Synthesis and Crystal Structures of γ-Type Octamolybdates Coordinated by Chiral Lysines

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The acidification of aqueous solutions containing $Na_2MoO_4 \cdot 2H_2O$ in the presence of a chiral lysine ligand (D- and L-form) gives octamolybdates coordinating two lysine ligands, $Na_2[Mo_8O_{26}(D\text{-}lysH_2)_2] \cdot 8H_2O$ (Mo_8-D) and $Na_2[Mo_8O_{26}(L\text{-}lysH_2)_2] \cdot 8H_2O$ (Mo_8-L) (where $lysH_2$ is 2,6-diammoniohexanoato), respectively. These two compounds crystallize with triclinic symmetry in the space group $P\bar{1}$, the cell parameters being $a=10.782(2)$, $b=11.241(5)$, $c=10.027(2)$ Å, $\alpha=93.21(2)$, $\beta=102.86(2)$, $\gamma=112.98(2)°$, $V=1077(1)$ Å^3, and $Z=1$ for the Mo_8-D, and $a=10.783(4)$, $b=11.246(3)$, $c=10.019(4)$ Å, $\alpha=93.21(3)$, $\beta=102.75(3)$, $\gamma=112.98(2)°$, $V=1077(2)$ Å^3, and $Z=1$ for Mo_8-L. The X-ray crystal structures of these two species have been solved by the MITHRIL direct method and refined to $R=0.0337$ and 0.0312 for Mo_8-D and -L, respectively. The chiral lysine ligands are coordinated via their carboxylate-oxygen atoms at the vacant sites on the two five-coordinate molybdenum for the centrosymmetric γ-$[Mo_8O_{26}]^{4-}$ anion to retain their configuration with a resultant formation of optically-active octamolybdate species.

As one of our studies on biological activities of polyoxometalates, the antitumor activity of polyoxomolybdates, especially, $[NH_3Pr^i]_6[Mo_7O_{24}] \cdot 3H_2O$, against animal transplantable tumors and human cancer xenografts has been investigated.[1] Recent studies of the biomedical studies of polyoxometalates have focused upon finding polyoxometalates with both good activity against HIV and improved clinical safety profiles. $K_7[PTi_2W_{10}O_{40}] \cdot 7H_2O$,[2] $[NH_4]_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4] \cdot 13H_2O$,[3] Cs^+ and $[NMe_4]^+$ salts of $[(RSi)_2OSiW_{11}O_{39}]^{4-}$ (R=CH_2CH_2COMe, $(CH_2)_3CN$, and $CH{=}CH_2$),[4] and $K_6[BVW_{11}O_{40}] \cdot xH_2O$[5] have been selected as candidate compounds for clinical treatment of HIV/AIDS. The antitumor mechanism on the basis of the repeated redox cycles of $[Mo_7O_{24}]^{6-}$ in tumor cells suggests that the formation of 1 : 1 $[Mo_7O_{24}]^{6-}$–FMN complex in the mitochondria on the tumor cell inhibits ATP generation.[6] It is important to investigate the interaction of polyoxomolybdates with enzymes to model polyoxomolybdates binding to peculiar functions of the protein. Therefore, structural chemistry of polyoxomolybdates with organic ligands are essential for understanding the antitumor/viral activities of polyoxometalates and modeling substrates involving in enzyme inhibition.[7] The most prominent binding sites for polyoxometalates in biogenetic molecules will be amine/amide functionalities, carboxylate, and OH groups. This paper deals with synthesis and crystal structures of optically-active γ-type octamolybdates coordinated by chiral lysine ligands, which are the first examples to our knowledge.

Octamolybdates $[Mo_8O_{26}]^{4-}$ have been observed as three isomers, α, β, and γ forms.[8] The α or β form of $[Mo_8O_{26}]^{4-}$ is normally selectively crystallized from an aqueous molybdate solution acidified to pH 3—4 by addition of a particular organic cation such as alkylammonium, alkylpyridinium, anilinium, or alkylphosphonium.[9,10] The γ-form as an intermediate in the $\alpha \rightleftharpoons \beta$ interconversion was recently isolated during acidification of molybdate in the presence of the $[Me_3N(CH_2)_6NMe_3]^{2+}$ cation.[11] Figure 1(a) shows the schematic structure of discrete crystallographically centrosymmetric γ-$[Mo_8O_{26}]^{4-}$, which has six MoO_6 octahedra and two MoO_5 trigonal bipyramids. The five-coordinate MoO_5 site is readily coordinated by a variety of oxygen-donating ligands, to form the six-coordinate MoO_6 octahedron, as exemplified by $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2] \cdot 2H_2O$,[12]

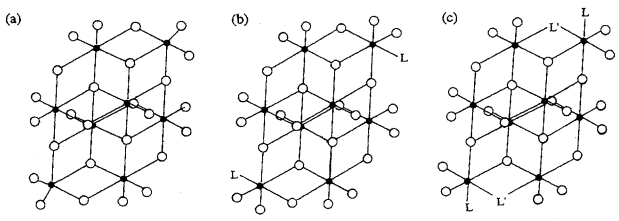

Fig. 1. Linkage isomers of γ-type octamolybdate. (a) $[Mo_8O_{26}]^{4-}$, (b) $[Mo_8O_{26}L_2]^{2n-4}$; L=OH ($n=-1$), HCOO ($n=-1$), C_5H_5N ($n=0$), $OC_6H_4CH{=}NPr\text{-}2$ ($n=-1$), MetO ($n=-1$), NCS ($n=-1$), and MoO_4 ($n=-2$), (c) $[Mo_8O_{24}L_2L'_2]^{2n}$; L=MoO_4 and L'=O ($n=-2$), and L=L'=CH_3O ($n=-1$).

$[NH_4]_6[Mo_8O_{26}(HCO_2)_2]\cdot 2H_2O$,[13] $[NH_3Me]_8[Mo_8O_{26}(MoO_4)_2]\cdot 2H_2O$,[14—16] $[NH_3Pr]_2[H_4Mo_8O_{26}(OC_6H_4CH{=}NPr\text{-}2)_2]\cdot 6MeOH$ ($(OC_6H_4CH{=}NPr\text{-}2)$ = *N*-propylsalicylideneiminate),[17] and $[Hmorph]_4[H_2Mo_8O_{26}(MetO)_2]\cdot 4H_2O$ (MetO=methioninate, morph=morpholine).[17] Figures 1(b) and 1(c) show schematic structures of anions in these compounds. Referring to the coordination of the tetrahedral MoO_4^{2-} into the MoO_5 site in the γ-form, two linkage isomers for $[Mo_8O_{26}(MoO_4)_2]^{8-}$ are known: MoO_4 group in $[NH_4]^+$ [14] and Tl^+ salts[15] of $[Mo_8O_{26}(MoO_4)_2]^{8-}$ can be related to cis to that (Fig. 1(b)) in the $[NH_3Me]^+$ salt.[16] $[Hpy]_4[Mo_8O_{26}(py)_2]\cdot 2Me_2SO$ (py=pyridine) and $K_6[Mo_8O_{26}(NCS)_2]\cdot 6H_2O$ with nitrogen-donating ligands have also been prepared,[18] and their schematic anion structures are also shown in Fig. 1(b). In $Na_4[Mo_8O_{24}(OMe)_4]\cdot 8MeOH$ with four methoxy groups,[19] two groups are terminal and other two bridging, cis to each other, as shown in Fig. 1(c).

