Bull. Chem. Soc. Jpn., 72, 2271—2275 (1999) 2271

# Sulfur-Bridged Incomplete Cubane-Type Iminodiacetato Molybdenum Clusters:
# Geometrical Isomers and Their Isomerization

**Takashi Shibahara,* Shun Yoshida, Masataka Maeyama, and Masaaki Kojima†**

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridai-cho Okayama 700-0005

†Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700-8530

(Received June 7, 1999)

Reaction of the incomplete cubane-type aqua clusters $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**A**) with $H_2ida$ (=iminodiacetic acid) followed by ion exchange separation gave four geometrical isomers of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(ida)_3]^{2-}$ (hereafter $[Mo_3S_4(ida)_3]^{2-}$; **A1**, **A2**, **A3**, and **A4** based on the elution sequence), which were isolated as solid samples: $Ca[Mo_3S_4(ida)_3]\cdot 12H_2O$ (**A1′**), $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (**A2′**), $Ca[Mo_3S_4(ida)_3]\cdot 10H_2O$ (**A3′**), and $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (**A4′**), respectively. The X-ray structural analyses of **A2′** and **A4′** revealed that the three nitrogen atoms of three ida ligands in each isomer have the configuration of "*trans*, *trans*, *cis*" and "*cis*, *cis*, *cis*" to $\mu_3$-S's, respectively. The X-ray structure of **A1′** has already been determined to have "*trans*, *trans*, *trans*" configuration, therefore, that of **A3′** is estimated to have "*trans*, *cis*, *cis*" configuration. HPLC analysis reveals that each isomer isomerizes, *cis*–*trans* conversion of the ida ligand occurring one by one, and that in equilibrium the anions **A1** (18%), **A2** (68%), and **A3** (14%) exist and **A4** does not exist. The advent of **A4** is possible only in the course of preparation from **A** and $H_2ida$.

We have previously reported the preparation and structures of sulfur/oxygen-bridged incomplete cubane-type iminodiacetato molybdenum clusters $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(ida)_3]^{2-}$ (hereafter $[Mo_3S_4(ida)_3]^{2-}$, $H_2ida$ = iminodiacetic acid)[1] and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(ida)_3]^{2-}$ (hereafter $[Mo_3OS_3(ida)_3]^{2-}$),[2] whose schematic structures are shown in Fig. 1. It is interesting that in $[Mo_3S_4(ida)_3]^{2-}$ all the three nitrogen atoms are *trans* to $\mu_3$-S, while in $[Mo_3OS_3(ida)_3]^{2-}$ one of three nitrogen atoms is *cis* to $\mu_3$-S.

Detailed examination of the synthetic procedures made clear that the cluster $[Mo_3S_4(ida)_3]^{2-}$ had four kinds of isomers, each of which isomerizes to other isomers. Although many geometrical isomers of mononuclear complexes with tridentate ligand(s), such as ida, dien (diethylenetriamine), and edma (ethylenediamine-*N*-acetate), have been reported,[3] examples of isomeric complexes with incomplete cubane-type cores are rather limited,[4] and no reports, to our knowledge, have appeared on the isomers of incomplete cubane-type metal clusters with ida ligands.

