the type A and the type B molecules possess the C25–C26′ (type A[3a]) and the C25–C26 (type B[3a]) ethyl groups, respectively. Therefore, there exist, theoretically, three types of dimers, AA, BB, and AB, which are composed of molecules A and A, B and B, and A and B, respectively, where an exact 2-fold symmetry exists for the first two but not for the last; two ethyl groups in the dimer come close to each other in the dimer AA, go away from each other in the dimer BB, or are directed synchronously in the dimer AB. However, as noted before, the very short C26′···C26′ contact precludes the existence of the dimer AA. Indeed, form I of the Na^+(5-Br-L^-) salt,[6c] which forms a "head-to-tail" dimer having a pseudo-2-fold symmetry, involves only a BB-type dimer. The $Ag^+(L^-)$ salt[6d] is an exception: it forms the AA-type "head-to-tail" dimer with a pseudo-2-fold symmetry, where unfavorable C26···C26 contact is, however, avoided by mutual sliding of the pairing molecules toward the phenyl group of the partner molecule to form Ag^+–phenyl bondings or vice versa. On the other hand, there seems to be no restriction in the mutual arrangement of the two ethyl groups for the "head-to-head" dimer structure; form II of Na^+(5-Br-L^-)[6c] and 5-Br-L free acid[4c] both contain the AA-type dimer with a pseudo-2-fold symmetry. Furthermore, occupancy factors for the C26 and C26′ atoms of 0.7 and 0.3 respectively indicate that the BB- and AB-type dimers exist in a 4:6 ratio, respectively, in the present crystal.[17] It is of interest to note here that monomeric lasalocid A–methanol[4a] can be crystallized to give two crystalline forms that contain only the A- and B-type ionophore molecules, respectively, while the present salt consists of the BB- and AB-type dimers in one crystalline form in a disordered manner.

Conclusion

The most novel structural feature of the complex is the existence of an exact 2-fold symmetry in the dimer, and this complex may, therefore, be regarded as a prototype for the 2:2 "head-to-tail" dimeric structure. The salt forms two types of "head-to-tail" dimers, BB and AB, but no AA (defined above), which differ in the mutual arrangement of the C25–C26 ethyl groups; the existence of the AA dimer may be allowed only in the cases in which the 2-fold symmetry in the dimer is significantly broken or the dimer adopts a peculiar structural feature(s), e.g., metal–phenyl bonding in the $Ag^+(L^-)$ salt.[6d] This suggests that the terminal ethyl group arrangement could play an important role in controlling the "head-to-tail" dimer structure, possibly an essential process in lasalocid A functions, e.g., metal release, since the dimer structure is believed[3] to be a metal-transporting form in membranes (though it is not known whether the dimer with a "head-to-tail" arrangement is an actual form or not). Clearly, further X-ray studies of metal salts involving different circumstances, possibly crystallization from solvents of different polarity, are necessary to understand the whole mechanism of metal ion capture and release by lasalocid A.[3]

Registry No. $Ag^+(C_{34}H_{53}O_8)^-$, 60208-69-7.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table V), atomic coordinates of hydrogen atoms (Table VI), torsion angles (Table VII), and least-squares planes (Table VIII) (3 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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(17) It should be noted here that there remains some ambiguity in this ratio value since we cannot rule out some deviation from these site occupations for C26 and C26′, which have not been refined because of a limited number of reflections.

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Preparation and Characterization of Sulfur-Capped Trinuclear Molybdenum(IV) Complexes with Mo_3O_3S Cores and of Sulfur-Bridged Dinuclear Molybdenum(V) Complexes with Mo_2O_3S Cores. Crystal and Molecular Structures of $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ and $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$

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New preparative routes to μ-oxo μ-sulfido cysteinato (**1A**) and edta (**1B**) Mo(V) dimer complexes containing Mo_2O_3S cores are reported, with use of Na_2MoO_4, $N_2H_4\cdot 2HCl$, Na_2S, and L-cysteine hydrochloride (for **1A**) or disodium ethylenediaminetetraacetic acid (for **1B**). Aqua ion, $Mo_2O_3S(aq)^{2+}$ (**1C**), is obtained by the aquation of **1A** in 1 M HCl. The sulfur-capped triangular Mo(IV) aqua ion $Mo_3O_3S(aq)^{4+}$ (**2A**) is obtained from **1C** and $NaBH_4$ in high yield (ca. 70%). The following derivatives of **2A** have been prepared: nitrilotriacetato (Ba^{2+} salt, **2B**; Na^+ salt, **2C**), iminodiacetato (Ca^{2+} salt, **2D**; Na^+ salt, **2E**), L-cysteinato (K^+ salt, **2F**), and thiocyanato (pyH^+ salt, **2G**) complexes. The crystallographic results obtained are as follows: $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**), triclinic, $P\bar{1}$, $a = 15.603$ (3) Å, $b = 11.315$ (2) Å, $c = 11.151$ (2) Å, $\alpha = 110.89$ (1)°, $\beta = 95.42$ (1)°, $\gamma = 99.70$ (1)°, $V = 1939.4$ (7) Å^3, $Z = 2$, 4245 unique data ($F_o^2 \geq 3\sigma(F_o^2)$), $R = 3.35\%$; $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**), triclinic, $P1$, $a = 11.727$ (5) Å, $b = 12.146$ (5) Å, $c = 11.241$ (6) Å, $\alpha = 107.11$ (4)°, $\beta = 118.72$ (4)°, $\gamma = 76.70$ (4)°, $V = 1334.5$ (11) Å^3, $Z = 2$, 4614 unique data ($F_o \geq 6\sigma(F_o)$), $R = 4.12\%$. The cluster anions of **2B′** and **2F′** have approximate symmetries of C_{3v} and C_3, respectively, and contain the same type of incomplete cubane-type core as $Mo_3(\mu\text{-}O)_3(\mu_3\text{-}S)$. The substitution of μ_3-S for μ_3-O causes elongation of Mo–Mo distances by ca. 0.1 Å. As for the electronic spectra of **2A–2F** and the relevant complexes with $Mo_3O_{4-n}S_n$ cores, only a slight red shift is observed on substitution of μ_3-S for μ_3-O, while a rather large red shift is observed on the introduction of μ-S. Reduction of **2A** in 1 and 4 M HCl by use of amalgamated zinc gives Mo^{III}_3 species, the oxidation state of which has been determined through titration with Fe^{3+} ion. In 4 M HCl, a mixed oxidation state of $Mo^{IV}Mo^{III}_2$ appears by the addition of Fe^{3+} to Mo^{III}_3. The spectrum of Mo^{III}_3 in 1 M HCl corresponds to that of $Mo^{IV}Mo^{III}_2$ as the HCl concentration increases to 8 M, the former reducing H^+ to give H_2 quantitatively. Cyclic voltammograms of $Mo_3O_3S(aq)^{4+}$ show that the midpoint potential shifts in the positive direction with increasing HCl concentration and that the second reduction peak develops at 8 M HCl. It seems that two- and one-electron processes develop. The cyclic voltammogram of **2D** shows three quasi-reversible waves, whereas that of **2F** shows only one quasi-reversible wave.

Previous investigations in this and other laboratories have demonstrated the preparation, characterization, and structures of a sequence of incomplete cubane-type molybdenum(IV) complexes with Mo_3O_4,[1] Mo_3O_3S,[2] $Mo_3O_2S_2$,[3] Mo_3OS_3,[4] and Mo_3S_4[5]

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Table I. Summary of Crystal Data, Intensity Collections, and Structure Refinement Parameters for $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**) and $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**)

	2B	**2F**
formula	$C_{18}H_{41}Mo_3BaSO_{31}N_3$	$C_9H_{27}Mo_3K_2S_4O_{15}N_3$
mol wt	1252.74	911.58
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P1$
a, Å	15.603 (3)	11.727 (5)
b, Å	11.615 (2)	12.146 (5)
c, Å	11.151 (2)	11.241 (6)
α, deg	100.89 (1)	107.11 (4)
β, deg	95.42 (1)	118.72 (4)
γ, deg	99.70 (1)	76.70 (4)
V, Å^3	1939.4 (7)	1334.5 (11)
Z	2	2
d_{calcd}, g/cm^3	2.146	2.269
d_{obsd}, g/cm^3		2.70
cryst size, mm	0.20 × 0.18 × 0.11	0.4 × 0.2 × 0.2
radiation (λ, Å)	Mo Kα (0.71073)[a]	Mo Kα (0.71073)[a]
abs coeff, μ, cm^{-1}	13.1	20.4
data collecn instrument	Phillips 1100	Rigaku AFC-6A
scan method	ω	ω ($2\theta < 30°$), ω–2θ ($2\theta > 30°$)
scan speed, deg/min	2	2
scan range, deg	$1.0 + 0.3 \tan\theta$	$1.04 + 0.5 \tan\theta$
bkgd measurement, s	10	10
data collected	$\pm h,\pm k,+l$ ($4 \le 2\theta \le 46°$)	$\pm h,\pm k,+l$ ($2 \le 2\theta \le 50°$)
total no. of reflcns	5396	5072
no. of unique data	4245[b]	4614[c]
no. of variables	515	590
R (R_w),[d] %	3.35 (4.31)[e]	4.12 (5.78)[f]

[a] Graphite monochromatized. [b] $F_o^2 \ge 3\sigma(F_o^2)$. [c] $F_o \ge 6\sigma(F_o)$. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [e] $w = 1/\sigma^2(|F_o|)$. [f] $w = 1/[\sigma^2(|F_o|) + g|F_o|^2]$; $g = 0.003$.

cores. An XPS study on these complexes has also been performed.[6]

In the course of the detailed study of complexes with Mo_3O_3S cores, we found a new route to the aqua ion $Mo_3O_3S(aq)^{4+}$, which enabled us to access complexes with the core easily. In addition to $Mo_3O_3S(aq)^{4+}$ and $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ described earlier[2] (H_3nta = nitrilotriacetic acid), iminodiacetato (ida) and cysteinato (cys) complexes have been prepared. The last complex, the structure of which has been determined by X-ray crystallography, is the first example of a cysteinato complex having an incomplete cubane-type trinuclear molybdenum(IV) core. The redox chemistry is one of the most attractive parts of the Mo chemistry, and we have investigated the redox properties of the complexes with Mo_3O_3S cores. Two kinds of reduced species of $Mo^{IV}{}_3O_3S(aq)^{4+}$ are identified, the oxidation state of them being $Mo^{III}{}_3$ and $Mo^{IV}Mo^{III}{}_2$. The former reacts with hydrogen ion to give the latter and hydrogen gas. We also describe here a facile preparative way to the molybdenum(V) dimeric complex with μ-oxo and μ-sulfido bridges $Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$,[7] which is the starting material for the Mo(IV) aqua ion $Mo_3O_3S(aq)^{4+}$.