It may provide insight into the molecular level for the antitumor/viral activities of polyoxometalates that the centrosymmetric $Mo_8O_{26}^{4-}$ can be converted into the chiral octamolybdates during the coordination of chiral amino acids.

Experimental

All the reagents required for the preparation were used without further purifications. $Na_2[Mo_8O_{26}$(D-$lysH_2)_2]\cdot 8H_2O$ (Mo_8-D), in which $lysH_2$ is 2,6-diammoniohexanoato, was prepared as follows: $Na_2MoO_4\cdot 2H_2O$ (10 g) was dissolved in a solution of D-lysine (2 g) in water (30 ml) at 25 °C and pH of the solution was adjusted to 3 by $HClO_4$. A white precipitate was filtered off and recrystallized from hot water at 70 °C. Colorless crystals were collected on a glass frit, and dried at room temperature, to give 2.3 g (27%) of pure material. IR spectrum: 3462vs, 3126vs, 1640vs, 1535m, 1497w, 1460w, 1400m, 1346m, 1330m, 1294m, 1238w, 1195w, 1141w, 1075w, 998w, 940vs, 917s, 886vs, 853vs, 685vs, 634m, 586m, 567m, 538m, 487w, 437w cm^{-1}. $Na_2[Mo_8O_{26}$(L-$lysH_2)_2]\cdot 8H_2O$ (Mo_8-L) was prepared according to the same procedure with L-lysine. The recrystallization from hot water gave 2.2 g (26%) of pure crystalline material. IR spectrum: 3464vs, 3138vs, 1642vs, 1535s, 1497s, 1460m, 1398s, 1346m, 1330m, 1294w, 1238w, 1195w, 1141w, 1075w, 998w, 938vs, 917s, 886vs, 853s, 692vs, 634m, 588m, 567m, 538m, 487w, 441w cm^{-1}. Similarly, $Na_2[Mo_8O_{26}$(D-$lysH_2$)(L-$lysH_2)]\cdot 8H_2O$ (Mo_8-*meso*) was prepared by the use of racemic DL-lysine and pure crystallines of 4.0 g (48%) were obtained by the recrystallization. IR spectrum: 3518vs, 3136vs, 1649vs, 1531m, 1499m, 1458m, 1406s, 1344m, 1330m, 1296m, 1241w, 1199w, 1141w, 1077w, 998w, 942vs, 919s, 888vs, 855s, 692vs, 642s, 594s, 565s, 538s, 489m, 445m cm^{-1}. The magnitudes of the optical activity, measured by a JASCO DIP-370 polarimeter were $[\alpha]_D=-3.680°$, $+3.500°$, and $+0.107°$ for Mo_8-D, -L and -*meso* species of 0.5 g cm^{-3} at 298 K in water, respectively. It is unlikely that the racemization of chiral lysines proceeded during the reaction with the octamolybdate in water. The small value of the optical activity for Mo_8-*meso* implies unequal proportions of the D- and L-enantiomers of lysine, due to the low purity of DL-lysine.

Data collection for X-ray structure analysis was done on a Rigaku AFC-5 diffractometer with a graphite monochromator and Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) generated at 45 kV and 25 mA. Crystal data and experimental conditions of the Mo_8-D and -L species are listed in Table 1. The cell dimensions were obtained from the setting angles of 25 reflections in the range $7<\theta<30°$ for two species. No significant decay of intensity of the three standards was observed. The molybdenum positions were located by a direct method using MITHRIL,[20] and the sodium, oxygen, nitrogen, and carbon atoms were located from difference syntheses. Lorenz and polarization factors were applied and an absorption correction was made based on the isotropically refined structure, using the program DIFABS.[21] The collection factors were 0.95—1.03 and 0.89—1.10 for Mo_8-D and -L, respectively. Subsequently, the molybdenum were refined with anisotropic thermal parameters. The quantity minimized was $\Sigma w(|F_o|-|F_c|)^2$. The weighting scheme used was $w^{-1}=\sigma^2(F_o)$, where $\sigma^2(I_o)=\sigma^2(I_{counting})+(0.03I_o)^2$. The maximum and minimum heights in the final difference synthesis were 0.9 and -1.2 e Å^{-3} for Mo_8-D (0.9 and -1.0 e Å^{-3} for Mo_8-L), respectively. All calculations were done on a Micro VAXII computer using the TEXSAN software package.[22] Table 2 shows atomic coordinates for Mo_8-D and -L. The complete F_o-F_c data and the anisotropic thermal parameters of Mo atoms are deposited as Document No. 68060 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The lysine is a chiral ligand which can exist in two different forms with different hands, D- or L-form. Figures 2(a) and 2(b) show structures of the octamolybdates coordinating D- and L-lysine ligands, respectively. The lysine ligand is coordinated to the Mo(1) and Mo(5) atoms through carboxylate oxygen O(27) and O(28) atoms as a monodentate 2,6-diammoniohexanoato ($lysH_2$) ligand, with resultant Mo–O bond lengths of 2.089(8) Å (Mo(1)–O(27)) and 2.130(9) Å (Mo(5)–O(28)) in Mo_8-D and 2.092(9) and 2.108(9) Å in Mo_8-L. To each of carbon atoms C(2) and C(8) in the lysine ligand are attached an amino N(1) and N(3) atoms, a carboxyl C(1) and C(7), and aliphatic side chains C(3—6) and C(9—12) atoms terminating in the ε nitrogen atoms N(2) and N(4), respectively. There is no significant difference in lattice parameters between Mo_8-D and -L (Table 1). We also characterized Mo_8-*meso*: Crystal data were triclinic space group $P\bar{1}$, $a=10.785(1)$, $b=11.207(1)$, $c=9.989(2)$ Å, $\alpha=92.88(2)$, $\beta=102.58(1)$, $\gamma=112.72(1)°$, $V=1074.7(3)$ Å^3, $Z=1$, $R=0.048$ and $R'=0.038$. Table 3 shows selected bond distances and angles for the two species of Mo_8-D and -L. The octamolybdate anion consists of centrosymmetrically condensed eight edge-sharing MoO_6 octahedra with 16 terminal positions, two of which are occupied by $lysH_2$ ligands. The same type of this anion was first observed for $[NH_3Pr^i]_6[Mo_8O_{26}(OH)_2]\cdot 2H_2O$.[12] In addition, the first carboxyl-oxygen coordinated octamolybdate of the same type was found for the formylated oc-

Table 1. Crystal Data, Structure Determination and Refinement Data for Mo_8-D (a) and -L (b)

	(a)	(b)
Formula	$Mo_8O_{38}C_{12}N_4Na_2$	$Mo_8O_{38}C_{12}N_4Na_2$
M.W.	1622	1622
Space group	$P1$	$P1$
a/Å	10.784(2)	10.783(4)
b/Å	11.241(3)	11.246(3)
c/Å	10.027(2)	10.019(4)
α/deg.	93.21(2)	93.21(3)
β/deg.	102.86(2)	102.75(3)
γ/deg.	112.98(2)	112.98(2)
V/Å^3	1077(1)	1077(2)
Z	1	1
D_c/g cm^{-3}	2.571	2.571
μ/cm^{-1}	23.31	23.31
$F(000)$	808	808
Cryst. size/mm	0.3×0.3×0.1, plate	0.3×0.3×0.1, plate
Radiation	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71069	0.71069
Scan method	ω–2θ	ω–2θ
Data collcn range	$2° \leq 2\theta \leq 60°$	$2° \leq 2\theta \leq 60°$
Standard reflcns	Three every 100 reflcns	Three every 100 reflcns
No. of data measd	6602	6611
No. of unique data	6269	6278
No. of obsd data [$F > 2.0\sigma(F)$]	5681	6012
No. of variables	251	251
(Mo anisotropic; C, N, O, and Na isotropic)		
Solution	Direct method	Direct method
Refinement	Full matrix least squares	Full matrix least squares
R/%	3.37	3.12
R'/%	4.26	3.10
S, goodness of fit	1.841	4.990
Max shift/error	0.051	0.129

tamolybdate, $[NH_4]_6[Mo_8O_{26}(HCO_2)_2]\cdot 2H_2O$.[13] Furthermore, methioninato (MetO) octamolybdate of the same type has been prepared recently as the morpholinium salt, $[Hmorph]_4[H_2Mo_8O_{26}(MetO)_2]\cdot 4H_2O$, and characterized as a crystal in triclinic $P\bar{1}$ and $Z=1$, indicating the coordination of two forms of D- and L-methionine ligands to give a *meso*-form.[17]