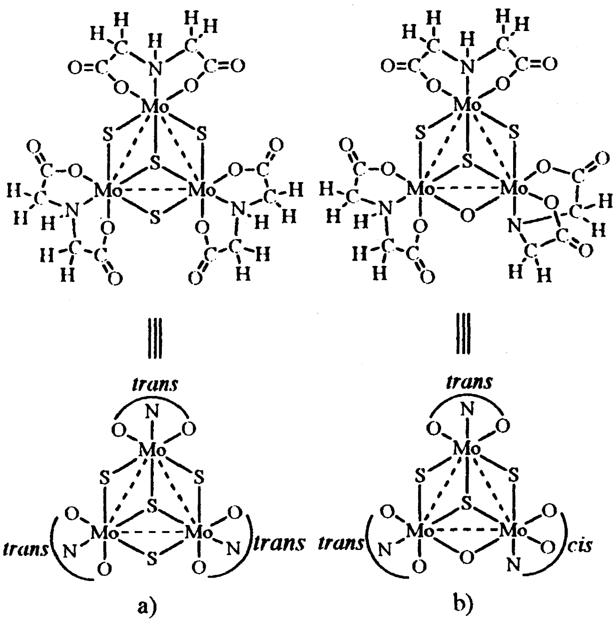

Fig. 1. Schematic structures of sulfur/oxygen-bridged incomplete cubane-type iminodiacetato molybdenum clusters $[Mo_3S_4(ida)_3]^{2-}$ and $[Mo_3OS_3(ida)_3]^{2-}$.

## Experimental

**Materials.** The aqua cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (**A**) was obtained according to the published procedures.[5]

**Preparation and Isolation of Geometrical Isomers of Sulfur-Bridged $[Mo_3S_4(ida)_3]^{2-}$ Clusters.** Iminodiacetic acid (23.0 g, $H_2ida/A \approx 30$) dissolved in a minimum amount of concentrated KOH was added dropwise to a solution of the aqua cluster **A** (0.115 M per trimer, 50 $cm^3$; M = mol $dm^{-3}$) in 2 M HCl, and the pH was adjusted to 7.0 with concentrated KOH, then the mixture was allowed to stand overnight and was filtered. The solution was diluted to ca. ten times its original volume with water, and was adsorbed on a Dowex 1-X2 anion exchanger (diameter 2.3 cm, length 56.5 cm), which was washed with 0.05 M $CaCl_2$. Elution with 0.3 M $CaCl_2$ (1st band, **A1**), 0.5 M $CaCl_2$ (2nd band, **A2**), 1.0 M $CaCl_2$ (3rd band, **A3**), and 2.0 M $CaCl_2$ (4th band, **A4**) gave four green bands, respectively.

**Isolation of $Ca[Mo_3S_4(ida)_3]\cdot 12H_2O$ (A1′) from 1st Band A1.** The solution **A1** from the 1st band (1.51 mM in 0.3 M $CaCl_2$, 240 cm$^3$) was diluted to 5 times its original volume with water and was adsorbed on a short Dowex 1-X2 column (diameter 1.7 cm, length 6 cm). Elution with 1.0 M $CaCl_2$ gave a green solution, which was stored in a refrigerator for a couple of days. Green crystals which deposited were collected by filtration and air-dried. Yield: 0.13 g (33% based on the amount used of the 1st band). Anal. Found: C, 13.48; H, 3.68; N, 3.87%. Calcd for $Mo_3CaS_4O_{24}N_3C_{12}H_{39}$: C, 13.53; H, 3.69; N, 3.94%.

**Isolation of $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (A2′) from 2nd Band A2.** A similar procedure for the preparation of **A1′** was applied to the solution from the 2nd band (10.4 mM in 0.5 M $CaCl_2$, 200 cm$^3$), 2.0 M $CaCl_2$ being used as an eluent. Yield: 0.96 g (38%). Anal. Found: C, 11.75; H, 4.12; N, 3.44%. Calcd for $Mo_3CaS_4O_{33}N_3C_{12}H_{57}$: C, 11.74; H, 4.68; N, 3.42%.

**Isolation of $Ca[Mo_3S_4(ida)_3]\cdot 10H_2O$ (A3′) from 3rd Band A3.** A similar procedure for the preparation of **A1′** was applied to the solution from the 3rd band (2.10 mM in 1.0 M $CaCl_2$, 300 cm$^3$), 5.0 M $CaCl_2$ being used as an eluent. Yield: 0.27 g (41%). Anal. Found: C, 13.98; H, 3.12; N, 4.10%. Calcd for $Mo_3CaS_4O_{22}N_3C_{12}H_{35}$: C, 14.00; H, 3.43; N, 4.08%.