Experimental Section

Preparation of Compounds. Sodium (μ-Oxo)(μ-sulfido)bis[(L-cysteinato)oxomolybdate(V)] Tetrahydrate, $Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$ (1A). Concentrated HCl (50 mL) was added to sodium molybdate dihydrate (9.6 g, 0.04 mol) dissolved in water (150 mL). Hydrazine dihydrochloride (10 g, 0.1 mol) was added to the solution, which was then heated at over 90 °C for $1^1/_2$ h. The hot solution was then poured into a polyethylene bottle that contained sodium sulfide nonahydate (9.6 g, 0.04 mol) and a magnetic follower, and the bottle was tightly stoppered. The solution was allowed to stand with magnetic stirring until the solution was brought to room temperature. The bottle was dented due to the low inside pressure. L-Cysteine hydrochloride hydrate (7 g, 0.04 mol) was dissolved in the solution, which was then filtered. After the solution was cooled in an ice bath, the pH of the solution was raised to ca. 12 with concentrated sodium hydroxide (ca. 13 M) and the solution was kept in a refrigerator overnight. The precipitate was filtered and washed with methanol and diethyl ether successively; yield ca. 7.5 g (58%). Recrystallization was as follows. The crude solid was dissolved in hot water (60 mL), the solution filtered, and the volume of the solution reduced to ca. one-third by heating over a water bath. The solution was kept in a refrigerator, and the crystals that deposited were collected and washed as above; yield 5.7 g.

Magnesium (μ-Ethylenediaminetetraacetato)(μ-oxo)(μ-sulfido)bis-oxomolybdate(V)] Hexahydrate, $Mg[Mo_2O_3S(edta)]\cdot 6H_2O$ (1B). Method A. The same procedure was followed up to the addition of L-cysteine hydrochloride hydrate. Disodium ethylenediaminetetraacetate dihydrate ($Na_2(H_2edta)\cdot 2H_2O$; 7.5 g, 0.02 mol) dissolved in a small amount of water was added to the solution. The pH of the solution was raised to ca. 6.5 with concentrated NaOH, the solution having been cooled in an ice bath. Solid magnesium chloride (20 g) was added, and the solution was kept in a refrigerator overnight. The crystals that deposited were filtered and washed with methanol and diethyl ether successively; yield 7.9 g (57%). Recrystallization from hot water gave 5.8 g.

Method B. The cysteinato complex **1A** (1.2 g) and $Na_2(H_2edta)\cdot 2H_2O$ (0.8 g) were dissolved in hot water (18 mL), to which concentrated HCl

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(8) During the addition of the NaOH solution, yellow precipitates appear at pH ca. 3 but disappear at pH ca. 6.

Table II. Atom Coordinates of $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**)

atom	*x*	*y*	*z*
Ba	0.45549 (3)	0.74268 (4)	0.66317 (4)
Mo1	0.23413 (4)	0.7493 (1)	0.3060 (1)
Mo2	0.25277 (4)	0.8188 (1)	0.1003 (1)
Mo3	0.30752 (4)	0.6293 (1)	0.1386 (1)
S	0.3716 (1)	0.8229 (2)	0.2506 (2)
O1	0.1544 (3)	0.7924 (4)	0.1887 (4)
O2	0.2324 (3)	0.6585 (4)	0.0062 (4)
O3	0.2105 (3)	0.5843 (4)	0.2271 (4)
O11	0.2427 (3)	0.9130 (4)	0.4305 (4)
O12	0.2929 (3)	0.7102 (4)	0.4693 (4)
O13	0.1818 (4)	1.0138 (5)	0.5768 (6)
C14	0.2689 (4)	0.6499 (5)	0.6412 (5)
O15	−0.0466 (3)	0.6362 (5)	0.4875 (5)
O16	−0.1136 (4)	0.5767 (7)	0.2968 (5)
O21	0.3380 (3)	0.8727 (4)	−0.0206 (4)
O22	0.2593 (3)	1.0032 (5)	0.1530 (4)
O23	0.3484 (4)	0.8953 (5)	−0.2122 (5)
O24	0.1885 (4)	1.1511 (6)	0.1378 (5)
O25	0.0120 (4)	0.8491 (5)	−0.2272 (5)
O26	−0.0463 (4)	0.6638 (5)	−0.2175 (6)
O31	0.3854 (3)	0.5492 (4)	0.2466 (4)
O32	0.4104 (3)	0.6359 (4)	0.0308 (4)
O33	0.4106 (4)	0.3786 (5)	0.2883 (5)
O34	0.4305 (3)	0.5891 (5)	−0.1649 (5)
O35	0.2197 (3)	0.2121 (5)	−0.1338 (5)
O36	0.0821 (4)	0.2326 (5)	−0.1090 (5)
N1	0.1175 (4)	0.7074 (5)	0.4069 (5)
N2	0.1575 (4)	0.8537 (5)	−0.0487 (5)
N3	0.2878 (4)	0.4420 (5)	0.0224 (5)
C11	0.1798 (5)	0.9237 (7)	0.4968 (7)
C12	0.2415 (5)	0.6674 (6)	0.5410 (7)
C13	0.1009 (5)	0.8247 (7)	0.4735 (6)
C14	0.1440 (5)	0.6317 (7)	0.4946 (6)
C15	0.0391 (5)	0.6409 (7)	0.3178 (7)
C16	−0.0427 (5)	0.6194 (7)	0.3787 (7)
C21	0.3038 (5)	0.8827 (6)	−0.1275 (6)
C22	0.1966 (5)	1.0477 (7)	0.1057 (7)
C23	0.2070 (5)	0.8736 (7)	−0.1550 (7)
C24	0.1263 (5)	0.9640 (9)	0.0101 (7)
C25	0.0834 (5)	0.7494 (7)	−0.0853 (7)
C26	0.0137 (5)	0.7621 (7)	−0.1839 (7)
C31	0.3816 (5)	0.4348 (7)	0.2162 (7)
C32	0.3934 (5)	0.5684 (7)	−0.0772 (6)
C33	0.3421 (4)	0.3699 (6)	0.0869 (6)
C34	0.3198 (5)	0.4594 (7)	−0.0971 (6)
C35	0.1923 (5)	0.3881 (7)	0.0024 (6)
C36	0.1687 (5)	0.2686 (7)	−0.0861 (7)
OW1	0.401 (0)	0.499 (0)	0.537 (0)
OW2	0.437 (0)	0.951 (1)	0.573 (1)
OW3	0.371 (0)	0.134 (1)	0.372 (1)
OW4	0.342 (1)	0.172 (1)	0.660 (1)
OW5	0.486 (0)	0.308 (0)	0.573 (0)
OW6	0.189 (0)	0.329 (1)	0.341 (1)
OW7	0.251 (0)	0.369 (1)	0.599 (1)
OW8	−0.038 (0)	−0.061 (0)	0.306 (0)
OW9	0.456 (1)	0.100 (1)	0.123 (1)
OW10	0.445 (1)	0.167 (1)	−0.109 (1)

(2.5 mL) was added, and the solution was maintained over 90 °C for ca. 5 min. After the solution was ice-cooled, the pH of the solution was adjusted to ca. 6.5 by use of concentrated NaOH. Then, $MgCl_2$ (0.8 g) dissolved in water (2 mL) was added and the solution was kept in a refrigerator overnight; yield 1.0 g (75%).

(μ-Oxo)(μ-sulfido)bis[oxomolybdenum(V)](2+) Aqua Dimer, $Mo_2O_3S(aq)^{2+}$ (1C). The procedure was essentially as described in ref 9, where $HClO_4$ was used. The compound **1A** (7 g) was dissolved in 1 M HCl (70 mL), the solution was stirred for ca. 30 min and filtered, and then Sephadex G-10 column chromatography (column diameter 3.5 cm, length 63 cm) was applied for separation (1 M HCl). The second band (>95%) contained the aqua ion **1C**. The first and third bands contained small amounts of $Mo_2O_4(aq)^{2+}$ and $Mo_2O_2S_2(aq)^{2+}$, respectively.

Barium (μ-Ethylenediaminetetraacetato)(μ-oxo)(μ-sulfido)bis[oxomolybdate(V)] Trihydrate, $Ba[Mo_2O_3S(edta)]\cdot 3H_2O$ (1D). A procedure similar to the preparation of the magnesium salt **1B** (method B) was employed. The following amounts of materials were used: **1A**, 1.2 g; $Na_2(H_2edta)\cdot 2H_2O$, 0.8 g; water, 50 mL; concentrated NaOH (to adjust the pH of the solution to ca. 6.5); $BaCl_2$, 0.9 g in 20 mL of water. The yield was 1.2 g (83%).