The structures of the centrosymmetric γ-octamolybdate frameworks for Mo_8-D and -L are very similar (Fig. 2). The bond strength of the Mo–O (carboxyl) interaction is calculated from $s=(d/1.882)^{-6.0}$, where s = bond strength of the Mo–O bond, d = crystallographic Mo–O bond length in Å, and the values of 1.882 (Mo–O bond of unit strength) and −6.0 are fitted parameters.[23] The calculated values of Mo(1)–O(27) and Mo(5)–O(28) interactions are 0.53 and 0.48 for Mo_8-D (0.53 and 0.51 for Mo_8-L), respectively. These values are very close to 0.49 and 0.51 for $[Hmorph]_4[H_2Mo_8O_{26}(MetO)_2]\cdot 4H_2O$[17] and $[NH_4]_6[Mo_8O_{26}(HCO_2)_2]\cdot 2H_2O$,[13] respectively. The weak Mo–O($lysH_2$) interactions are compensated within Mo(1) or Mo(5) octahedra by some other strong Mo–O bonds, so that the sums of the bond lengths Σs corresponding to the bond orders of molybdenum, amount to 5.67 and 5.87 for the Mo(1) and Mo(5) octahedra in Mo_8-D (5.89 and 6.03 in Mo_8-L), respectively. The octamolybdate coordinated by $lysH_2$ seems to be formed via lysine carboxylate coordination at the vacant sites on the two five-coordinate molybdenums for the γ-$[Mo_8O_{26}]^{4-}$ anion, which is composed of six MoO_6 octahedra interlinked along edges and two MoO_5 trigonal bipyramids each sharing two edges with the octahedra (Fig. 1(a)), which has been prepared as an intermediate in the $\alpha \rightleftharpoons \beta$ $[Mo_8O_{26}]^{4-}$ conversion in water.[11] As shown in Table 3, the 14 Mo=O bond lengths for Mo_8-D species range from 1.67(1) to 1.766(9) Å (1.66(1) to 1.768(9) Å for Mo_8-L). The Mo–O distances in the single bridge Mo–O–Mo vary from 1.74(1) to 2.400(9) Å in Mo_8-D and from 1.721(9) to 2.463(9) Å in Mo_8-L, in the triply-bridging Mo_3O core from 1.859(9) to 2.33(1) Å in Mo_8-D and from 1.87(1) to 2.31(1) Å in Mo_8-L, and finally in the Mo_4O core from 1.932(9) to 2.48(1) Å in Mo_8-D and from 1.94(1) to 2.49(1) Å in Mo_8-L. For the Mo(2) site we see the expected trend of increasing Mo–O bond length for two<three<four-coordinate oxygens, but the trend is not so apparent for the other six-coordinate molybdenums: for the Mo(4) site the Mo(4)–O(19) (three-coordinated) bond length

Table 2. Atomic Coordinations ($\times 10^4$) and Isotropic Thermal Parameters for Mo_8-D (a) and -L (b)