**Isolation of $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (A4′) from 4th Band A4.** A similar procedure for the preparation of **A1′** was applied to the solution from the 4th band (6.3 mM in 2.0 M $CaCl_2$, 75 cm$^3$), 5.0 M $CaCl_2$ being used as an eluent. Yield: 0.055 g (11%). Anal. Found: C, 12.77; H, 3.87; N, 3.82%. Calcd for $Mo_3CaS_4O_{26}N_3C_{12}H_{43}$: C, 13.08; H, 3.93; N, 3.81%.

**Structural Determination of $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (A2′) and $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (A4′).** A green crystal of **A2′** and a green crystal of **A4′** were mounted in glass capillaries, respectively. Crystal data and collection and refinement parameters are summarized in Table 1. No appreciable decay was observed for either crystal. An empirical absorption correction based on azimuthal scans of several reflections was applied for both the crystals. The structures of **A2′** and **A4′** were solved by SHELXS-86 (direct method),[6] and SIR-92 (direct method),[7] respectively, and the remaining non-hydrogen atoms were located from difference maps. All the other calculations were performed using the teXsan crystallographic software package.[8] The calcium ion in **A2′** is disordered, and is separated into two parts, occupancy factors for the two calcium ions being fixed to 0.6 and 0.4. In addition, some of the water molecules of crystallization in **A2′** are disordered heavily, and were not refined, the isotropic thermal parameters being fixed to $B = 25$ Å$^2$. The number of the water molecules was deduced from the elemental analyses of C, H, and N, and density measurements.

The atomic coordinates, thermal parameters, bond distances and angles, and $F_o - F_c$ tables are deposited as Document No.72037 at the Office of the Editor of the Bull. Chem. Soc. Jpn. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 133094—133095.

**Apparatus.** UV, visible, and near-infrared spectra were recorded on a Hitachi U2000 spectrophotometer. Carbon, hydrogen, and nitrogen were determined with a Perkin–Elmer 2400II CHN analyzer. The chromatographic system consisted of a JASCO 880-PU HPLC pump and a JASCO 875-UV/vis detector. Chromatograms were recorded on a JASCO 807-IT integrator. The anion-exchange column used in this study was a YMC-Pack IES-AX (length 25 cm × diameter 4.6 mm) from YMC Co., Ltd. (Kyoto, Japan). The isomers were detected at 380 nm, and the column temperature was 20 °C. The eluent was a 0.8 M NaCl or 0.5 M $BaCl_2$, and the flow-rate was 1.0 cm$^3$ min$^{-1}$.

## Results and Discussion

**Preparation and Characterization of Geometrical Isomers of Sulfur-Bridged Clusters $[Mo_3S_4(ida)_3]^{2-}$:**

Table 1. Crystallographic Data and Refinement Details for $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (**A2′**) and $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (**A4′**)

| Complex | A2′ | A4′ |
|---|---|---|
| Chemical formula | $Mo_3CaS_4O_{33}N_3C_{12}H_{57}$ | $Mo_3CaS_4O_{26}N_3C_{12}H_{43}$ |
| Formula weight | 1227.72 | 1101.62 |
| Crystal size/mm | 0.21 × 0.06 × 0.05 | 0.45 × 0.05 × 0.05 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$/Å | 10.823(1) | 13.528(5) |
| $b$/Å | 23.336(1) | 22.72(1) |
| $c$/Å | 16.904(1) | 13.133(3) |
| $\beta$/deg | 107.59(1) | 116.33(2) |
| $V$/Å$^3$ | 4069.6(4) | 3617(2) |
| $Z$ | 4 | 4 |
| $D_{calc}$/g cm$^{-3}$ | 2.004 | 2.022 |
| $D_{obs}$/g cm$^{-3}$ | 2.00 | 1.98 |
| $\mu$ / cm$^{-1}$ | 114.50 | 14.88 |
| $2\theta_{max}$ /deg | 140 | 50 |
| Radiation, $\lambda$/Å | Cu $K\alpha$, 1.54178[a] | Mo $K\alpha$, 0.71069[a] |
| No. of reflns measured | 7823 | 6869 |
| No. of reflns unique | 7413 | 6578 |
| No. of reflns observed | 3834 ($I > 1.5\sigma(I)$) | 4303 ($I > 1.5\sigma(I)$) |
| No. of Variables | 425 | 443 |
| $R$[b] | 0.081 | 0.039 |
| $R_w$[c] | 0.121 | 0.049 |

a) Graphite monochromated. b) $R = \sum||F_o| - |F_c||/\sum|F_o|$. c) $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o)+p^2/4(F_o)^2]^{-1}$.

