkl} $	$ F_{\bar{h}\bar{k}\bar{l}} $
1 1 0	1638	1633	6.027	m+	45	45
1 0 1	2021	2019	5.420	vvs	119	119
2 0 0	3263	3267	4.262	s	130	130
0 0 2	4809	4811	3.512	vvw	43	43
2 1 1	5288	5286	3.350	vs	84	108
1 1 2	6446	6444	3.034	m+	76	76
2 2 0	6523	6534	3.013	w	59	59
2 0 2	8074	8077	2.710	vw	37	37
3 1 0	8170	8167	2.695	m+	41	72
3 0 1	8551	8553	2.634	vvw	25	25
1 0 3	11635	11640	2.258	vvw	55	55
3 2 1	11824	11820	2.240	m	54	77
3 1 2	12979	12977	2.138	s	80	111
4 0 0	13068	13067	2.131	vw	83	83
2 1 3	14921	14907	1.9950	w	38	66
4 1 1	15100	15086	1.9831	m	62	96
4 2 0	16330	16334	1.9059	m	67	101
4 0 2	17857	17878	1.8217	vvw	25	25
3 0 3	18169	18174	1.8068	vvw	43	43
0 0 4	19263	19242	1.7559	vvw	70	70
3 3 2	19525	19511	1.7438	m	99	99
1 1 4	20867	20876	1.6858	vvw	28	28
4 2 2	21137	21144	1.6751	vvw	37	24
3 2 3	21455	21441	1.6635	vw	55	68
5 0 1	21630	21620	1.6566	m	62	62
4 3 1					48	67
2 0 4	22507	22509	1.6235	vvw	63	63
4 1 3	24697	24708	1.5496	m-	53	74
5 2 1	24897	24887	1.5440	m-	60	63
5 1 2	26020	26044	1.5093	w	74	71
1 0 5	30897	30883	1.3860	vvw	57	57
4 3 3	31250	31241	1.3781	vvw	50	46
5 0 3					44	44
6 1 1	31436	31420	1.3741	vvw	36	30
4 0 4	32305	32309	1.3551	vvw	58	58
5 3 2	32622	32578	1.3495	vw	74	51
6 2 0		32668	1.3476		76	76
2 1 5	34186	34149	1.3181	vvw	25	33
6 0 2		34211	1.3169		<17	<17
5 4 1	34680	34687	1.3078	vvw	36	28
4 2 4	35576	35576	1.2914	vw	46	66
6 2 2	37487	37478	1.2582	vvw	30	<17
6 3 1	37991	37954	1.2503	vw	42	31
3 2 5	40663	40683	1.2076	vvw	29	34
7 0 1	41217	41220	1.1997	vvw	30	30
6 4 0	42470	42468	1.1820	vvw	38	46
4 1 5	43952	43950	1.1619	vvw	28	40
7 2 1	44450	44487	1.1548	vvw	33	<17
7 1 2	45633	45645	1.1401	vvw	45	33
5 5 2					39	39

REFINEMENT

The structure was refined by the structure factor least squares method using the full matrix programme LALS⁵ and 151 observed, independent reflexions. In the initial cycles, besides the atomic coordinates and isotropic temperature factors, a separate scale factor was refined for each layer, but in the final cycles of refinement the atomic coordinates, isotropic temperature factors, and an overall scale factor were refined. The structure factors were weighted according to Cruickshank,⁶ $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$, with $a=400$, $c=0.007$ and $d=0$.

The final R value, obtained after six cycles of refinement, was 0.075 for all observed reflexions and 0.11 for both observed and non-observed reflexions. The parameters, together with their standard deviations, are given in Table 2, the weight analysis in Table 3, and observed and calculated structure factors in Table 4. The contribution to the structure factors from the hydrogen atoms has not been taken into consideration.

Table 2. Atomic coordinates (expressed in fractions of the cell edges) and isotropic thermal parameters with their standard deviations for $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_3)_4]$.

The temperature factor = $\exp(-B \sin^2\theta/\lambda^2)$. Space group $I\bar{4}$. Two formula units in the cell. $R=0.075$.