Table IV. Atom Coordinates of $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**)

atom	*x*	*y*	*z*
Mo1	0.7174 (1)	0.6078 (1)	0.4935 (1)
Mo2	0.7542 (1)	0.7479 (1)	0.7331 (1)
Mo3	0.7146 (1)	0.8305 (1)	0.5233 (1)
Mo4	0.2241 (1)	0.3201 (1)	0.0046 (1)
Mo5	0.2251 (1)	0.0993 (1)	−0.0182 (1)
Mo6	0.2455 (1)	0.2453 (1)	0.2132 (1)
K1	0.7010 (2)	0.4071 (2)	0.7167 (2)
K2	0.1816 (2)	−0.0792 (2)	0.2134 (2)
K3	0.8627 (2)	0.1460 (2)	0.9021 (2)
K4	0.1987 (2)	0.6082 (2)	0.3181 (2)
S1	0.9046 (2)	0.7096 (2)	0.6388 (2)
S2	0.4084 (2)	0.2008 (2)	0.1351 (2)
O1	0.6355 (5)	0.6257 (5)	0.6103 (6)
O2	0.6334 (5)	0.8662 (5)	0.6526 (6)
O3	0.5945 (5)	0.7249 (5)	0.3910 (6)
O4	0.1088 (5)	0.2121 (5)	−0.1305 (6)
O5	0.1269 (5)	0.1244 (5)	0.0853 (6)
O6	0.1333 (5)	0.3633 (5)	0.1255 (6)
S11	0.8556 (2)	0.4274 (2)	0.5447 (2)
S21	0.9059 (2)	0.8727 (2)	0.9390 (2)
S31	0.8095 (2)	0.8518 (2)	0.3828 (2)
S41	0.3378 (2)	0.3400 (2)	−0.1174 (3)
S51	0.3596 (2)	−0.0783 (2)	0.0515 (2)
S61	0.3980 (2)	0.3649 (2)	0.4254 (2)
O11	0.7565 (5)	0.5512 (4)	0.3123 (6)
O12	0.7497 (8)	0.3972 (6)	0.1430 (8)
O21	0.8533 (5)	0.6200 (4)	0.8627 (6)
O22	0.9565 (7)	0.6160 (6)	1.0860 (7)
O31	0.7929 (6)	0.9983 (5)	0.6440 (6)
O32	0.7892 (7)	1.1740 (5)	0.6267 (7)
O41	0.2954 (5)	0.4910 (5)	0.1275 (6)
O42	0.2782 (8)	0.6717 (6)	0.1128 (8)
O51	0.2888 (5)	0.0402 (5)	−0.1800 (6)
O52	0.3130 (7)	−0.1154 (6)	−0.3329 (7)
O61	0.3256 (5)	0.1191 (4)	0.3464 (6)
O62	0.4033 (8)	0.1149 (6)	0.5667 (8)
N1	0.5756 (7)	0.4856 (6)	0.3449 (7)
N2	0.6648 (7)	0.7728 (6)	0.8779 (7)
N3	0.5692 (6)	0.9652 (6)	0.4183 (7)
N4	0.0836 (7)	0.4490 (6)	−0.1120 (7)
N5	0.0958 (7)	−0.0339 (6)	−0.1786 (8)
N6	0.1385 (6)	0.2843 (6)	0.3444 (7)
C11	0.7239 (9)	0.4490 (7)	0.2380 (9)
C12	0.6527 (8)	0.3905 (7)	0.2834 (9)
C13	0.7515 (9)	0.3266 (6)	0.3967 (9)
C21	0.8713 (8)	0.6575 (7)	0.9891 (9)
C22	0.7773 (8)	0.7619 (7)	1.0144 (8)
C23	0.8517 (9)	0.8708 (7)	1.0686 (8)
C31	0.7508 (8)	1.0780 (7)	0.5786 (9)
C32	0.6463 (8)	1.0490 (7)	0.4258 (9)
C33	0.716 (1)	0.9905 (9)	0.335 (1)
C41	0.2531 (9)	0.5714 (7)	0.0617 (9)
C42	0.1657 (8)	0.5362 (7)	−0.0943 (9)
C43	0.249 (1)	0.4734 (9)	−0.173 (1)
C51	0.2679 (9)	−0.0636 (7)	−0.2514 (8)
C52	0.1820 (8)	−0.1233 (7)	−0.2250 (9)
C53	0.273 (1)	−0.1845 (7)	−0.1036 (9)
C61	0.3301 (9)	0.1603 (7)	0.4670 (9)
C62	0.2430 (8)	0.2733 (7)	0.4858 (8)
C63	0.3267 (9)	0.3738 (7)	0.5445 (9)
OW1	0.7577 (7)	0.1572 (6)	1.0895 (7)
OW2	1.0045 (6)	1.0929 (6)	0.2983 (7)
OW3	1.0989 (7)	0.8355 (6)	0.3877 (8)
OW4	0.5524 (8)	0.5497 (7)	0.8414 (9)
OW5	0.3874 (7)	−0.3510 (6)	0.6123 (7)
OW6	0.6034 (7)	0.2554 (6)	0.7983 (7)
OW7	0.5375 (9)	0.6531 (8)	1.090 (1)
OW8	0.8646 (6)	0.3782 (6)	0.9782 (7)
OW9	0.3644 (7)	−0.1906 (6)	0.4176 (8)
OW10	0.5570 (7)	0.0275 (6)	0.8647 (8)
OW11	0.016 (1)	−0.4586 (9)	0.362 (1)
OW12	0.0384 (9)	0.1255 (8)	0.574 (1)

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(9) $[(Mo_2O_3S(ox)_2)_2(ox)]^{6-}$: Shibahara, T.; Ooi, S.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3742–3746.

Table VI. Analytical Data for Mo(V) (**1A**, **1B**, and **1C**) and Mo(IV) (**2A**, **2B**, **2C**, **2C′**, **2D**, **2E**, **2F**, and **2G**) Complexes

		N, %	C, %	H, %
$Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$ (**1A**)	found	4.39	11.60	2.97
	calcd	4.45	11.47	2.88
$Mg[Mo_2O_3S(edta)]\cdot 6H_2O$ (**1B**)	found	4.05	17.28	3.48
	calcd	4.04	17.34	3.49
$Ba[Mo_2O_3S(edta)]\cdot 3H_2O$ (**1D**)	found	3.70	15.94	2.28
	calcd	3.73	15.98	2.41
$Mo_3O_3S(aq)^{4+}$ (**2A**)[a]				
$Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**)	found	3.52	17.40	2.95
	calcd	3.35	17.25	3.29
$Na_2[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2C**)	found	3.67	18.78	3.67
	calcd	3.61	18.61	3.55
$Na_2[Mo_3O_3S(Hnta)_3]\cdot 3H_2O$ (**2C′**)	found	4.02	20.43	2.68
	calcd	4.05	20.88	2.62
$Ca[Mo_3O_3S(ida)_3]\cdot 7H_2O$ (**2D**)	found	4.54	15.38	2.97
	calcd	4.53	15.54	3.15
$Na_2[Mo_3O_3S(ida)_3]\cdot 3H_2O$ (**2E**)	found	4.83	16.45	2.17
	calcd	4.87	16.73	2.45
$K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**)	found	4.60	11.88	2.80
	calcd	4.60	11.85	2.98
$(pyH)_5[Mo_3O_3S(NCS)_9]\cdot 3H_2O$ (**2G**)	found	14.81	30.03	2.42
	calcd	14.57	30.35	2.69

[a] Mo/S = 3.0.

Table VII. Electronic Spectral Data for Mo(IV) Trimers (Experiments 1–8) and Mo(V) Dimers (Experiments 9–11)[a,b]

expt no.	compd	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)	ref
1	$Mo_3O_4(aq)^{4+}$	303 (795), 505 (189)	1i
2	$Mo_3O_3S(aq)^{4+}$	333 (932), 512 (153)	2a
3	$Mo_3O_2S_2(aq)^{4+}$	338 (2760), 450 sh (177), 572 (202)	3
4	$Mo_3OS_3(aq)^{4+}$	307 (3080), 370 sh (2200), 410 sh (1760), 588 (263)	4
5	$Mo_3S_4(aq)^{4+}$	367 (5190), 500 sh (290), 602 (351)	5a,b
6	$Na_2[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$	236 (21 900), 330 (1520), 533 (272)	*c*
7	$Ca[Mo_3O_3S(ida)_3]\cdot 7H_2O$	236 (25 810), 327 (1790), 420 sh (468), 540 (342)	*c*
8	$K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$	230 sh (25 400), 273 (11 500), 381 (9180), 543 (925)	*c*
9	$Mo_2O_3S(aq)^{2+}$	220 sh (5600), 278 (3950), 314 (3250), 450 sh (57)	9
10	$Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$	214 (26 000), 245 sh (11 230), 284 (12 610), 320 sh (8010), 470 sh (192)	*c*
11	$Mg[Mo_2O_3S(edta)]\cdot 6H_2O$	235 (9500), 281 (7950), 311 (5920), 480 sh (110)	*c*

[a] Data for experiments 1–5 in 2 M HPTS, for experiments 6–8, 10, and 11 in water, and for experiment 9 in 1 M $HClO_4$. [b] ϵ values per trimer for Mo(IV) complexes and per dimer for Mo(V) complexes. [c] This work.

(μ_3-Sulfido)tris(μ-oxo)-*triangulo*-trimolybdenum(IV)(4+) Aqua Trimer, $Mo_3O_3S(aq)^{4+}$ (2A). To the aqua ion **1C** obtained as above (350 mL, 0.0565 M per monomer) was added $NaBH_4$ (8 g) little by little with stirring; concentrated HCl (20 mL) was then added slowly, the solution turning from orange-red to brown. The resultant brown solution was heated in a boiling water bath for ca. 2 h with introduction of an air stream to give a red-brown solution with a tint of purple. The volume of the solution was decreased to ca. 100 mL by use of a rotary evaporator, and the solution was cooled to room temperature. After the precipitates of boric acid were filtered off, the filtrate was subjected to Sephadex G-15 column chromatography (1 M HCl; diameter 5 cm, length 75 cm). The first eluate, which is red-purple, was collected (ca. 240 mL, 0.0576 M per monomer, yield ca. 70%). Then, the following were eluted from the column in order: $Mo_3O_2S_2(aq)^{4+}$ (4.7%), $Mo_2O_4(aq)^{2+}$ (1.0%), $Mo_3OS_3(aq)^{4+}$ (1.3%), $Mo_2O_3S(aq)^{2+}$ (15.6%), $Mo_3S_4(aq)^{4+}$ (0.1%), and unidentified green species. This aqua ion has sufficient purity (>95%) for the preparation of other complexes (described below). For further purification, Dowex 50W-X2 column chromatography was used (1 M HCl). Concentrated fractions (>90%) of the eluate were collected: the diluted fraction that was eluted first contained a very small amount of $Mo_3O_4(aq)^{4+}$.