**$Ca[Mo_3S_4(ida)_3]\cdot 12H_2O$ (A1′), $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (A2′), $Ca[Mo_3S_4(ida)_3]\cdot 10H_2O$ (A3′), $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (A4′).** Four kinds of the isomers were obtained by column chromatography from the reaction products of the aqua cluster **A** and $H_2$ida. The typical yields were 6% (**A1**), 35% (**A2**), 34% (**A3**), and 6% (**A4**) in solution based on the aqua cluster **A**, respectively. The respective yield is changeable, but the total yield of the four species remains rather constant (see the section of Equilibration of the Geometrical Isomers of Sulfur-Bridged Clusters $[Mo_3S_4(ida)_3]^{2-}$). From each solution, a solid sample was isolated successfully.[9] Electronic spectra of the four isomers are shown in Fig. 2. The peak positions and ε values are summarized in Table 2. Corresponding peak positions are similar to each other.

**X-Ray Structures of $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (A2′) and $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (A4′).** X-Ray structures of the two geometrical isomers **A2′** and **A4′** were determined, and the structures of the anions in them are shown in Figs. 3 and 4 respectively. Although the crystals of **A2′** suffered heavy disorder in some of water molecules of crystallization, the configuration of the cluster anion has no ambiguity. It is clear that the configuration of the three nitrogen atoms of ida ligands in **A2′** is "*trans*, *trans*, *cis*" to the $\mu_3$-S atom of the $Mo_3S_4$ core, and that the configuration of **A4′** is "*cis*, *cis*, *cis*" to the $\mu_3$-S atom. Since the configuration of **A1′** has been determined to be "*trans*, *trans*, *trans*", it is supposed that the configuration of **A3′** is "*trans*, *cis*, *cis*" as is shown in Fig. 6.[10] It is interesting that the sequence of elution from the ion exchange resin is related to the configuration of the clusters: The more the number of *trans* configuration(s) of the ida ligands, the faster the elution from the anion exchange resin. Interatomic distances and angles are collected in Table 3 for **A2′** and in Table 4 for **A4′**. No large difference was observed among the dimensions of **A1′**, **A2′**, and **A4′**.

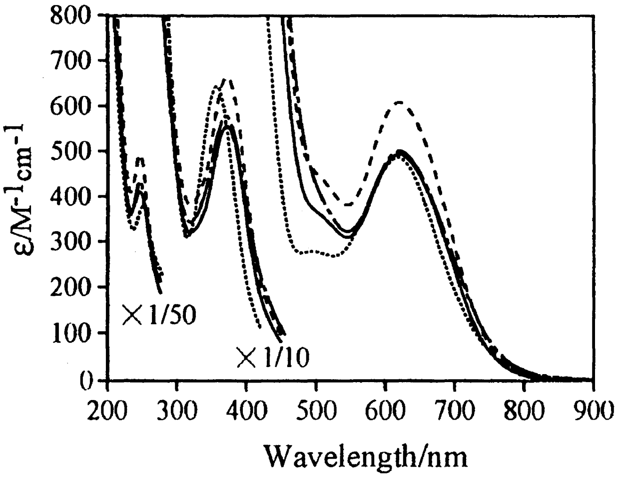

Fig. 2. Electronic spectra of the four isomers of $[Mo_3S_4(ida)_3]^{2-}$ in water. **A1** ———, **A2** - - - - - -, **A3** —•——•—, **A4** ••••••••.