Atom	Position	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
Mo	2a	0	0	0	2.5 ± 0.1
Zn	2c	0	$\frac{1}{2}$	$\frac{1}{2}$	3.9 ± 0.3
O ₁	8g	0.089 ± 0.002	0.217 ± 0.002	-0.007 ± 0.005	4.7 ± 0.5
O ₂	8g	0.051 ± 0.003	0.144 ± 0.003	-0.203 ± 0.004	5.3 ± 0.6
N	8g	0.057 ± 0.003	0.316 ± 0.003	0.424 ± 0.004	3.9 ± 0.6

Table 3. Weight analysis.

$ F_o $ -interval	$\overline{w\Delta^2}$	No. of reflexions
0 — 24.5	0.54	28
24.5— 31.7	0.98	30
31.7— 38.3	1.14	30
38.3— 55.4	1.09	30
55.4— 130.3	1.25	31

The results of the refinement were confirmed by a three-dimensional difference electron density calculation in which the largest discrepancy corresponded to a peak of $1 \text{ e}/\text{\AA}^3$, which is less than one eighth of the nitrogen peak in the F_o synthesis. Furthermore, all distances and angles were found to be within the normal range, thus supporting the correctness of the structure.

Table 4. Observed and calculated structure factors for $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$.

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $
2 0 0	130	127	1 4 1	96	86
4 0 0	83	83	3 4 1	67	64
6 0 0	55	54	5 4 1	36	40
8 0 0	23	30	2 5 1	63	64
10 0 0	26	22	4 5 1	28	33
1 1 0	45	48	1 6 1	30	28
3 1 0	41	41	3 6 1	31	40
5 1 0	<12	6	0 0 2	43	52
7 1 0	<14	14	2 0 2	37	34
9 1 0	<14	15	4 0 2	25	27
2 2 0	59	65	6 0 2	<17	12
4 2 0	67	69	8 0 2	<18	9
6 2 0	76	70	1 1 2	76	90
8 2 0	42	37	3 1 2	80	73
10 2 0	24	24	5 1 2	74	71
1 3 0	72	66	7 1 2	45	43
3 3 0	15	18	9 1 2	27	32
5 3 0	<13	12	2 2 2	<10	3
7 3 0	<15	18	4 2 2	37	41
9 3 0	<13	7	6 2 2	30	32
2 4 0	101	95	8 2 2	<18	10
4 4 0	50	54	1 3 2	111	117
6 4 0	38	42	3 3 2	99	92
8 4 0	29	29	5 3 2	74	70
1 5 0	34	37	7 3 2	35	37
3 5 0	<13	19	9 3 2	14	19
5 5 0	<14	8	2 4 2	24	72
7 5 0	23	21	4 4 2	<16	15
2 6 0	69	72	6 4 2	<18	11
4 6 0	46	52	8 4 2	<16	4
6 6 0	32	32	1 5 2	71	67
8 6 0	26	25	3 5 2	51	46
1 7 0	<14	16	5 5 2	39	38
3 7 0	<15	17	7 5 2	33	33
5 7 0	<14	9	2 6 2	<17	9
7 7 0	<11	10	4 6 2	<18	11
2 8 0	42	40	6 6 2	<17	13
4 8 0	40	34	1 7 2	33	35
6 8 0	18	18	3 7 2	35	36
1 9 0	<14	12	5 7 2	34	31
3 9 0	<12	12	2 8 2	<18	13
2 10 0	21	20	4 8 2	<16	15
1 0 1	119	123	1 9 2	27	30
3 0 1	25	27	3 9 2	22	26
5 0 1	62	60	1 0 3	55	56
7 0 1	30	33	3 0 3	43	48
2 1 1	84	82	5 0 3	44	42
4 1 1	62	62	7 0 3	34	28
6 1 1	36	41	2 1 3	38	48
1 2 1	108	104	4 1 3	53	51
3 2 1	54	46	6 1 3	39	35
5 2 1	60	63	8 1 3	22	25
7 2 1	33	32	1 2 3	66	70
2 3 1	77	72	3 2 3	55	53
4 3 1	48	46	5 2 3	54	54
6 3 1	42	46	7 2 3	29	29

Table 4. Continued.