Barium (μ_3-Sulfido)tris(μ-oxo)-*triangulo*-[tris(nitrilotriacetato(2−))-molybdate(IV)] Decahydrate, $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (2B) (H_3nta = Nitrilotriacetic Acid). The aqua ion **2A** in 1 M HCl (20 mL, 0.0173 M per monomer) was diluted to 3 times the original volume with water in which H_3nta (0.081 g, H_3nta/Mo = 1.2) was dissolved, and the pH was adusted to 1.2 with concentrated NaOH. Dark red plate crystals were obtained by addition of $BaCl_2$ (ca. 0.1 g) after storage for several days; yield 0.067 g (46%).

Sodium (μ_3-Sulfido)tris(μ-oxo)-*triangulo*-[tris(nitrilotriacetato(2−))-molybdate(IV)] Decahydrate, $Na_2[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (2C), and Its Trihydrate Analogue (2C′). H_3nta (0.656 g, H_3nta/Mo = 1.2) dissolved in a minimum amount of concentrated NaOH was added to a solution of **2A** (50 mL, 0.0572 M per monomer), and the pH was adjusted to 1.2 with concentrated NaOH. Dark red crystals were obtained after several days, which were collected by filtration and air-dried; yield 0.93 g (84%). The crystalline compound turns to a powdered one, if it is washed with methanol. The compound dried in vacuo has three waters of crystallization per trimer.

Calcium (μ_3-Sulfido)tris(μ-oxo)-*triangulo*-[tris(iminodiacetato)molybdate(IV)] Heptahydrate, $Ca[Mo_3O_3S(ida)_3]\cdot 7H_2O$ (2D) (H_2ida = Iminodiacetic Acid). H_2ida (17 g, H_2ida/Mo = 10) dissolved in a minimum amount of 10 M KOH was added to a solution of **2A** (100 mL, 0.127 M per monomer), and the pH was adjusted to ca. 1 by the slow addition of 10 M KOH. After the solution was allowed to stand overnight, the pH of the solution was raised to ca. 7 by the slow addition of 10 M KOH and the resultant solution was kept to stand overnight. The solution was diluted with water to 10 times its original volume and absorbed on a Dowex 1-X2 anion exchanger. The red eluate obtained by use of 1 M $CaCl_2$ was stored in a refrigerator for several days, and dark red columnar crystals were obtained; yield 1.12 g (28%).

Sodium (μ_3-Sulfido)tris(μ-oxo)-*triangulo*-[tris(iminodiacetato)molybdate(IV)] Trihydrate, $Na_2[Mo_3O_3S(ida)_3]\cdot 3H_2O$ (2E). The corresponding calcium salt **2D** (0.20 g) and water (3 mL) were stirred with Dowex 50W-X2 cation-exchange resin (Na^+ form, 10 mL), and the resultant suspension was filtered by means of suction. To the red solution obtained was added methanol, and needlelike crystals were obtained.

Potassium (μ_3-Sulfido)tris(μ-oxo)-*triangulo*-tris[(L-cysteinato)molybdate(IV)] Hexahydrate, $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (2F). L-(+)-Cysteine hydrochloride hydrate (8.8 g) was dissolved in water (50 mL) so as to make a 1 M solution, and the pH of the solution was adjusted to 5 with 10 M KOH. To the 1 M L-cysteine solution was added the aqua ion **2A** (0.127 M per monomer, 40 mL, L-cysteine/Mo = 10), the pH of the solution being maintained between 4 and 6 during the addition. Then, the pH of the solution was adjusted to 10 with 10 M KOH and the solution was allowed to stand for 2 days under a dinitrogen atmosphere. The solution was filtered and diluted to 10 times its original volume with water, and Dowex 1-X2 column chromatography was applied (3 M KCl). A red band from the column was collected and stored in a refrigerator under a dinitrogen atmosphere. Dark red cube-shaped crystals were obtained after 3 days. This compound has an approximate formula of $K_2[Mo_3O_3S(cys)_3]KCl\cdot 8H_2O$; yield 1.03 g. For recrystallization, the crystals (1.03 g) were dissolved in water (20 mL) at 40 °C and a few drops of 1 M KCl was added to the solution, which was kept in a refrigerator under a dinitrogen atmosphere. Dark red hexagonal-shaped crystals were obtained after 2 days; yield 0.87 g (56%). The crystals lose some of their water of crystallization in air.

Structural Determinations of $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (2B) and $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (2F). The crystallographic and machine parameters are given in Table I. Intensities were corrected for polarization and Lorentz factors but not for absorption. A crystal of **2B** was mounted on a glass fiber with an adhesive, and a crystal of **2F** was mounted in a glass capillary. For **2B**, the intensities of standard reflections monitored every 4 h decreased ca. 3% during the data collection; however, no correction was made. For **2F**, the intensities of standard reflections monitored after every 150 reflections did not show any appreciable decay. For both complexes, the coordinates of three Mo atoms, a μ_3-S atom, and three μ-O atoms were determined by means of MULTAN[10] and the remaining non-hydrogen atoms were located from difference maps. No attempt was made to locate hydrogen atoms. The refinement of the

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(10) Main, P.; Hull, S. E.; Lessinger, L.; Germain, L.; Declercq, J.-P.; Woolfson, M. M.; "MULTAN-78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York: York, England, 1978.

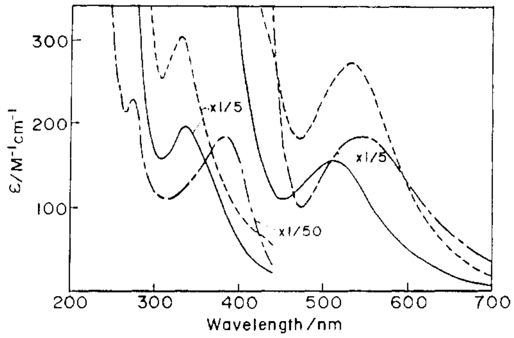

Figure 1. Electronic spectra of (—) $Mo_3O_3S(aq)^{4+}$ (**2A**), (- - -) $[Mo_3O_3S(Hnta)_3]^{2-}$ (anion of **2C**), and (- - -) $[Mo_3O_3S(cys)_3]^{2-}$ (anion of **2F**) (ε values per trimer).

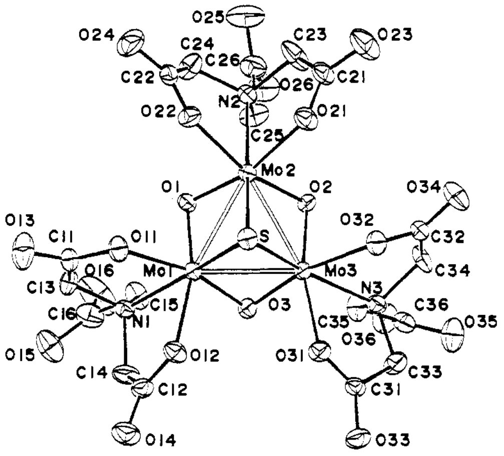

Figure 2. Perspective view of $[Mo_3O_3S(Hnta)_3]^{2-}$ showing the atom-labeling scheme. In Figures 2 and 3 the 50% probability vibrational ellipsoids are shown.

structure was performed by the block-diagonal least-squares method. No chemically significant peaks were observed on the final difference Fourier maps for **2B** and **2F**. The atomic coordinates and thermal parameters for **2B** are listed in Tables II and III, and those for **2F** are listed in Tables IV and V, respectively (Tables III and V are given in the supplementary material). Most of the computations were performed on Melcom Cosmo 700 III (for **2B**) and FACOM M380 (for **2F**) computers at the Okayama University of Science. The programs in the UNICS[11] system were employed. The figure was drawn by use of ORTEP.[12]

Other Physical Measurements. UV, visible, and near-infrared spectra were recorded on a Hitachi 320 or 330 spectrophotometer. Infrared spectra were recorded on a Hitachi 285 grating infrared spectrophotometer for compounds in KBr disks. Cyclic voltammograms were recorded on a Yanaco P1100 polarographic analyzer. The working electrode was a hanging Hg drop. The saturated calomel electrode (SCE) was isolated from the test solution by means of a glass frit. The auxiliary electrode was a platinum wire. Hydrogen gas was analyzed by use of a Yanaco G 3800 gas chromatograph with 5A molecular sieves.

Reduction of $Mo^{IV}{}_3O_3S(aq)^{4+}$ Ion. Reduction of the aqua ion **2A** by use of amalgamated zinc was as follows; all of the procedures were performed under a dinitrogen atmosphere. The aqua ion (ca. 2 × 10^{-3} M per trimer, 20 mL) in 1 or 4 M HCl was put into a bottle containing Zn/Hg (ca. 3 g), and the mixture was stirred magnetically for ca. 15 min. To prepare the reduced species in 8 M HCl, the aqua ion (ca. 5 × 10^{-3} M per trimer) was reduced in 1 M HCl and a calculated amount of concentrated HCl was added to get the desired HCl concentration.

A weighed amount of solid iron alum was used to oxidize the reduced species ($Mo^{III}{}_3$ and $Mo^{IV}Mo^{III}{}_2$) of the aqua ion **2A**.

Elemental Analyses. Carbon, hydrogen, and nitrogen analyses were determined by standard microanalytical procedures. Molybdenum was determined according to the literature procedure[13] and sulfur by gravimetry as $BaSO_4$. The results of elemental analyses of compounds described above are summarized in Table VI.