	(a)				(b)			
Atom	x	y	z	B_{iso}(Å^2)	x	y	z	B_{iso}(Å^2)
Mo(1)	−242	3177	−1488	1.53(4)	6668	6080	4606	1.63(5)
Mo(2)	2606(2)	3026(2)	176(2)	1.67(4)	9516(2)	5945(2)	6285(2)	1.61(5)
Mo(3)	2804(2)	266(2)	652(2)	1.49(4)	9709(2)	3175(2)	6755(2)	1.66(5)
Mo(4)	−129(2)	200(2)	−1789(2)	1.35(4)	6785(2)	3105(2)	4317(2)	1.47(4)
Mo(5)	179.0(7)	−2927.9(6)	1417.9(7)	1.55(4)	7087.6(7)	−28.6(7)	7511.6(7)	1.69(5)
Mo(6)	−2670(2)	−2784(2)	−287(2)	1.65(4)	4240(2)	135(2)	5821(3)	1.95(5)
Mo(7)	−2867(2)	−17(2)	−742(2)	1.51(4)	4040(2)	2893(2)	5357(2)	1.57(5)
Mo(8)	64(2)	52(2)	1704(2)	1.32(4)	6979(2)	2957(2)	7810(2)	1.43(4)
Na(1)	−1427(5)	5676(5)	5322(5)	2.94(9)	5233(6)	8553(6)	907(6)	3.5(1)
Na(2)	1617(6)	5400(5)	5115(6)	3.1(1)	8293(6)	−2523(6)	11354(6)	3.2(1)
O(1)	−1340(10)	3740(10)	−900(10)	2.7(2)	5560(10)	6600(10)	5160(10)	2.3(2)
O(2)	810(10)	4360(10)	−2270(10)	2.1(2)	7711(8)	7259(8)	3810(10)	1.6(1)
O(3)	3488(8)	4280(8)	−570(10)	2.0(1)	10340(10)	7116(9)	5320(10)	2.2(2)
O(4)	3465(9)	3548(8)	1960(10)	2.0(2)	10350(10)	6461(9)	8070(10)	2.1(2)
O(5)	3910(10)	910(10)	2230(10)	2.1(2)	10840(10)	3840(10)	8300(10)	2.7(2)
O(6)	3419(9)	−782(8)	−40(10)	1.8(2)	10330(10)	2170(8)	5970(10)	2.0(2)
O(7)	−1140(10)	−470(10)	−3440(10)	2.9(2)	5840(10)	2450(10)	2660(10)	1.8(2)
O(8)	1334(9)	−3484(8)	1050(10)	2.0(1)	8200(10)	−620(10)	7130(10)	2.6(2)
O(9)	−830(10)	−4200(10)	2110(10)	2.3(2)	6080(10)	−1310(10)	8170(10)	2.8(2)
O(10)	−3470(10)	−3940(10)	710(10)	2.5(2)	3350(10)	−1119(9)	6580(10)	2.3(2)
O(11)	−3590(10)	−3440(10)	−1930(10)	2.8(2)	3290(10)	−520(10)	4210(10)	2.6(2)
O(12)	−3960(10)	−760(10)	−2370(10)	2.8(2)	2960(10)	2200(10)	3710(10)	2.2(2)
O(13)	−3580(10)	880(10)	−40(10)	2.4(2)	3360(10)	3850(10)	5960(10)	2.1(2)
O(14)	950(10)	640(9)	3390(10)	1.6(1)	7900(10)	3510(10)	9480(10)	2.9(3)
O(15)	1030(10)	3420(10)	250(10)	2.8(2)	7970(10)	6370(10)	6340(10)	2.0(2)
O(16)	3446(9)	1848(9)	−140(10)	1.4(1)	10298(8)	4729(8)	5811(9)	1.4(1)
O(17)	1113(9)	−473(8)	−1570(10)	1.3(1)	8120(10)	2540(10)	4620(10)	1.8(2)
O(18)	1010(10)	2020(10)	−1800(10)	1.6(2)	7910(10)	4910(10)	4300(10)	1.9(2)
O(19)	−1290(10)	1250(10)	−1190(10)	1.7(2)	5660(10)	4190(10)	4910(10)	1.4(2)
O(20)	1250(10)	1074(9)	620(10)	1.4(2)	8150(10)	4010(10)	6720(10)	1.6(2)
O(21)	−1116(8)	−3233(8)	−343(9)	1.0(1)	5820(10)	−290(10)	5760(10)	1.7(2)
O(22)	−3430(10)	−1560(10)	190(10)	2.0(2)	3400(10)	1304(9)	6110(10)	1.9(2)
O(23)	−1250(10)	610(10)	1430(10)	2.3(2)	5785(9)	3639(9)	7620(10)	1.5(2)
O(24)	−1000(10)	−1680(10)	1790(10)	1.5(2)	5890(10)	1210(10)	7880(10)	1.5(2)
O(25)	1250(10)	−970(10)	1190(10)	1.4(2)	8210(10)	1960(10)	7310(10)	1.8(2)
O(26)	−1310(10)	−910(10)	−730(10)	1.6(2)	5580(10)	2020(10)	5370(10)	1.7(2)
O(27)	−1599(8)	2261(7)	−3442(8)	1.6(1)	5300(10)	5147(9)	2660(10)	2.1(2)
O(28)	1406(9)	−1938(8)	3450(10)	2.2(2)	8280(10)	938(9)	9530(10)	2.1(2)
O(29)	−1418(8)	3764(7)	−4791(8)	2.6(1)	5502(8)	6664(8)	1316(9)	2.8(2)
O(30)	987(7)	−3586(6)	4757(6)	1.8(1)	7904(8)	−679(7)	10858(8)	2.1(1)
O(31)	−180(10)	6440(10)	−2700(10)	3.3(2)	6470(10)	9210(10)	3270(10)	2.8(2)
O(32)	−3500(10)	4304(9)	−7280(10)	2.6(2)	3430(10)	7220(10)	−1220(10)	3.2(2)
O(33)	−3580(10)	5570(10)	−4580(10)	4.9(2)	3290(10)	8431(9)	1480(10)	4.9(2)
O(34)	−1517(9)	7680(8)	−5714(9)	3.3(1)	5818(8)	10693(7)	559(8)	2.4(1)
O(35)	338(9)	−6077(9)	2750(10)	2.4(2)	7030(10)	−3280(10)	8740(10)	3.0(2)
O(36)	3520(10)	3880(10)	7410(10)	3.6(2)	10460(10)	−970(10)	13450(10)	3.6(3)
O(37)	3550(10)	−5860(10)	4580(10)	5.7(2)	10410(10)	−2960(10)	10670(10)	5.2(2)
O(38)	1023(7)	−7538(6)	5445(7)	2.1(1)	8342(8)	−4539(8)	11724(9)	3.2(2)
N(1)	−2400(10)	2160(10)	−7170(10)	2.3(2)	4250(10)	5070(10)	−1090(10)	2.1(2)
N(2)	−5960(10)	−3170(10)	−9080(10)	2.4(2)	900(10)	−120(10)	−3150(10)	2.6(2)
N(3)	2570(10)	−1930(10)	7090(10)	2.2(2)	9190(10)	940(10)	13180(10)	2.1(2)
N(4)	5900(10)	3240(10)	9170(10)	2.2(2)	12740(10)	6270(10)	15090(10)	2.4(2)
C(1)	−1600(10)	2700(10)	−4630(10)	1.5(2)	5130(10)	5570(10)	1440(10)	1.8(2)
C(2)	−2230(9)	1551(8)	−5859(8)	2.0(1)	4070(10)	4567(9)	230(10)	2.4(1)
C(3)	−3555(9)	418(8)	−5767(9)	2.3(1)	4050(10)	3230(10)	240(10)	3.1(2)
C(4)	−3970(10)	−760(10)	−6950(10)	2.6(2)	2710(10)	2200(10)	−770(10)	3.1(3)
C(5)	−5248(9)	−1902(8)	−6770(10)	2.5(1)	2600(10)	860(10)	−660(10)	4.8(3)
C(6)	−5530(10)	−3190(10)	−7700(10)	2.6(2)	1180(10)	−240(10)	−1560(10)	2.4(2)
C(7)	1720(10)	−2380(10)	4550(10)	2.1(2)	8410(10)	480(10)	10620(10)	2.1(2)
C(8)	2791(9)	−1408(8)	5794(9)	2.2(1)	9065(9)	1599(8)	11886(9)	2.0(1)
C(9)	2810(10)	−70(10)	5790(10)	2.9(1)	10408(9)	2744(8)	11795(9)	2.1(1)
C(10)	4160(10)	950(10)	6810(10)	2.6(2)	10830(10)	3910(10)	12990(10)	2.6(2)
C(11)	4260(10)	2330(10)	6770(10)	4.0(2)	12097(9)	5059(8)	12777(9)	2.3(1)
C(12)	5670(10)	3390(10)	7530(10)	3.1(2)	12310(10)	6390(10)	13650(10)	3.3(3)

Table 3. Bond Distances and Angles for Mo_8-D (a) and -L (b)

		(a)/Å	(b)/Å			(a)/Å	(b)/Å
Mo(1)	O(1)	1.73(1)	1.70(1)	Mo(5)	O(8)	1.694(9)	1.68(1)
	O(2)	1.732(9)	1.732(9)		O(9)	1.71(1)	1.70(1)
	O(15)	1.89(1)	1.90(1)		O(21)	1.910(9)	1.90(1)
	O(18)	2.27(1)	2.26(1)		O(24)	2.298(9)	2.30(1)
	O(19)	2.09(1)	2.05(1)		O(25)	2.10(1)	2.14(1)
	O(27)	2.089(8)	2.092(9)		O(28)	2.130(9)	2.108(9)
Mo(2)	O(3)	1.686(8)	1.752(9)	Mo(6)	O(10)	1.757(9)	1.697(9)
	O(4)	1.766(9)	1.768(9)		O(11)	1.67(1)	1.66(1)
	O(15)	1.92(1)	1.92(1)		O(21)	1.940(8)	1.95(1)
	O(16)	1.921(9)	1.952(8)		O(22)	1.94(1)	1.903(9)
	O(18)	2.21(1)	2.23(1)		O(24)	2.33(1)	2.31(1)
	O(20)	2.248(9)	2.24(1)		O(26)	2.18(1)	2.19(1)
Mo(3)	O(5)	1.68(1)	1.66(1)	Mo(7)	O(12)	1.72(1)	1.73(1)
	O(6)	1.743(9)	1.759(9)		O(13)	1.70(1)	1.68(1)
	O(16)	1.927(9)	1.984(8)		O(19)	1.91(1)	1.95(1)
	O(17)	2.400(9)	2.30(1)		O(22)	1.97(1)	1.914(9)
	O(20)	2.192(9)	2.22(1)		O(23)	2.34(1)	2.463(9)
	O(25)	1.922(9)	1.88(1)		O(26)	2.27(1)	2.23(1)
Mo(4)	O(7)	1.71(1)	1.69(1)	Mo(8)	O(14)	1.696(9)	1.69(1)
	O(17)	1.759(9)	1.758(9)		O(20)	1.932(9)	1.94(1)
	O(18)	1.93(1)	1.92(1)		O(23)	1.74(1)	1.721(9)
	O(19)	2.18(1)	2.17(1)		O(24)	1.859(9)	1.87(1)
	O(20)	2.45(1)	2.45(1)		O(25)	2.15(1)	2.16(1)
	O(26)	1.96(1)	1.95(1)		O(26)	2.48(1)	2.49(1)
C(1)	O(27)	1.32(1)	1.34(2)	C(7)	O(28)	1.27(2)	1.24(2)
	O(29)	1.16(1)	1.16(1)		O(30)	1.33(1)	1.26(1)
	C(2)	1.55(1)	1.51(1)		C(8)	1.52(1)	1.55(2)
C(2)	N(1)	1.52(1)	1.48(1)	C(8)	N(3)	1.49(1)	1.54(1)
	C(3)	1.52(1)	1.49(1)		C(9)	1.50(1)	1.54(1)
C(3)	C(4)	1.57(1)	1.54(2)	C(9)	C(10)	1.54(1)	1.57(2)
C(4)	C(5)	1.53(1)	1.47(2)	C(10)	C(11)	1.52(2)	1.53(2)
C(5)	C(6)	1.56(1)	1.57(2)	C(11)	C(12)	1.51(2)	1.60(2)
C(6)	N(2)	1.37(2)	1.58(2)	C(12)	N(4)	1.64(2)	1.44(2)