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $
233	68	67	105	57	64
433	50	49	305	35	36
633	37	38	505	25	28
833	<17	16	705	21	17
143	74	71	215	25	28
343	46	49	415	28	25
543	36	32	615	27	25
743	27	22	815	25	16
253	37	40	125	33	43
453	28	25	325	29	26
653	28	28	525	31	30
163	27	24	725	27	24
363	24	23	235	34	36
563	21	21	435	33	30
273	24	24	635	24	24
473	19	23	145	40	41
183	23	24	345	28	27
383	23	24	545	22	18
004	70	98	745	18	18
204	63	68	255	31	32
404	58	56	455	22	23
604	44	36	655	19	18
114	28	29	165	34	29
314	18	15	365	23	27
514	<23	18	565	19	17
714	<24	11	275	22	22
224	52	62	206	<17	14
424	46	46	406	<23	13
624	38	43	116	47	50
134	30	26	316	30	32
334	21	15	516	37	36
534	<24	18	226	<20	14
244	66	69	426	<23	8
444	41	41	136	33	37
644	35	34	336	32	32
154	<23	20	536	34	31
354	<24	15	246	23	22
554	<24	8	446	<23	9
264	<25	40	156	34	32
464	35	29	356	32	28
174	<24	9			

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ contain tetramminezinc(II) ions and tetraperoxomolybdate(VI) ions packed as indicated in the projection of the unit cell shown in Fig. 1. The configuration about the molybdenum atom is illustrated in Fig. 2.

Zinc is regularly tetrahedrally coordinated by four nitrogen atoms, whereas the eight oxygen atoms coordinated to the molybdenum atom form a somewhat distorted dodecahedron of the $[\text{Mo}(\text{CN})_8]^{4-}$ type.⁷

Fig. 1. The crystal structure of $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ viewed along the c -direction.

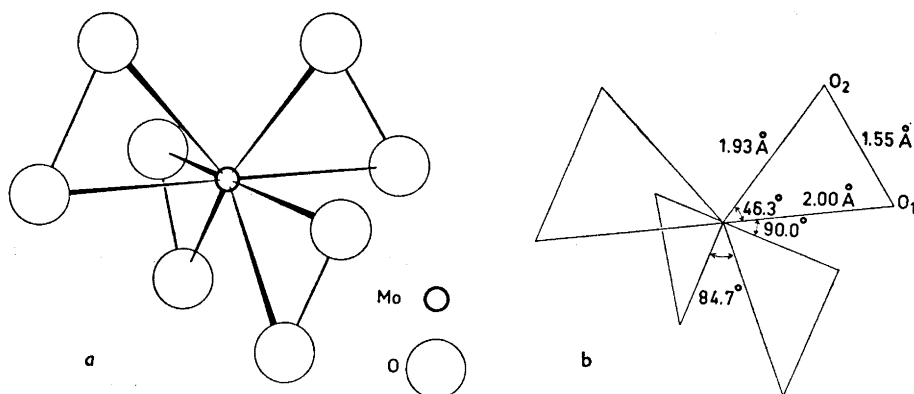
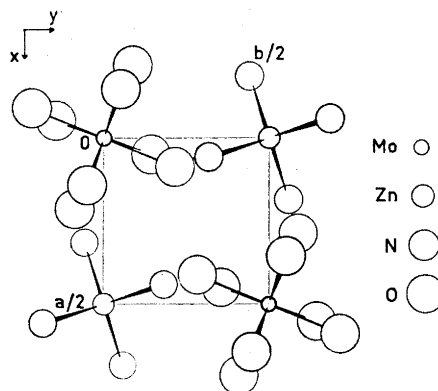


Fig. 2. a) The $[\text{Mo}(\text{O}_2)_4]^{2-}$ ion. b) Bond distances and angles in the $[\text{Mo}(\text{O}_2)_4]^{2-}$ ion.

A similar configuration has been found for the $[\text{Cr}(\text{O}_2)_4]^{3-}$ ion,⁸⁻¹⁰ which has exactly $\bar{4}2m$ symmetry. Since the atoms $\text{O}_1(1)$, $\text{O}_2(1)$, Mo , $\text{O}_1(2)$, and $\text{O}_2(2)$ all lie in a plane, within the limits of experimental error (0.05 Å), the $[\text{Mo}(\text{O}_2)_4]^{2-}$ ion has $\bar{4}2m$ symmetry and is thus isomorphous with the $[\text{Cr}(\text{O}_2)_4]^{3-}$ ion. Bond distances and angles are given in Table 5. From the table it is evident that one molybdenum-oxygen bond, $\text{Mo}-\text{O}_1$, is probably slightly longer (0.07 Å) than the other, $\text{Mo}-\text{O}_2$. This was also found in the $[\text{Cr}(\text{O}_2)_4]^{3-}$ ion, the difference in bond length being 0.10 Å. The mean $\text{Mo}-\text{O}$ distance is 1.97 Å which is in good agreement with the value 1.96 Å found in $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$,¹¹ 1.94 Å in $\text{K}_2[\text{MoO}(\text{O}_2)\text{F}_4](\text{H}_2\text{O})$,¹² 1.91 Å in $(\text{NH}_4)_3\text{F}[\text{MoO}(\text{O}_2)\text{F}_4]$ ¹³ and 1.94 Å in $\text{K}_2[\text{MoO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$.¹⁴