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) in $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**)

Mo1–Mo2	2.596 (1)	Mo1–N1	2.260 (6)
Mo1–Mo3	2.587 (1)	Mo2–N2	2.264 (6)
Mo2–Mo3	2.584 (1)	Mo3–N3	2.267 (6)
mean	2.589 [6]	mean	2.264 [4]
Mo1–S	2.354 (2)	O11–C11	1.292 (9)
Mo2–S	2.367 (2)	O12–C12	1.292 (9)
Mo3–S	2.358 (2)	O21–C21	1.293 (10)
mean (Mo–(μ_3-S))	2.360 [7]	O22–C22	1.295 (9)
Mo1–O1	1.913 (5)	O31–C31	1.298 (9)
Mo1–O3	1.909 (5)	O32–C32	1.284 (9)
Mo2–O1	1.914 (5)	mean	1.292 [5]
Mo2–O2	1.916 (5)	O13–C11	1.234 (10)
Mo3–O2	1.915 (5)	O14–C12	1.224 (10)
Mo3–O3	1.935 (5)	O23–C21	1.240 (11)
mean (Mo–(μ-O))	1.917 [9]	O24–C22	1.219 (10)
Mo1–O11	2.108 (5)	O33–C31	1.227 (9)
Mo1–O12	2.121 (5)	O34–C32	1.224 (10)
Mo2–O21	2.088 (5)	mean	1.228 [8]
Mo2–O22	2.093 (5)	O15–C16	1.200 (11)
Mo3–O31	2.078 (5)	O25–C26	1.202 (10)
Mo3–O32	2.094 (5)	O35–C36	1.211 (10)
mean	2.097 [15]	mean	1.204 [6]
		O16–C16	1.326 (12)
		O26–C26	1.317 (10)
		O36–C36	1.330 (9)
		mean	1.324 [7]
Mo2–Mo1–Mo3	59.81 (2)	O1–Mo1–O12	162.9 (2)
Mo1–Mo2–Mo3	59.93 (2)	O3–Mo1–O11	164.3 (2)
Mo2–Mo3–Mo1	60.26 (2)	O1–Mo2–O21	164.3 (2)
mean	60.0 [2]	O2–Mo2–O22	162.8 (2)
S–Mo1–O1	102.5 (2)	O2–Mo3–O31	163.0 (2)
S–Mo1–O3	103.7 (2)	O3–Mo3–O32	167.0 (2)
S–Mo2–O1	102.0 (2)	mean	164.1 [16]
S–Mo2–O2	103.0 (1)	O1–Mo1–N1	86.3 (2)
S–Mo3–O2	103.4 (1)	O3–Mo1–N1	87.2 (2)
S–Mo3–O3	102.7 (2)	O1–Mo2–N2	86.4 (2)
mean	102.9 [6]	O2–Mo2–N2	85.8 (2)
S–Mo1–O11	89.2 (2)	O2–Mo3–N3	84.5 (2)
S–Mo1–O12	92.0 (2)	O3–Mo3–N3	91.8 (2)
S–Mo2–O21	91.5 (2)	mean	87.0 [25]
S–Mo2–O22	92.3 (1)	O11–Mo1–O12	79.4 (2)
S–Mo3–O31	92.6 (1)	O21–Mo2–O22	82.0 (2)
S–Mo3–O32	89.2 (2)	O31–Mo3–O32	84.8 (2)
mean	91.1 [15]	mean	82.1 [27]
S–Mo1–N1	165.3 (2)	O11–Mo1–N1	78.7 (2)
S–Mo2–N2	167.1 (2)	O12–Mo1–N1	77.7 (2)
S–Mo3–N3	163.0 (2)	O21–Mo2–N2	79.0 (2)
mean	165.1 [21]	O22–Mo2–N2	77.9 (2)
O1–Mo1–O3	94.1 (2)	O31–Mo3–N3	78.5 (2)
O1–Mo2–O2	94.9 (2)	O32–Mo3–N3	75.7 (2)
O2–Mo3–O3	92.9 (2)	mean	77.9 [12]
mean	94.0 [10]	Mo1–S–Mo2	66.7 (1)
O1–Mo1–O11	91.8 (2)	Mo1–S–Mo3	66.6 (1)
O3–Mo1–O12	91.1 (2)	Mo2–S–Mo3	66.3 (1)
O1–Mo2–O22	89.5 (2)	mean	66.5 [2]
O2–Mo2–O21	89.7 (2)	Mo1–O1–Mo2	85.4 (2)
O2–Mo3–O32	89.5 (2)	Mo2–O2–Mo3	84.9 (2)
O3–Mo3–O31	89.2 (2)	Mo1–O3–Mo3	84.6 (2)
mean	90.1 [11]	mean	85.0 [4]

Results and Discussion

Preparation and Properties of Molybdenum(V) Complexes with Mo_2O_3S Cores. Water-soluble dimeric molybdenum(V) complexes containing μ-oxo μ-sulfido cores (Mo_2O_3S) were first prepared and electrochemically and spectrally characterized by Schultz and

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(13) Rao, G. G.; Suryanarayana, M. *Fresenius' Z. Anal. Chem.* **1959**, *168*, 177–181.

(14) $[Mo_2O_3S(pdta)]^{2-}$: Suzuki, K. Z.; Sasaki, Y.; Ooi, S.; Saito, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1288–1298. Kojima, A.; Ooi, S.; Sasaki, Y.; Suzuki, K. Z.; Saito, K.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2457–2465.

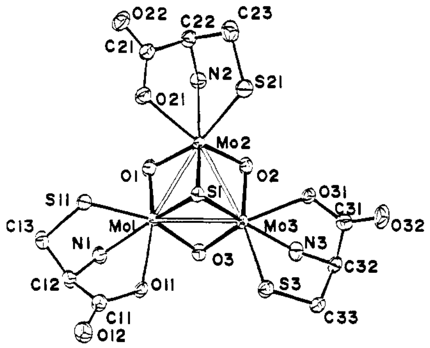

Figure 3. Perspective view of $[Mo_3O_3S(cys)_3]^{2-}$ showing the atom-labeling scheme.

co-workers.[7] Characterization of the aqua ion $Mo_2O_3S(aq)^{2+}$ and X-ray structure determinations[9,14-16] of the derivatives were reported. Studies on the complexes with Mo_2O_3S cores in organic solvents have also been developed.[17-22] The procedure described previously[7] to give $[Mo_2O_3S(cys)_2]^{2-}$ requires a relatively long time and the yield was not high.[23] We have found a new preparative technique that is more convenient and gives a higher yield of the complex. We used the easily obtainable sodium molybdate and hydrazine hydrochloride instead of molybdenum pentachloride, and sodium sulfide instead of bubbling H_2S gas. Another merit of employing this preparative method is that a relatively large amount of the compound is obtainable at once. The pH of the solution has been kept low by using 3 M HCl[7] so as to minimize the formation of the bis(μ-sulfido) species. In the final stage of the preparation, the pH of the solution was raised to ca. 12, which gave the cysteinato complex in a fairly pure form, since the bis(μ-oxo) Mo(V) cysteinato complex, which is the main byproduct in the preparation, is decomposed in solutions of high pH. Corresponding calcium, barium, and magnesium salts can be easily prepared by the addition of $CaCl_2{\cdot}2H_2O$, $BaCl_2{\cdot}2H_2O$, and $MgCl_2{\cdot}6H_2O$, respectively.[16] At the final stage of the preparation of the edta complex **1B**, the pH was adjusted to 6.5. The complex seems to be decomposed at pHs higher than 8, since lower yields with low purity were observed at pHs higher than 8. The edta complexes **1B** and **1D** can also be prepared from the cysteinato complex before recrystallization has sufficient high purity (>95%) as a starting material for the preparation of other complexes. The purity of the cysteinato and edta complexes has been checked against the complexes prepared from the pure aqua ion **1C** and the corresponding ligand through the comparison of the electronic spectra (ϵ values) of the complexes. Electronic spectra of the Mo(V) dimers are slightly different from those of Schultz and co-workers. The spectroscopic data are summarized in Table VII.

Preparation and Properties of Molybdenum(IV) Complexes with Mo_3O_3S Cores. In the early stage of this research,[2a] the aqua trimer **2A** was prepared from the ethylenediaminetetraacetato

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(15) $[Mo_2O_3S(NCS)_9]^{4-}$: Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2945–2948.

(16) $[Mo_2O_3S(cys)_2]^{2-}$: Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2277–2279.

(17) $[Mo_2O_3S(p_rdtc)_2]$: Dirand-Colin, J.; Ricard, L.; Weiss, R. *Inorg. Chim. Acta* **1976**, *18*, L21–L22.

(18) Newton, W. E.; Chen, G. J.-J.; Mcdonald, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5387–5388.

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(22) Newton, W. E.; McDonald, J. W. In *Abstracts of Papers*, Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum, Oxford, England; Mitchell, P. C. H.; Ed.; Climax Molybdenum: Ann Arbor, MI, 1976; pp 25–30; *J. Less-Common Met.* **1977**, *54*, 51–62.

(23) Hydrogen sulfide gas was bubbled through the solution of molybdenum pentachloride dissolved in 3 M HCl, and then, L-(+)-cysteine hydrochloride was added to the solution, the pH of which was raised to 6.0 to give the cysteinato complex.