Table 2. Electronic Spectral Data for $[Mo_3S_4(ida)_3]^{2-}$ Isomers in Water

| Compound | $\lambda_{max}$/nm $(\varepsilon/M^{-1}\,cm^{-1})$[a)] |
|---|---|
| **A1** | 246 (21700), 380 (5330), 622 (494) |
| **A2** | 247 (24686), 372 (6644), 619 (608) |
| **A3** | 247 (20544), 371 (5784), 620 (501) |
| **A4** | 251 (18930), 357 (6445), 494 (279), 619 (486) |

a) ε per trimer.

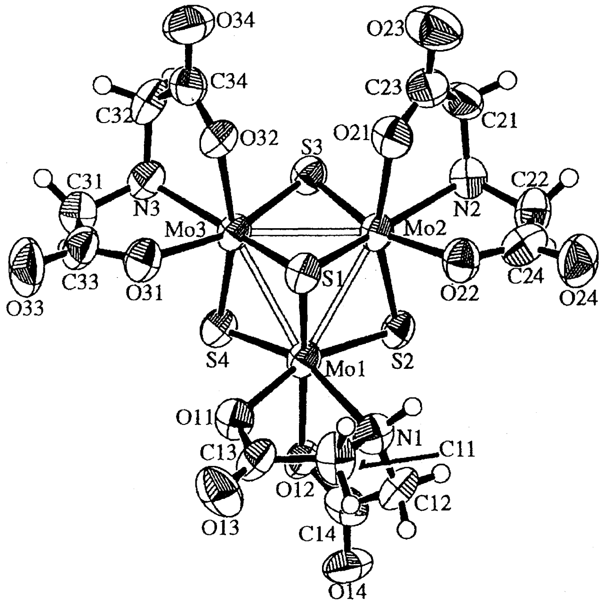

Fig. 3. ORTEP drawing of the anion of $Ca[Mo_3S_4(ida)_3]\cdot 21H_2O$ (**A2′**).

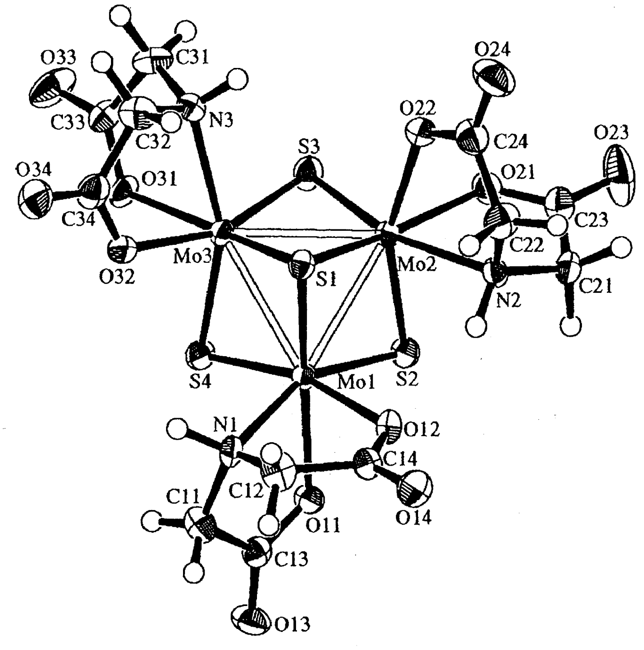

Fig. 4. ORTEP drawing of the anion of $Ca[Mo_3S_4(ida)_3]\cdot 14H_2O$ (**A4′**).