The distance between the two oxygen atoms of the peroxo group is 1.55 ± 0.05 Å and does not, therefore, deviate significantly from the values 1.48 Å found in $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$ ¹¹ and 1.47 Å in $\text{K}_3[\text{Cr}(\text{O}_2)_4]$. Values between 1.40 and 1.47 Å have been obtained for peroxochromium compounds¹⁵ and

Table 5. Bond distances and angles in $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$. The figures in parentheses refer to the generated equivalent positions as they appear in the *International Tables for X-ray Crystallography*, Vol. I (1952).

	Distance (Å)	e.s.d. (Å)
Mo—O ₁	2.00	0.02
Mo—O ₂	1.93	0.03
O ₁ —O ₂	1.55	0.05
Zn—N	2.05	0.03
	Angle (°)	e.s.d. (°)
Mo—O ₁ —O ₂	64.5	1.3
Mo—O ₂ —O ₁	69.2	1.5
O ₁ —Mo—O ₂	46.3	1.4
O ₁ (1)—Mo—O ₁ (2)	177.2	2.2
O ₁ (1)—Mo—O ₁ (3)	90.0	0.0
O ₁ (1)—Mo—O ₂ (2)	130.9	1.4
O ₁ (1)—Mo—O ₂ (3)	89.2	1.2
O ₁ (1)—Mo—O ₂ (4)	92.8	1.2
O ₂ (1)—Mo—O ₂ (2)	84.7	1.6
O ₂ (1)—Mo—O ₂ (3)	123.1	1.0
N(1)—Zn—N(2)	106.7	1.6
N(1)—Zn—N(8)	110.8	0.8

the value 1.50 Å for $\text{K}_2\text{W}_2\text{O}_{11} \cdot 4\text{H}_2\text{O}$.¹⁶ The angles in the Mo—O₁—O₂ triangle are within the normal range.

The Zn—N distance, 2.05 Å, is in good agreement with the value 2.06 Å found in $\text{Zn}(\text{C}_6\text{H}_6\text{ON})_2(\text{H}_2\text{O})_2$ ¹⁷ and 2.10 Å in $\text{Zn}(\text{C}_6\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$.¹⁸ The average N—Zn—N angle is 109°.

Table 6. Interatomic distances, other than bond distances, less than 4.0 Å in $[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$.

	Distance (Å)	e.s.d. (Å)
O ₁ (1)—O ₁ (3)	2.81	0.03
O ₁ (1)—O ₂ (2)	3.58	0.04
O ₁ (1)—O ₂ (3)	2.76	0.04
O ₁ (1)—O ₂ (4)	2.85	0.04
O ₁ (1)—O ₂ (6)	3.92	0.04
O ₁ (1)—N(1)	3.15	0.05
O ₁ (1)—N(6)	3.07	0.03
O ₁ (1)—N(7)	3.08	0.04
O ₁ (1)—N(8)	3.06	0.03
O ₁ (1)—Zn(1)	3.10	0.03
O ₂ (1)—O ₂ (2)	2.60	0.05
O ₂ (1)—O ₂ (3)	3.40	0.05
O ₂ (1)—N(1)	3.00	0.04
O ₂ (1)—N(3)	3.23	0.04
O ₂ (1)—N(4)	3.57	0.04
O ₂ (1)—N(6)	3.48	0.04
O ₂ (1)—N(7)	3.79	0.04
N(1)—N(2)	3.29	0.06
N(1)—N(7)	3.38	0.05

$[\text{Zn}(\text{NH}_3)_4][\text{Mo}(\text{O}_2)_4]$ is somewhat more stable than $\text{K}_2[\text{Mo}(\text{O}_2)_4]$ (hexagonal). This may be due to the existence of hydrogen bonding in the former compound (five O—N distances are less than 3.2 Å as can be seen in Table 6).

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