Table IX. Selected Interatomic Distances (Å) and Angles (deg) in $K_2[Mo_3O_3S(cys)_3]{\cdot}6H_2O$ (**2F**)[a]

I		II	
Mo1–Mo2	2.619 (1)	Mo4–Mo5	2.617 (1)
Mo1–Mo3	2.621 (1)	Mo4–Mo6	2.641 (2)
Mo2–Mo3	2.629 (1)	Mo5–Mo6	2.618 (1)
mean	2.623 [5]	mean	2.625 [14]
Mo1–S1	2.373 (2)	Mo4–S2	2.384 (2)
Mo2–S1	2.363 (2)	Mo5–S2	2.349 (2)
Mo3–S1	2.375 (2)	Mo6–S2	2.359 (3)
mean	2.370 [6]	mean	2.365 [18]
Mo1–O1a	1.909 (8)	Mo4–O4a	1.878 (5)
Mo2–O2a	1.867 (5)	Mo5–O5a	1.921 (8)
Mo3–O3a	1.881 (5)	Mo6–O6a	1.864 (5)
mean	1.886 [21]	mean	1.888 [30]
Mo1–O3b	1.964 (6)	Mo4–O6b	1.994 (8)
Mo2–O1b	1.986 (5)	Mo5–O4b	1.958 (6)
Mo3–O2b	1.994 (8)	Mo6–O5b	1.983 (5)
mean	1.981 [16]	mean	1.976 [25]
Mo1–S11	2.443 (2)	Mo4–S41	2.411 (4)
Mo2–S21	2.457 (2)	Mo5–S51	2.448 (2)
Mo3–S31	2.421 (4)	Mo6–S61	2.461 (2)
mean	2.440 [18]	mean	2.440 [26]
Mo1–O11	2.183 (7)	Mo4–O41	2.217 (6)
Mo2–O21	2.182 (6)	Mo5–O51	2.161 (7)
Mo3–O31	2.207 (6)	Mo6–O61	2.193 (6)
mean	2.191 [14]	mean	2.190 [28]
Mo1–N1	2.184 (7)	Mo4–N4	2.197 (6)
Mo2–N2	2.245 (10)	Mo5–N5	2.225 (6)
Mo3–N3	2.212 (6)	Mo6–N6	2.251 (9)
mean	2.214 [31]	mean	2.224 [27]
S11–C13	1.815 (7)	S41–C43	1.815 (11)
S21–C23	1.885 (13)	S51–C53	1.820 (8)
S31–C33	1.856 (10)	S61–C63	1.858 (13)
mean	1.842 [23]	mean	1.831 [24]
O11–C11	1.299 (9)	O41–C41	1.263 (12)
O21–C21	1.283 (12)	O51–C51	1.285 (9)
O31–C31	1.254 (12)	O61–C61	1.280 (12)
mean	1.279 [23]	mean	1.276 [12]
O12–C11	1.206 (14)	O42–C41	1.221 (11)
O22–C21	1.218 (10)	O52–C51	1.220 (14)
O32–C31	1.221 (11)	O62–C61	1.232 (12)
mean	1.215 [8]	mean	1.224 [6]
Mo2–Mo1–Mo3	60.23 (3)	Mo5–Mo4–Mo6	59.73 (3)
Mo1–Mo2–Mo3	59.91 (4)	Mo4–Mo5–Mo6	60.59 (3)
Mo1–Mo3–Mo2	59.85 (3)	Mo4–Mo6–Mo5	59.68 (5)
mean	60.00 [20]	mean	60.00 [51]
S1–Mo1–O1	103.7 (2)	S2–Mo4–O4	102.9 (2)
S1–Mo1–O3	101.1 (2)	S2–Mo4–O6	99.2 (2)
S1–Mo2–O1	101.6 (2)	S2–Mo5–O4	101.7 (2)
S1–Mo2–O2	104.5 (3)	S2–Mo5–O5	104.0 (2)
S1–Mo3–O2	100.1 (2)	S2–Mo6–O5	101.7 (2)
S1–Mo3–O3	103.6 (2)	S2–Mo6–O6	104.0 (3)
mean	102.4 [17]	mean	102.3 [18]
S1–Mo1–S11	88.9 (1)	S2–Mo4–S41	90.1 (1)
S1–Mo2–S21	88.6 (1)	S2–Mo5–S51	88.5 (1)
S1–Mo3–S31	89.8 (1)	S2–Mo6–S61	87.3 (1)
mean	89.1 [6]	mean	88.6 [14]
S1–Mo1–O11	95.8 (2)	S2–Mo4–O41	98.2 (1)
S1–Mo2–O21	95.0 (2)	S2–Mo5–O51	93.1 (2)
S1–Mo3–O31	97.3 (1)	S2–Mo6–O61	96.8 (2)
mean	96.0 [12]	mean	96.0 [26]
S1–Mo1–N1	167.1 (2)	S2–Mo4–N4	168.6 (2)
S1–Mo2–N2	163.1 (2)	S2–Mo5–N5	163.0 (2)
S1–Mo3–N3	167.3 (2)	S2–Mo6–N6	164.1 (2)
mean	165.8 [24]	mean	165.2 [30]
Mo1–S1–Mo2	67.2 (1)	Mo4–S2–Mo5	67.1 (1)
Mo1–S1–Mo3	67.0 (1)	Mo4–S2–Mo6	67.6 (1)
Mo2–S1–Mo3	67.4 (1)	Mo5–S2–Mo6	67.6 (1)
mean	67.2 [2]	mean	67.4 [3]
Mo1–O1–Mo2	84.5 (3)	Mo4–O4–Mo5	86.0 (2)
Mo2–O2–Mo3	85.8 (3)	Mo5–O5–Mo6	84.2 (3)
Mo1–O3–Mo3	85.9 (2)	Mo4–O6–Mo6	86.3 (2)
mean	85.4 [8]	mean	85.5 [11]

[a] Ligand: O*n*a, trans to O_{cys}; O*n*b, trans to S_{cys}.

Table X. Comparison of Mo–Mo Bond Lengths (Å) in Complexes with $Mo^{IV}{}_3O_{4-n}S_n$ or $Mo^{V}{}_2O_{2-n}S_n$ Cores[a]

Mo(IV) Trimers

Mo–Mo			
μ_3-O, μ-O[b]	μ_3-S, μ-O[b]	μ_3-S, μ-S[b]	ref
2.495 [10]			1a
2.486 [1]			1j
2.491 (1)			1j
2.506 [13]			1b
2.494 [6]			1g
2.518 [5]			1h
	2.589 [6]		this work[c]
	2.624 [9]		this work[c]
	2.635 [10]	2.715 (4)	3[d]
	2.612 (2)	2.725 [12]	4[e]
		2.754 [11]	5b
		2.766 [24]	5f
		2.790 [5]	5f
		2.769 (1)	5j
		2.775 [8]	5l
		2.765 [7]	5m
		2.783 [12]	5n
		2.812 [1]	5o
		2.766 (4)	5q
		2.773 [7]	5r
		2.758 [18]	5s
		2.744 [12]	5t
		2.756 [9]	5u

Mo(V) Dimers

Mo–Mo			
2 μ-O[b]	μ-O, μ-S[b]	2 μ-S[b]	ref
2.569 (2)			*f, i*
2.541			*g, j*
	2.718 (1)		15*f*
		2.82 (0.3)	*f, k*
		2.799 (1)	*h, l*

[a] Parentheses indicate esd of one value; brackets indicate $[\sum_i(x_i - \bar{x})^2/(n-1)]^{1/2}$, in which $\bar{x}$ is the mean of n values. [b] Bridges between two Mo atoms. [c] $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$ core. [d] $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_2(\mu\text{-}S)$ core. [e] $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2$ core. [f] Mo(V) cysteinato complex. [g] Mo(V) aqua oxalato complex. [h] Mo(V) ethylenediaminetetracetato complex. [i] Knox, J. R.; Prout, C. K. *Acta Crystallogr., Sect. B* **1969**, 1857–1866. [j] Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *4*, 1377–1381. [k] Brown, D. H.; Jeffreys, J. A. D. *J. Chem. Soc., Dalton Trans.* **1973**, 732–735. [l] Spivack, S.; Dori, Z. *J. Chem. Soc., Dalton Trans.* **1973**, 1173–1177.

Table XI. Short Contacts (Å) in $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (**2B**)[a]

Ba–O12	3.096 (5)	Ba–OW2	2.839 (7)
Ba–O14	2.898 (6)	Ba–O33^{b}	2.777 (5)
Ba–O23^{a}	2.893 (7)	Ba–OW3^{b}	2.936 (7)
Ba–O34^{a}	2.865 (6)	Ba–OW5^{b}	2.857 (6)
Ba–OW1	2.863 (5)	Ba–OW9^{b}	2.788 (9)
O33–OW1	2.887 (8)	O23–OW2^{d}	2.992 (10)
OW1–OW5	2.844 (8)	O24–OW6^{e}	2.754 (9)
OW1–OW7	2.783 (9)	O36–OW8^{f}	2.621 (8)
OW3–OW5	2.937 (9)	O25–OW8^{g}	2.746 (8)
OW4–OW5	2.872 (11)	O26–OW6^{g}	2.534 (9)
OW6–OW7	2.872 (9)	O32–OW10^{h}	2.868 (12)
OW9–OW10	2.841 (14)	O13–OW8^{i}	2.780 (8)
OW3–O22^{c}	2.866 (9)	O16–OW7^{i}	2.641 (11)
OW4–O13^{c}	2.807 (11)	OW5–O31^{b}	2.771 (8)
OW6–O24^{c}	2.754 (9)		

[a] Symmetry operations: (a) $x, y, z + 1$; (b) $1 - x, 1 - y, 1 - z$; (c) $x, y - 1, z$; (d) $x, y, z - 1$; (e) $x, y + 1, z$; (f) $-x, -y, -z$; (g) $-x, 1 - y, -z$; (h) $1 - x, 1 - y, -z$; (i) $-x, 1 - y, 1 - x$.