**Equilibration of the Geometrical Isomers of Sulfur-Bridged Clusters $[Mo_3S_4(ida)_3]^{2-}$.** Isomerization of each of the four isomers **A1′**, **A2′**, **A3′**, and **A4′** was detected. Accordingly, each of the solid samples was dissolved in water and the isomerization of each isomer was followed at 40 °C by the use of HPLC analysis. The changes of isomer ratio

Table 3. Selected Bond distances (Å) and Angles (°) for Ca[$Mo_3S_4$(ida)$_3$]·21$H_2O$ (**A2′**)

| Bond distances | | Bond distances | |
|---|---|---|---|
| Mo1–Mo2 | 2.767(2) | Mo1–Mo3 | 2.739(2) |
| Mo2–Mo3 | 2.731(2) | Mo1–S1 | 2.348(5) |
| Mo2–S1 | 2.345(5) | Mo3–S1 | 2.353(5) |
| Mo1–S2 | 2.286(4) | Mo1–S4 | 2.276(5) |
| Mo2–S2 | 2.289(5) | Mo2–S3 | 2.280(5) |
| Mo3–S3 | 2.287(5) | Mo3–S4 | 2.294(5) |
| Mo1–O11 | 2.10(1) | Mo1–O12 | 2.16(1) |
| Mo2–O21 | 2.13(1) | Mo2–O22 | 2.15(1) |
| Mo3–O31 | 2.17(1) | Mo3–O32 | 2.10(1) |
| Mo1–N1 | 2.25(2) | Mo2–N2 | 2.26(2) |
| Mo3–N3 | 2.23(2) | | |
| **Bond angles** | | **Bond angles** | |
| Mo2–Mo1–Mo3 | 59.47(5) | Mo1–Mo2–Mo3 | 59.74(5) |
| Mo1–Mo3–Mo2 | 60.79(5) | S2–Mo1–S4 | 98.0(2) |
| S2–Mo2–S3 | 95.7(2) | S3–Mo3–S4 | 93.8(2) |
| S1–Mo1–S2 | 104.6(2) | S1–Mo1–S4 | 106.6(2) |
| S1–Mo2–S2 | 104.6(2) | S1–Mo2–S3 | 107.2(2) |
| S1–Mo3–S3 | 106.7(2) | S1–Mo3–S4 | 105.9(2) |
| Mo1–S1–Mo2 | 72.3(1) | Mo2–S1–Mo3 | 71.1(1) |
| Mo1–S1–Mo3 | 71.3(1) | Mo1–S2–Mo2 | 74.4(1) |
| Mo2–S3–Mo3 | 73.4(1) | Mo1–S4–Mo3 | 73.6(1) |
| S1–Mo1–N1 | 91.8(5) | S1–Mo2–N2 | 159.3(4) |
| S1–Mo3–N3 | 158.6(4) | | |

Table 4. Selected Bond Distances (Å) and Angles (°) for Ca[$Mo_3S_4$(ida)$_3$]·14$H_2O$ (**A4′**)

| Bond distances | | Bond distances | |
|---|---|---|---|
| Mo1–Mo2 | 2.732(1) | Mo1–Mo3 | 2.768(1) |
| Mo2–Mo3 | 2.772(1) | Mo1–S1 | 2.347(2) |
| Mo2–S1 | 2.348(2) | Mo3–S1 | 2.357(2) |
| Mo1–S2 | 2.285(2) | Mo1–S4 | 2.281(2) |
| Mo2–S2 | 2.276(2) | Mo2–S3 | 2.292(2) |
| Mo3–S3 | 2.287(2) | Mo3–S4 | 2.290(2) |
| Mo1–O11 | 2.153(5) | Mo1–O12 | 2.145(5) |
| Mo2–O21 | 2.139(5) | Mo2–O22 | 2.114(5) |
| Mo3–O31 | 2.171(4) | Mo3–O32 | 2.137(5) |
| Mo1–N1 | 2.272(6) | Mo2–N2 | 2.280(5) |
| Mo3–N3 | 2.268(6) | | |
| **Bond angles** | | **Bond angles** | |
| Mo2–Mo1–Mo3 | 60.54(3) | Mo1–Mo2–Mo3 | 60.37(2) |
| Mo1–Mo3–Mo2 | 59.09(3) | S2–Mo1–S4 | 97.14(7) |
| S2–Mo2–S3 | 95.97(7) | S3–Mo3–S4 | 100.18(8) |
| S1–Mo1–S2 | 106.60(7) | S1–Mo1–S4 | 104.99(6) |
| S1–Mo2–S2 | 106.85(7) | S1–Mo2–S3 | 104.97(7) |
| S1–Mo3–S3 | 104.81(7) | S1–Mo3–S4 | 104.36(7) |
| Mo1–S1–Mo2 | 71.16(5) | Mo2–S1–Mo3 | 72.20(5) |
| Mo1–S1–Mo3 | 72.08(5) | Mo1–S2–Mo2 | 73.57(6) |
| Mo2–S3–Mo3 | 74.52(6) | Mo1–S4–Mo3 | 74.54(6) |
| S1–Mo1–N1 | 90.5(2) | S1–Mo2–N2 | 90.6(1) |
| S1–Mo3–N3 | 93.9(1) | | |