(2.18(1) and 2.17(1) Å) is larger than the Mo(4)–O(26) (four-coordinated) one (1.96(1) and 1.95(1) Å in Mo_8-D and -L, respectively); similarly for the Mo(7) site, the Mo(7)–O(23) (two-coordinated) (2.34(1) and 2.463(9) Å) is larger than both bond lengths of the Mo(7)–O(19) (three-coordinated) (1.91(1) and 1.95(1) Å) and the Mo(7)–O(26) (four-coordinated) (2.27(1) and 2.23(1) Å in Mo_8-D and -L, respectively). These variations are no doubt a consequence of departure from regular octahedral symmetry as evidenced by large deviations of bond angles from 180° and 90° for trans- and cis-coordinated oxygens (Table 3). The distortion of MoO_6 octahedra has been also observed for other γ-octamolybdates containing organic ligands.[12—17]

Selected interatomic separations ($\leq$3.2 Å) for Mo_8-D and -L are shown in Table 4. Sodium–water or $-Mo_8(lysH_2)_2$ oxygen distances vary from 2.2 to 2.9 Å. Each atom of Na(1) and Na(2) is surrounded by four water molecules and two anion oxygen atoms to result in the distorted octahedral configuration. The fact that the $Mo_8(lysH_2)_2$ compounds can be prepared at pH=3 indicates that each nitrogen atom in the lysine ligand has an extra proton because of the pK_a ($\alpha-NH_3^+$)=9.0 and pK_a (side chain)=10.5 for lysine. Thus, that only two Na atoms in the molecule were found satisfies the chemical neutrality of the molecule. The protonation at four amino groups of the lysine ligands in the anion would lead to the hydrogen-bonding between the amino nitrogen atoms N(1—4) and neighboring octamolybdate-oxygen atoms. Observable short distances (2.7—2.9 Å) between each N atom and octamolybdate O atoms support strongly the presence of this type of hydrogen-bonding with a resultant formation of the three-dimensional hydrogen and ionic bonding system (Table 4). Figure 3 exemplifies packing of the Mo_8-D anions in the unit cell together with the hydrogen-bonding network.

Two C–O bond lengths of the carboxyl group in the $lysH_2$ ligand are slightly different between the two ligands in the anion: 1.32(1) Å (C(1)–O(27)) and 1.16(1) Å (C(1)–O(29)) against 1.27(2) Å (C(7)–O(28)) and 1.33(1) Å (C(7)–O(30)) for Mo_8-D (1.34(2) and 1.16(1) Å against 1.24(2) and 1.26(1) Å for Mo_8-L). The C(7)–O(30) bond length is significantly longer than the corresponding C(1)–O(29) bond length. This asymmetry is attributed to the coordination of the O(30) atom into two Na atoms (Table 4 and Fig. 3). Table 5 shows dihedral angles (°) among carboxyl group, side chain, and central octamolybdate Mo(2)Mo(4)Mo(6)Mo(8) planes. Table 6 shows distances (Å) of carbon and nitrogen atoms from least-squares planes of selected atoms. Chiral C(2) and C(8) atoms lie 0.45

Table 3. (Continued)