Table XII. Short Contacts (Å) in $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (**2F**)[a]

K1–O1	3.019 (7)	K2–O5	3.014 (7)
K1–O21	3.062 (7)	K2–O42^{a}	3.058 (10)
K1–O32^{a}	2.843 (8)	K2–O61	2.867 (7)
K1–OW4	2.743 (10)	K2–OW2^{b}	2.855 (9)
K1–OW6	2.918 (9)	K2–OW3^{b}	3.054 (9)
K1–OW8	2.706 (9)	K2–OW9	2.731 (9)
K3–O5^{c}	2.779 (7)	K4–O22^{d}	2.790 (8)
K3–O31^{a}	2.764 (7)	K4–O41	2.774 (7)
K3–O32^{a}	2.893 (8)	K4–OW3^{e}	2.780 (9)
K3–OW1	2.866 (9)	K4–OW5^{f}	2.931 (9)
K3–OW6	2.831 (9)	K4–OW9^{f}	3.080 (9)
K3–OW8	2.698 (9)	K4–OW11^{f}	2.744 (13)
OW1–OW10	2.838 (12)	OW4–OW7	2.782 (15)
O3–OW7^{g}	2.998 (13)	O4–OW12^{g}	2.925 (13)
O11–OW7^{g}	2.924 (13)	O12–OW1^{g}	2.786 (12)
O12–OW8^{g}	2.704 (12)	O51–OW10^{g}	2.910 (11)
O52–OW5^{g}	2.768 (12)	O52–OW9^{g}	2.978 (12)
O6–OW8^{d}	2.757 (10)	OW5–O1^{a}	2.868 (10)
OW5–OW4^{a}	2.791 (13)	OW9–O3^{a}	2.783 (11)
OW10–O2^{a}	2.971 (11)	OW9–OW3^{b}	2.917 (13)
OW11–O11^{b}	2.799 (15)	OW12–OW2^{b}	2.839 (14)
O52–OW3^{h}	2.921 (12)	OW1–OW2^{i}	2.929 (12)
O1–OW5^{f}	2.868 (10)		

[a] Symmetry operations: (a) $x, y - 1, z$; (b) $x - 1, y - 1, z$; (c) $x + 1, y, z + 1$; (d) $x - 1, y, z - 1$; (e) $x - 1, y, z$; (f) $x, y + 1, z$; (g) $x, y, 1 - z$; (h) $x - 1, y - 1, z - 1$; (i) $x, y - 1, z + 1$.

Mo(V) dimer **1B** and K_2CO_3. However, the yield was not high (ca. 20%) and, therefore, we have developed a new procedure for the preparation of the aqua trimer. The procedure is essentially the same as we described earlier for the preparation of $Mo_3S_4(aq)^{4+}$ using $Na_2[Mo_2O_2S_2(cys)_2]$ and $NaBH_4$.[5a,b] While this paper was being prepared, Sykes and colleagues reported another preparative method of **2A** using **1C** and $[MoCl_6]^{3-}$;[2b] however, our method, we believe, has merits of its own, which we will describe. The Mo(V) aqua dimer **1C** was reduced with $NaBH_4$, the resultant solution was air-oxidized, and then column chromatography was applied. This method is simpler, is easily scaled up, and gives a higher yield (ca. 70%) than the previous one.[2a] This new method together with that of preparing an Mo(V) dimer with an Mo_2O_3S core (described above) enables us to access the Mo(IV) chemistry easily. The Hnta (**2B**, **2C**, and **2C′**), ida (**2D** and **2E**), and cys (**2F**) complexes have been prepared from the aqua ion **2A** and the corresponding ligands. The preparation and characterization of the thiocyanato complex $(pyH)_5[Mo_3O_3S(NCS)_9]\cdot 3H_2O$ has also been reported.[6] Electronic spectra of **2A**, **2C**, and **2F** are shown in Figure 1, and the peak positions and ϵ values of **2A**, **2C′**, **2D**, and **2F** are included in Table VII together with those of the relevant complexes with $Mo_3O_{4-n}S_n$ cores. Only a slight red shift is observed on the substitution of μ_3-S for μ_3-O, while a rather large red shift is observed on the introduction of μ-S. The aqua, Hnta, and ida complexes are air-stable; however, the cysteinato complex is slightly air-sensitive and the solution must be stored under a dinitrogen atmosphere if it is to be stored a relatively long time. A diamagnetic susceptibility value greater than the calculated value has been obtained for **2B** and will be discussed elsewhere.[24]

Structures of $Ba[Mo_3O_3S(Hnta)_3]\cdot 10H_2O$ (2B) and $K_2[Mo_3O_3S(cys)_3]\cdot 6H_2O$ (2F). The structure of the anion $[Mo_3O_3S(Hnta)_3]^{2-}$ (**2B′**) is shown in Figure 2, and the interatomic distances and angles are collected in Table VIII. The unit cell of **2F** has two independent chemical units, but no significant structural difference can be seen between the two units. The cluster anion $[Mo_3O_3S(cys)_3]^{2-}$ (**2F′**) is shown in Figure 3, and selected interatomic distances and angles are collected in Table IX. The cluster anions **2B′** and **2F′** lack crystallographically imposed symmetry but have approximate symmetries of C_{3v} and C_3, respectively, and contain the same type of incomplete cubane-type core as $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3$. Either the substitution of μ_3-S for μ_3-O or that of μ-S for μ-O causes elongation of the Mo–Mo bond length by ca. 0.1 Å as seen in Table X. Elongation of Mo–Mo distances in the Mo(V) complexes with $Mo_2O_{2-n}S_n$ cores has also been observed on the substitution of sulfur for the oxygen. Some of the distances of Mo(V) complexes with $Mo_2O_{2-n}S_n$ cores are also included in Table X. The Mo---Mo distances in the Mo(V) complexes are longer than the corresponding Mo–Mo distances of Mo(IV) complexes. In **2B** and **2F**,

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(24) Kobayashi, H.; Shibahara, T.; Uryu, N. to be submitted for publication.

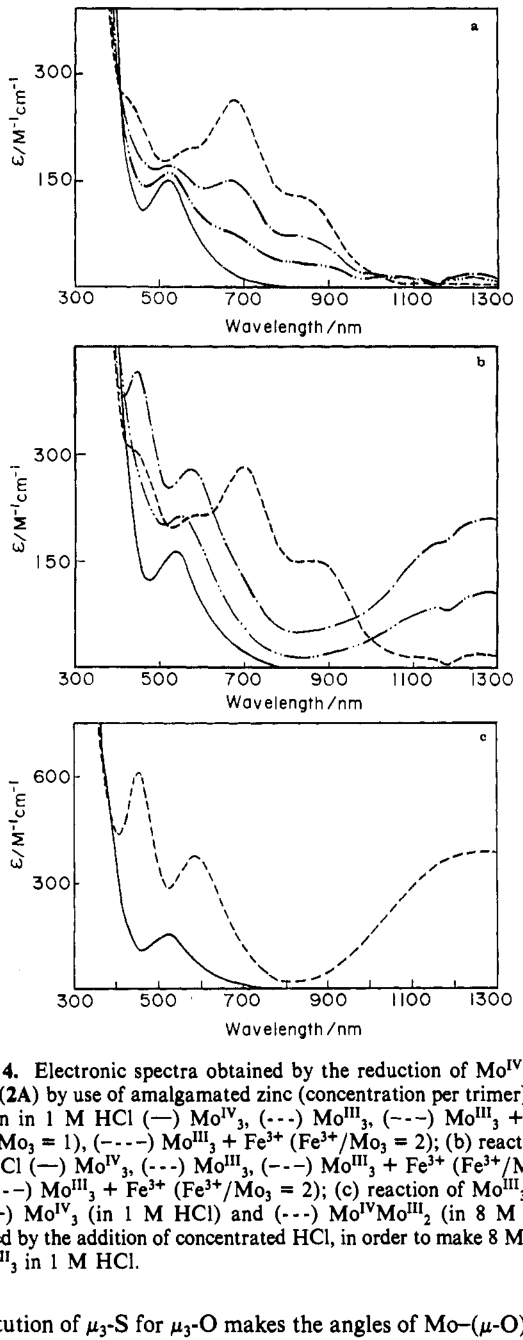

Figure 4. Electronic spectra obtained by the reduction of $Mo^{IV}{}_3O_3S(aq)^{4+}$ (**2A**) by use of amalgamated zinc (concentration per trimer): (a) reaction in 1 M HCl (—) $Mo^{IV}{}_3$, (---) $Mo^{III}{}_3$, (– – –) $Mo^{III}{}_3 + Fe^{3+}$ ($Fe^{3+}/Mo_3 = 1$), (– - - –) $Mo^{III}{}_3 + Fe^{3+}$ ($Fe^{3+}/Mo_3 = 2$); (b) reaction in 4 M HCl (—) $Mo^{IV}{}_3$, (---) $Mo^{III}{}_3$, (– – –) $Mo^{III}{}_3 + Fe^{3+}$ ($Fe^{3+}/Mo_3 = 1$), (– - - –) $Mo^{III}{}_3 + Fe^{3+}$ ($Fe^{3+}/Mo_3 = 2$); (c) reaction of $Mo^{III}{}_3$ with H^+ (—) $Mo^{IV}{}_3$ (in 1 M HCl) and (---) $Mo^{IV}Mo^{III}{}_2$ (in 8 M HCl) obtained by the addition of concentrated HCl, in order to make 8 M HCl, to $Mo^{III}{}_3$ in 1 M HCl.

substitution of μ_3-S for μ_3-O makes the angles of Mo–(μ-O)–Mo larger than those of the unsubstituted ones. The average Mo- - -Mo distance of **2F** is longer than that of **2B** by 0.035 Å; however, a larger range of Mo- - -Mo distances has been found for complexes with Mo_3S_4 cores (Table X).

If we ignore the difference between μ_3-S and μ_3-O, structure of the anion **2B′** has a structure similar to that of $[Mo_3O_4((O_2CCH_2)_2NCH_3)_3]^{2-}$ and to the local structure of $Na_4[(Mo_3O_4)_2(edta)_3]\cdot 14H_2O$, the three nitrogen ligand atoms occupying the δ positions trans to μ_3-S and the six carboxylate oxygen γ positions trans to μ-O.[1b] One uncoordinated CO_2 group in each $Hnta^{2-}$ ligand has a long (average 1.325 Å) and a short (1.205 Å) distance, indicating the existence of three –COOH groups in the whole complex anion, in accord with the presence of an absorption band at 1725 cm^{-1} in the infrared spectrum.