with the passage of time are shown in Figs. 5a, 5b, 5c, and 5d, respectively. Figure 5a shows that as **A1** decreases, **A2** starts to appear immediately, and **A3** turns up later. The isomer **A4**

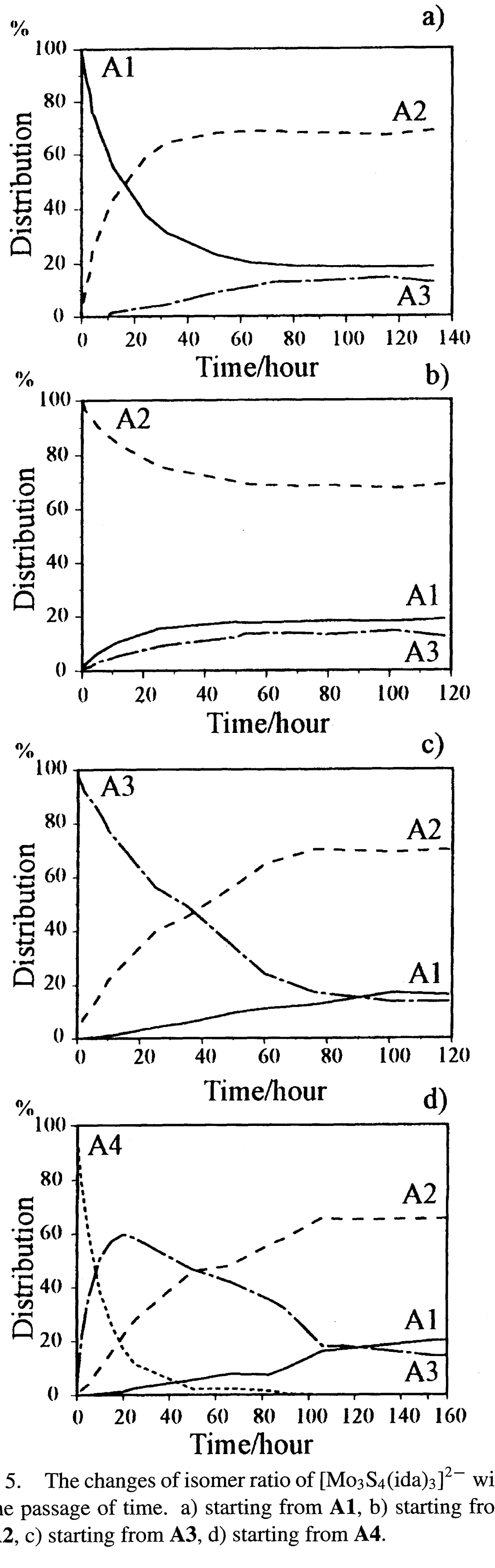

Fig. 5. The changes of isomer ratio of [$Mo_3S_4$(ida)$_3$]$^{2-}$ with the passage of time. a) starting from **A1**, b) starting from **A2**, c) starting from **A3**, d) starting from **A4**.