			(a)/°	(b)/°				(a)/°	(b)/°
O(1)	Mo(1)	O(2)	109.6(4)	110.1(4)	O(8)	Mo(5)	O(9)	101.3(4)	99.6(5)
O(1)	Mo(1)	O(15)	97.7(5)	98.2(5)	O(8)	Mo(5)	O(21)	103.1(4)	102.8(5)
O(1)	Mo(1)	O(18)	162.7(4)	161.7(5)	O(8)	Mo(5)	O(24)	165.3(4)	166.6(4)
O(1)	Mo(1)	O(19)	94.4(4)	94.1(4)	O(8)	Mo(5)	O(25)	97.1(4)	97.7(5)
O(1)	Mo(1)	O(27)	96.5(4)	95.2(4)	O(8)	Mo(5)	O(28)	96.1(4)	97.3(5)
O(2)	Mo(1)	O(15)	100.3(5)	99.4(5)	O(9)	Mo(5)	O(21)	98.4(4)	99.1(5)
O(2)	Mo(1)	O(18)	86.9(4)	87.8(4)	O(9)	Mo(5)	O(24)	93.1(4)	93.7(4)
O(2)	Mo(1)	O(19)	153.6(4)	153.1(4)	O(9)	Mo(5)	O(25)	157.3(4)	158.2(4)
O(2)	Mo(1)	O(27)	89.1(4)	89.3(4)	O(9)	Mo(5)	O(28)	90.0(4)	90.4(4)
O(15)	Mo(1)	O(18)	73.4(4)	74.2(5)	O(21)	Mo(5)	O(24)	77.0(3)	76.1(5)
O(15)	Mo(1)	O(19)	86.9(5)	88.1(5)	O(21)	Mo(5)	O(25)	90.2(4)	89.8(5)
O(15)	Mo(1)	O(27)	159.2(4)	160.4(5)	O(21)	Mo(5)	O(28)	156.9(3)	155.9(4)
O(18)	Mo(1)	O(19)	70.7(4)	69.4(4)	O(24)	Mo(5)	O(25)	68.3(3)	69.0(4)
O(18)	Mo(1)	O(27)	88.7(3)	88.8(4)	O(24)	Mo(5)	O(28)	81.2(3)	81.2(4)
O(19)	Mo(1)	O(27)	76.9(4)	76.6(4)	O(25)	Mo(5)	O(28)	74.7(3)	74.3(4)
O(3)	Mo(2)	O(4)	103.6(4)	110.6(4)	O(10)	Mo(6)	O(11)	104.9(4)	96.5(4)
O(3)	Mo(2)	O(15)	100.0(4)	99.7(5)	O(10)	Mo(6)	O(21)	98.8(4)	99.3(5)
O(3)	Mo(2)	O(16)	100.4(4)	95.2(4)	O(10)	Mo(6)	O(22)	95.4(4)	100.6(4)
O(3)	Mo(2)	O(18)	92.1(4)	86.6(4)	O(10)	Mo(6)	O(24)	85.3(4)	92.2(4)
O(3)	Mo(2)	O(20)	165.4(4)	158.5(4)	O(10)	Mo(6)	O(26)	158.1(4)	165.5(5)
O(4)	Mo(2)	O(15)	95.8(5)	95.3(5)	O(11)	Mo(6)	O(21)	96.2(4)	97.8(5)
O(4)	Mo(2)	O(16)	96.5(4)	101.4(4)	O(11)	Mo(6)	O(22)	103.3(5)	97.0(4)
O(4)	Mo(2)	O(18)	162.8(4)	161.6(4)	O(11)	Mo(6)	O(24)	168.0(4)	169.5(4)
O(4)	Mo(2)	O(20)	90.3(4)	90.0(4)	O(11)	Mo(6)	O(26)	96.6(4)	97.4(5)
O(15)	Mo(2)	O(16)	152.9(4)	152.1(4)	O(21)	Mo(6)	O(22)	151.9(4)	153.6(4)
O(15)	Mo(2)	O(18)	74.3(4)	74.6(5)	O(21)	Mo(6)	O(24)	75.7(3)	75.1(5)
O(15)	Mo(2)	O(20)	82.9(4)	83.7(5)	O(21)	Mo(6)	O(26)	83.1(4)	83.0(5)
O(16)	Mo(2)	O(18)	87.4(4)	82.9(4)	O(22)	Mo(6)	O(24)	81.6(4)	87.0(4)
O(16)	Mo(2)	O(20)	73.1(3)	74.1(4)	O(22)	Mo(6)	O(26)	75.0(4)	73.5(4)
O(18)	Mo(2)	O(20)	74.8(3)	73.8(4)	O(24)	Mo(6)	O(26)	73.9(3)	74.4(4)
O(5)	Mo(3)	O(6)	104.0(4)	105.5(5)	O(12)	Mo(7)	O(13)	106.4(5)	103.9(5)
O(5)	Mo(3)	O(16)	95.9(4)	98.2(5)	O(12)	Mo(7)	O(19)	101.4(5)	100.3(5)
O(5)	Mo(3)	O(17)	173.6(4)	171.7(5)	O(12)	Mo(7)	O(22)	97.7(5)	94.6(4)
O(5)	Mo(3)	O(20)	103.0(4)	103.6(5)	O(12)	Mo(7)	O(23)	167.9(5)	170.3(4)
O(5)	Mo(3)	O(25)	98.6(4)	99.6(5)	O(12)	Mo(7)	O(26)	98.3(5)	99.4(5)
O(6)	Mo(3)	O(16)	107.0(4)	101.8(4)	O(13)	Mo(7)	O(19)	104.4(5)	101.1(4)
O(6)	Mo(3)	O(17)	82.3(4)	81.3(4)	O(13)	Mo(7)	O(22)	100.8(4)	107.4(4)
O(6)	Mo(3)	O(20)	152.6(4)	151.0(5)	O(13)	Mo(7)	O(23)	84.6(4)	85.8(4)
O(6)	Mo(3)	O(25)	100.6(4)	102.7(5)	O(13)	Mo(7)	O(26)	155.1(4)	156.7(5)
O(16)	Mo(3)	O(17)	81.1(3)	75.4(3)	O(19)	Mo(7)	O(22)	142.4(4)	143.5(4)
O(16)	Mo(3)	O(20)	74.2(3)	73.9(4)	O(19)	Mo(7)	O(23)	80.2(4)	78.1(4)
O(16)	Mo(3)	O(25)	144.5(4)	144.4(4)	O(19)	Mo(7)	O(26)	72.9(4)	72.5(4)
O(17)	Mo(3)	O(20)	70.7(3)	69.8(4)	O(22)	Mo(7)	O(23)	74.8(4)	81.6(3)
O(17)	Mo(3)	O(25)	81.1(4)	83.3(4)	O(22)	Mo(7)	O(26)	72.5(4)	72.4(4)
O(20)	Mo(3)	O(25)	71.0(4)	72.1(4)	O(23)	Mo(7)	O(26)	70.5(4)	70.9(4)
O(7)	Mo(4)	O(17)	103.5(5)	105.6(5)	O(14)	Mo(8)	O(20)	106.4(4)	105.8(6)
O(7)	Mo(4)	O(18)	107.5(5)	106.3(5)	O(14)	Mo(8)	O(23)	104.5(5)	102.9(5)
O(7)	Mo(4)	O(19)	98.5(4)	100.6(4)	O(14)	Mo(8)	O(24)	101.3(4)	101.5(6)
O(7)	Mo(4)	O(20)	177.3(4)	179.0(4)	O(14)	Mo(8)	O(25)	98.6(4)	95.8(5)
O(7)	Mo(4)	O(26)	100.6(5)	102.4(5)	O(14)	Mo(8)	O(26)	177.1(4)	177.1(5)
O(17)	Mo(4)	O(18)	101.7(4)	98.6(5)	O(20)	Mo(8)	O(23)	101.5(5)	98.5(5)
O(17)	Mo(4)	O(19)	157.2(4)	153.8(4)	O(20)	Mo(8)	O(24)	140.0(4)	140.6(5)
O(17)	Mo(4)	O(20)	76.4(4)	73.8(4)	O(20)	Mo(8)	O(25)	71.9(4)	72.4(4)
O(17)	Mo(4)	O(26)	97.3(4)	100.1(5)	O(20)	Mo(8)	O(26)	76.4(3)	76.4(4)
O(18)	Mo(4)	O(19)	75.4(4)	73.9(4)	O(23)	Mo(8)	O(24)	98.9(4)	102.5(4)
O(18)	Mo(4)	O(20)	75.2(4)	74.5(4)	O(23)	Mo(8)	O(25)	156.9(4)	160.9(4)
O(18)	Mo(4)	O(26)	141.0(4)	139.9(5)	O(23)	Mo(8)	O(26)	75.7(4)	78.4(4)
O(19)	Mo(4)	O(20)	81.0(4)	80.0(4)	O(24)	Mo(8)	O(25)	75.9(4)	77.2(4)
O(19)	Mo(4)	O(26)	74.0(4)	73.7(4)	O(24)	Mo(8)	O(26)	75.8(4)	75.7(4)
O(20)	Mo(4)	O(26)	76.7(3)	77.1(4)	O(25)	Mo(8)	O(26)	81.2(3)	83.1(4)
O(27)	C(1)	O(29)	125(1)	124(1)	O(28)	C(7)	O(30)	123(1)	131(1)
O(27)	C(1)	C(2)	110.7(9)	116(1)	O(28)	C(7)	C(8)	118(1)	110(1)
O(29)	C(1)	C(2)	122(1)	118(1)	O(30)	C(7)	C(8)	118(1)	117(1)
N(1)	C(2)	C(1)	105.8(7)	109.6(8)	N(3)	C(8)	C(7)	109.9(8)	106.3(8)
N(1)	C(2)	C(3)	114.3(7)	112.8(8)	N(3)	C(8)	C(9)	112.7(8)	116.0(7)
C(1)	C(2)	C(3)	114.6(7)	113.8(8)	C(7)	C(8)	C(9)	112.4(8)	114.2(8)
C(2)	C(3)	C(4)	109.6(7)	111.0(9)	C(8)	C(9)	C(10)	110.2(8)	109.8(8)
C(3)	C(4)	C(5)	108.0(8)	112(1)	C(9)	C(10)	C(11)	111.7(9)	107.6(9)
C(4)	C(5)	C(6)	110.7(8)	114(1)	C(10)	C(11)	C(12)	114(1)	110.3(9)
N(2)	C(6)	C(5)	113.2(9)	112.9(9)	N(4)	C(12)	C(11)	107(1)	106(1)