As for the configuration of the cysteinato ligands in the complex anion **2F′**, the three nitrogen atoms occupy the δ positions and the three oxygens and the three sulfurs occupy the γ positions. The distances Mo–(μ-O) trans to S_{cys} are longer by ca. 0.1 Å than those trans to O_{cys} (Table IX). Short contacts in **2B** and **2F** are collected in Tables XI and XII, respectively.

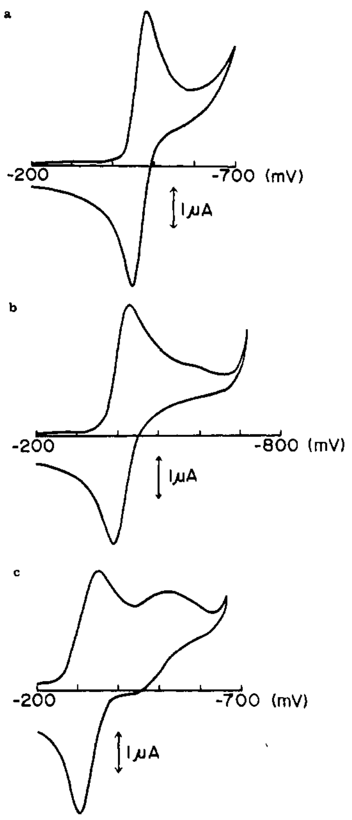

Figure 5. Cyclic voltammograms of $Mo_3O_3S(aq)^{4+}$ at a hanging-Hg-drop electrode (scan rate 100 mV/s, reference electrode SCE, concentration per trimer): (a) 0.408 mM complex, in 1 M HCl; (b) 0.397 mM complex, in 4 M HCl; (c) 0.404 mM complex, in 8 M HCl.

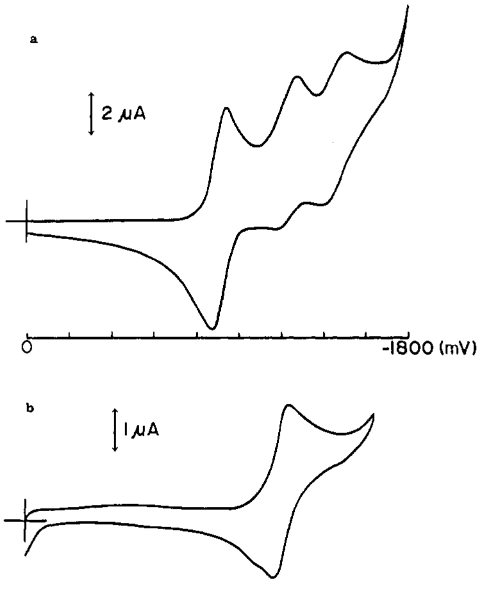

Figure 6. Cyclic voltammograms at a hanging-Hg-drop electrode (scan rate 100 mV/s, reference electrode, SCE, concentration per trimer): (a) $[Mo_3O_3S(ida)_3]^{2-}$ (anion of **2D**, 5.23 mM); (b) $[Mo_3O_3S(cys)_3]^{2-}$ (anion of **2F**, 0.417 mM).

Reduced Species, $Mo^{III}{}_3$ and $Mo^{IV}Mo^{III}{}_2$. Detailed electrochemistry of $Mo_3O_4(aq)^{4+}$ and $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$ has been reported, and the existence of the oxidation states $Mo^{IV}{}_3$, $Mo^{IV}Mo^{III}{}_2$, and $Mo^{III}{}_3$ has been established.[1e,f]

Electronic spectra of the reduced species of $Mo_3O_3S(aq)^{4+}$ (**2A**) in 1, 4, and 8 M HCl with use of amalgamated zinc under a dinitrogen atmosphere are shown in parts a–c, respectively, of Figure 4. Addition of portions of the Fe^{3+} ion (up to $Fe^{3+}/Mo_3 = 3$) to the reduced species in 1 and 4 M HCl results in the reoxidation of $Mo^{III}{}_3$ to the original $Mo^{IV}{}_3$ trimer, which indicates that the reduced species are Mo^{III}_3 in 1 and 4 M HCl.[25] During the addition of Fe^{3+} ion to Mo^{III}_3 in 4 M HCl, a characteristic spectrum appears and this is ascribed to that of the intermediate $Mo^{IV}Mo^{III}_2$, while no characteristic spectrum appears in the same procedure in 1 M HCl. It seems that the oxidation state $Mo^{IV}Mo^{III}_2$, is unstable in lower acidic concentration to give Mo^{IV}_3 and Mo^{III}_3 through a disproportionation reaction as in the case of the $Mo^{IV}Mo^{III}_2$ aqua ion having μ_3-O.[1e] An interesting phenomenon appears; that is, the spectrum of Mo^{III}_3 in 1 M HCl corresponds to that of $Mo^{IV}Mo^{III}_2$ as the HCl concentration increases to 8 M (Figure 4c). This indicates that Mo^{III}_3 in 8 M HCl reduces H^+, as shown in the reaction

$$\mathrm{Mo^{III}_3 + H^+ \rightarrow Mo^{IV}Mo^{III}_2 + \tfrac{1}{2}H_2}$$

Determination of the amount of hydrogen gas ($H_2/Mo_3 = 0.48$) by use of a gas chromatograph supports the reaction.

Cyclic voltammograms of $Mo_3O_3S(aq)^{4+}$ (Figure 5) in some acid concentrations show that the midpoint potential shifts in the positive direction with increasing HCl concentration and that the second reduction peak develops at 8 M HCl. It seems that two- and one-electron processes appear.

Cyclic voltammograms of $[Mo_3O_3S(ida)_3]^{2-}$ (**2D**) and $[Mo_3O_3S(cys)_3]^{2-}$ (**2F**) are shown in parts a and b of Figure 6, respectively. The former shows three quasi-reversible waves, which can be attributed to three one-electron waves as was found in the case of $[Mo_3S_4(ida)_3]^{2-}$.[5b] The cysteinato complex **2F** shows only one quasi-reversible wave in the region down to −1.65 V, three waves appearing to be collapsed. Attempts to obtain reasonable samples of the reduced species of **2B**–**2F** have yet not succeeded.

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Supplementary Material Available: Anisotropic thermal parameters (Tables III and V) and interatomic distances and angles for **2B** and **2F** (Tables VIIIS and IXS) (6 pages); tables of F_o and F_c values (26 pages). Ordering information is given on any current masthead page.

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[25] Mo^{III}_3 in 1 and 4 M HCl is also air-oxidized to give the Mo^{IV}_3 aqua ion.

Notes

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Triammineruthenium(II) Complexes Bound with the Novel Bridging Ligand 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz)

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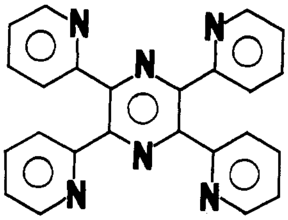
There has been recent interest in the preparation and study of polymetallic complexes bound through novel bridging ligands.[1] Previous investigations of bimetallic Ru(II) polyazine complexes for photocatalyzed intramolecular energy-transfer processes have focused on nitrogen aromatic heterocyclic bridging ligands such as pyrazine,[2,3] 2,3-bis(2-pyridyl)quinoxaline (dpq),[4] 2,2′-bipyrimidine (bpym),[5-8] 2,3-bis(2-pyridyl)pyrazine (dpp),[9,10] and biimidazole (bim).[11] To efficiently function as photon-capture, energy-transfer complexes, in addition to the prerequisites of being highly absorbing and photostable, the bridging ligand must also be efficient at communicating electronic density between the metal centers. The Creutz–Taube dimer[2,3] $(NH_3)_5Ru(pz)Ru(NH_3)_5{}^{4+}$ has served as a model complex in comparative bridging ligand communicative studies.[12] The elegance of the complex is derived in part from the photo- and electrochemical stability and from the facts that (1) each ruthenium(II) center is surrounded by NH_3 ligands that undergo only σ interactions with the metal center and are therefore uncompetitive with Ru(II) d_π–pz p_{π^*} interactions, (2) the monodentate NH_3 ligands circumvent steric difficulties of the peripheral ligands such as in $(bpy)_2$ complexes, and (3) the planar nitrogen heterocyclic pyrazine bridging ligand coordinated to the ruthenium at the pyrazine 1,4-positions provides effective π delocalization through the pyrazine bridging ligand. Similar bidentate ligands such as bpym and dpp have been utilized in the preparation of tetraammineruthenium(II) complexes.[8,10] The bpym ligand utilizes nitrogen coordination at the 1,3-positions on both pyrimidine rings to simultaneously chelate the two Ru(II) centers, while dpp incorporates the pyrazine nitrogen 1,4-coordination and 1′,1″-coordination of the remote pyridine rings. As evaluated from electrochemical and absorption spectral results of the tetraamineruthenium(II) complexes, the bpym ligand offers significantly less metal–metal communication than through analogous pyrazine-bridged dimer, while dpp appears to be competitive with the pyrazine-bridged pentaammineruthenium(II) complex, probably as a result of the direct pyrazine linkage of the two ruthenium centers.



tppz

Figure 1. 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz).

We have used the novel tridentate nitrogen aromatic heterocyclic ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) (Figure 1) to prepare mono- and bimetallic triammineruthenium(II) complexes bound to/through tppz. The bis-tridentate coordination through tppz in the bimetallic complex affords direct metal-bridging ligand–metal communication through the central pyrazine group, as well as through the remote pyridine rings. The ammine spectator ligands on the triammineruthenium(II) moiety provide a richer metal d_π electronic environment without competitive π

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[1] Novel Main Group Element Ligands Symposium, 3rd Chemical Congress of North America, Toronto, Ontario, Canada, June 5–10, 1988.

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