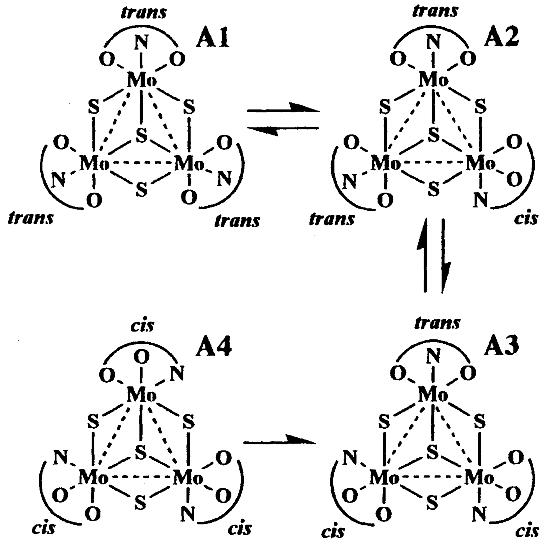

Fig. 6. Four kinds of isomers of $[Mo_3S_4(ida)_3]^{2-}$: **A1** (*trans, trans, trans*), **A2** (*trans, trans, cis*), **A3** (*trans, cis, cis*), **A4** (*cis, cis, cis*).

is not detected. Figure 5b indicates that as **A2** decreases, both **A1** and **A3** appear at the same time. The isomer **A4** is not detected. Figure 5c displays that as **A3** decreases, **A2** starts to appear immediately, and **A1** turns up later. The isomer **A4** is not detected. Figure 5d shows that as **A4** decreases rapidly, **A3** starts to appear immediately, and **A2** turns up later. Finally **A1** starts to be detected. All the Figs. 5a—d indicate that in equilibrium **A1** (18%), **A2** (68%), and **A3** (14%) exist, and **A4** does not exist. As is indicated in Fig. 6, *cis–trans* conversion of ida ligand occurs one by one.

The isomer **A4** does not exist in equilibrium and the advent of **A4** is possible only in the course of preparation from **A** and $H_2$ida. This is the reason why "the respective yield is changeable, but the total yield of the four species remains rather constant" (see preparation and characterization).

This work was partly supported by a Grant-in-Aid for Scientific Research No. 08454215 from the Ministry of Education, Science, Sports and Culture. We thank the Research Instruments Center, Okayama University of Science, for the use of instruments.

## References

1 T. Shibahara and H. Kuroya, *Polyhedron*, **5**, 357 (1986).

2 T. Shibahara, H. Miyake, K. Kobayashi, and H. Kuroya, *Chem. Lett.*, **1986**, 139.

3 For example: a) F. R. Keene and G. H. Searle, *J. Chem. Soc., Chem. Commun.*, **1970**, 784. b) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972). d) T. Yasui, K. Okamoto, J. Hidaka, T. Ama, and H. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **60**, 2573 (1987). e) T. Kawamoto, T. Yasui, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 841 (1988).

4 For example: $[Co_3(edma)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]Cl$: a) T. Ama, M. Shiro, A. Takeuchi, T. Yonemura, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **70**, 2685 (1997). b) Md. M. Rashid, T. Ama, T. Yonemura, H. Kawaguchi, and T. Yasui, "The 48th Symposium on Coordination Chemistry of Japan," Kochi (1998), Abstr., No. 1PA17.

5 a) T. Shibahara, M. Yamasaki, G. Sakane, K. Minami, T. Yabuki, and A. Ichimura, *Inorg. Chem.*, **31**, 640 (1992). b) T. Shibahara and H. Akashi, *Inorg. Synth.*, **29**, 260 (1992). c) H. Akashi, T. Shibahara, and H. Kuroya, *Polyhedron*, **9**, 1671 (1990).

6 G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany.

7 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, and G. Polidori, *J. Appl. Crystallogr.*, **27**, 435 (1994).

8 "Crystal Structure Analysis Package," Molecular Structure Corporation, The Woodlands, TX (1985 and 1992).

9 The elemental analysis of **A1′** indicates that the number of water of crystallization is 12 rather than 11.5 previously reported (Ref. 1).

10 Crystals of **A3′** suitable for X-ray crystal structure determination have not been obtained yet.