Table 4. Selected Interatomic Distances for Mo_8-D (a) and -L (b)

		(a)/Å	(b)/Å			(a)/Å	(b)/Å
N(1)	O(13^{i})	2.91(1)	2.96(1)	O(33)	O(11^{vi})	2.82(1)	2.91(1)
	O(23^{i})	2.96(1)	3.12(1)	O(34)	O(7^{vi})	2.84(1)	2.80(1)
N(2)	O(3^{iv})	2.93(1)	3.16(2)		O(24^{ix})	2.75(1)	
	O(6^{iii})	3.16(1)	3.00(1)	O(35)	O(15^{ii})	2.86(2)	2.86(2)
	O(8^{iii})	2.84(1)	2.82(2)	O(36)	O(11^{vii})	2.88(1)	2.81(2)
	O(10^{i})	3.17(1)		O(37)	O(4^{ii})	2.65(1)	2.63(1)
	O(22^{i})	2.90(1)	2.84(1)	O(38)	O(14^{ii})	2.79(1)	2.87(2)
N(3)	O(6^{v})	2.87(1)	2.82(1)	Na(1)	O(29)	2.245(9)	2.30(1)
	O(17^{v})	3.11(1)	2.96(1)		O(31)	2.59(1)	2.36(1)
N(4)	O(1^{vii})	2.83(1)	2.89(2)		O(32)	2.50(1)	2.47(1)
	O(3^{v})		3.13(1)		O(33)	2.56(1)	2.25(1)
	O(10^{viii})	3.19(1)	2.97(1)		O(34)	2.79(1)	2.87(2)
	O(13^{vii})	3.03(1)			O(30^{ix})	2.343(9)	2.306(9)
	O(16^{v})	2.76(1)	2.81(1)	Na(2)	O(30)	2.409(8)	2.330(9)
O(31)	O(21^{vi})	2.83(1)	2.82(2)		O(35)	2.37(1)	2.59(1)
O(32)	O(4^{iii})	2.94(1)	2.99(1)		O(36)	2.67(1)	2.67(1)
	O(9^{ix})	2.94(1)			O(37)	2.49(1)	2.73(1)
	O(10^{ix})	2.90(1)			O(38)	2.297(1)	2.34(1)
	O(10^{ix})	2.90(1)			O(2^{x})	2.94(1)	2.68(1)
Mo(1)	Mo(2)	3.225(2)	3.225(2)	Mo(4)	Mo(6)	4.031(2)	4.023(3)
	Mo(4)	3.395(2)	3.397(2)		Mo(7)	3.274(2)	3.277(2)
	Mo(7)	3.843(2)	3.841(3)		Mo(8)	3.4788(2)	3.477(2)
Mo(2)	Mo(3)	3.246(2)	3.256(2)	Mo(5)	Mo(6)	3.236(2)	3.242(2)
	Mo(4)	3.474(2)	3.486(3)		Mo(8)	3.399(2)	3.404(3)
	Mo(8)	4.040(2)	4.044(3)	Mo(6)	Mo(7)	3.249(2)	3.245(2)
Mo(3)	Mo(4)	3.514(2)	3.507(3)		Mo(8)	3.489(2)	3.485(3)
	Mo(5)	3.851(2)	3.852(3)	Mo(7)	Mo(8)	3.513(2)	3.528(3)
	Mo(8)	3.280(2)	3.268(2)				

symmetry code: i) $x, y, z-1$; ii) $x, y-1, z$; iii) $x-1, y, z-1$; iv) $x-1, y-1, z-1$; v) $x, y, z+1$; vi) $x, y+1, z$; vii) $x+1, y, z+1$; viii) $x+1, y+1, z+1$; ix) $x, y+1, z-1$; x) $x, y-1, z+1$.

Table 5. Dihedral Angles (°) between the Selected Least Square Planes for Mo_8-D and -L (in parentheses)

Plane[a)]	1	2	3	4	5	6	7	8
2	42.7(66.9)							
3	68.5(45.2)	108.8(109.5)						
4	173.8(146.8)	134.0(131.3)	116.1(117.0)					
5	147.2(174.2)	119.7(118.2)	129.1(130.8)	26.7(27.8)				
6	41.1(30.2)	53.9(50.6)	63.6(60.5)	144.0(177.0)	163.6(155.2)			
7	27.5(24.0)	69.9(47.9)	41.6(61.7)	156.0(168.3)	150.5(161.8)	45.5(9.8)		
8	34.5(27.0)	56.2(43.7)	56.9(65.8)	151.2(167.3)	173.0(158.9)	9.7(11.7)	35.8(4.2)	
9	24.0(27.0)	64.6(53.7)	44.8(57.0)	161.0(173.2)	158.5(158.1)	37.2(3.8)	8.4(9.5)	27.6(12.6)

a) Plane **1**, Mo(2)Mo(4)Mo(6)Mo(8); **2**, C(2)C(3)C(4)C(5)C(6); **3**, C(8)C(9)C(10)C(11)C(12); **4**, C(1)N(1)C(3); **5**, C(7)N(3)C(9); **6**, C(1)O(27)O(29); **7**, C(7)O(28)O(30); **8**, C(1)O(27)O(29)C(2); **9**, C(7)O(28)O(30)C(8).

and 0.44 Å for Mo_8-D (−0.43 and −0.44 Å for Mo_8-L) out of C(1)N(1)C(3) and C(7)N(3)C(9) planes, respectively. The opposite location of C(2) and C(8) atoms out of the C(1)N(1)C(3) and C(7)N(3)C(9) planes between Mo_8-D and -L indicates that the two species are optical-active compound as supported by the polarimetric measurement ($[\alpha]_D = -3.680°$ and $+3.500°$ for Mo_8-D and -L, respectively). The dihedral angle between the least-squares planes containing side chains C(2—6) and C(8—12) atoms is about 110° (108.8° and 109.5° for Mo_8-D and -L, respectively) with a large displacement from 180°, indicating that the geometry for two $lysH_2$ ligands in the anion is not the case of Mo_8-*meso* related by an inversion center.[17] In addition, the dihedral angle of 173.8° between the Mo(2,4,6,8) least-square plane and the C(1)N(1)C(3) plane for Mo_8-D (146.8° for Mo_8-L) is significantly different from 147.2° between the Mo(2,4,6,8) and C(7)N(3)C(9) planes (174.2° for Mo_8-L). The carboxyl group and the chiral carbon atoms are approximately coplanar, as indicated by bond angles (about 120°) of O(27)–C(1)–O(29) (125(1)°), O(29)–C(1)–C(2) (122(1)°), O(28)–C(7)–O(30) (123(1)°), and O(30)–C(7)–C(8) (118(1)°) in Mo_8-

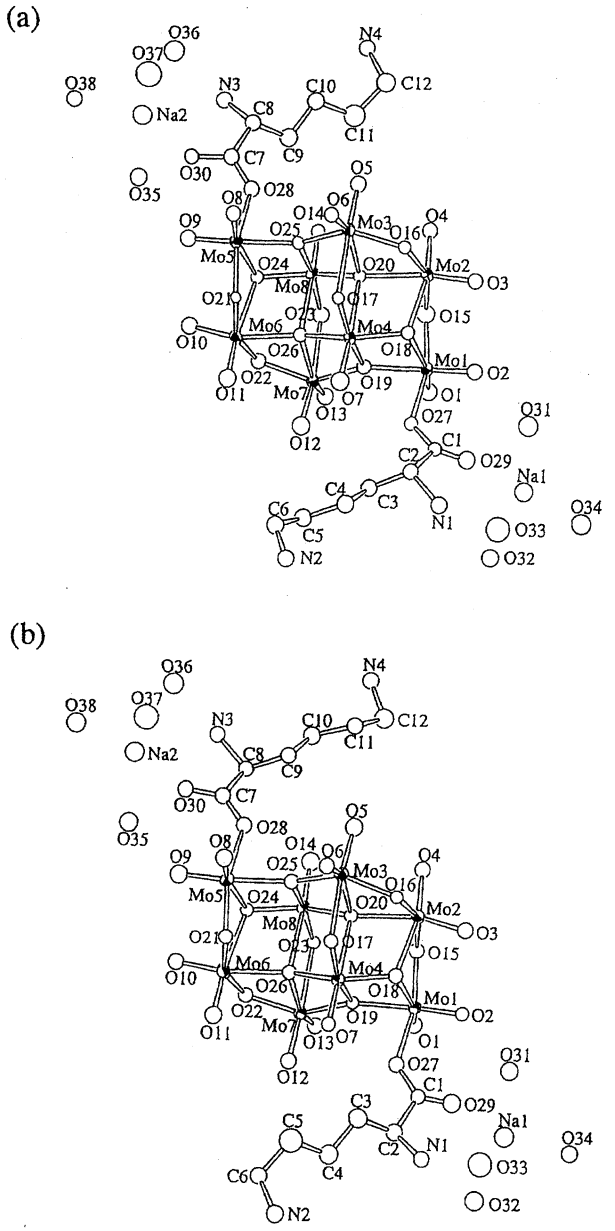

Fig. 2. Structures of Mo_8-D (a) and -L (b).

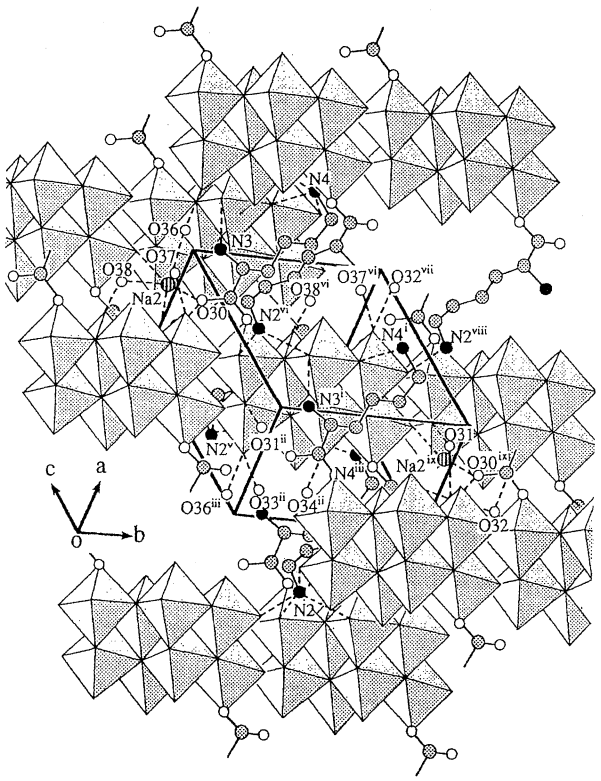

Fig. 3. Packing of Mo_8-D molecules in the unit cell together with hydrogen-bonding network. ○, ●, ○ and ◍ represent carbon, nitrogen, oxygen, and sodium atoms, respectively.

Table 6. Separations (Å) of Carbon and Nitrogen Atoms from the Selected Planes for Mo_8-D (a) and -L (b)

Plane	Atom	(a)/Å[a)]	(b)/Å[a)]
C(1)N(1)C(3)	C(2)	0.45	−0.43
C(7)N(3)C(9)	C(8)	0.44	−0.44
C(2)C(3)C(4)C(5)C(6)	C(1)	0.37	−0.50
	N(1)	−1.30	1.28
	N(2)	−1.01	1.24
C(8)C(9)C(10)C(11)C(12)	C(7)	0.54	−0.47
	N(3)	−1.31	1.33
	N(4)	−1.27	1.10

a) + direction is that in which a right-hand screw advances when turned from C(1)C(3)(C(7)C(9), C(2)C(3), or C(8)C(9)) vector to C(1)N(1) (C(7)N(3), C(2)C(4), or C(8)C(10)) vector through the smaller angle.

D (Table 3) (124(1), 118(1), 131(1), and 117(1)° in Mo_8-L). The C–C bond lengths vary from 1.49(1) to 1.60(2) Å with their average values of 1.55(1) and 1.52(2) Å for C(2—6) and C(8—12) side chains in Mo_8-D (1.52(2) and 1.56(2) Å in Mo_8-L) in good agreement with the average value 1.533(3) Å in the normal hydrocarbons butane through heptane.[24] Similarly, the average values of the four C–C–C angles are 110.7(8)° and 112.1(9)° for C(1—6) and C(7—12) in Mo_8-D (113(1)° and 110.5(9)° in Mo_8-L), respectively, in good agreement with the value of 112.4° found in *n*-butane.[24] The C atoms in each side chain of the $lysH_2$ ligand are also approximately coplanar. The deviations of ε-amino N atoms of N(2) and N(4) from the least-squares plane of side chain C atoms are −1.01 and −1.27 Å for Mo_8-D (1.24 and 1.10 Å for Mo_8-L). ε-Amino N(2) and N(4) atoms are located at the same side from the least-square plane including the side chain C atoms as the α-amino N(1) and N(3) atoms (at −1.30 and −1.31 Å for Mo_8-D and 1.28 and 1.33 Å for Mo_8-L), in contrast with the case of the L-lysine-hydrogen chloride–water (1/1/2) crystal where ε-amino nitrogen atom lies on the least-square plane of the side chain.[24] As shown in Table 2, the side chain C–N_ε bond lengths are appreciably asymmetric between the two $lysH_2$ ligands in the anion: 1.37(2) Å (C(6)–N(2)) and 1.64(2) Å (C(12)–N(4)) for Mo_8-D

(1.58(2) and 1.44(2) Å for Mo_8-L), while the chiral centered C–N_α bond lengths are nearly symmetric; 1.52(1) Å (C(2)–N(1)) and 1.49(1) Å (C(8)–N(3)) for Mo_8-D (1.48(1) and 1.54(1) Å for Mo_8-L). In L-lysine–hydrogen chloride–water (1/1/2) and Mo_8-*meso*, corresponding C–N_ε bond lengths were 1.482(4)[24] and 1.50(3) Å, respectively. The N(4)···O(16^v) distance (2.76(1) Å) in Mo_8-D is significantly shorter than corresponding N(2)···O(22^i) distance (2.90(1) Å) in another $lysH_2$ ligand. Since the former distance implies the presence of the strong hydrogen-bonding between ε-amino nitrogen N(4) and octamolybdate oxygen O(16^v) atoms, the asymmetric feature of the C–N_ε bond length between the two $lysH_2$ ligands in the anion might be associated with the difference in hydrogen bonds deployed in the NH_3^+ group.

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