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# Synthesis, characterization and properties of $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ and related $M_6S_8L_6$ cluster complexes (M = Mo, W)†

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Octahedral molybdenum chalcogenide clusters are the building blocks of the well-known Chevrel phases. Although the synthesis of molecular $Mo_6S_8L_6$ (L = $PEt_3$ and pyridine) clusters has been previously reported, a high yield and larger scale synthetic procedure is needed to produce soluble $Mo_6S_8L_6$ (L = Lewis base ligand) clusters, so that they can be used as precursors for the construction of novel network structures. Using the previously developed $W_6S_8$(4-*tert*-butylpyridine)$_6$ synthesis as a starting point, a facile, high yield (70%) synthesis of $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ from $(Bu_4N)_2Mo_6Cl_8Cl_6$ was developed. This general sulfidation reaction scheme can be extended to the direct preparation of many $M_6S_8L_6$ (M = W, Mo; L = Lewis base ligand) complexes. Three $Mo_6S_8L_6$ complexes (L = $PEt_3$, methylamine, 4,4′-bipyridine) were also prepared *via* ligand exchange reactions with $Mo_6S_8$(4-*tert*-butylpyridine)$_6$. The above $Mo_6S_8L_6$ complexes were characterized and their reactivity was compared with their tungsten counterparts. Crystal structures were found for $Mo_6S_8$(4-*tert*-butylpyridine)$_6$, $Mo_6S_8$(4,4′-bipyridine)$_6$, and $Mo_6S_8$(methylamine)$_6$.

## Introduction

Octahedral molybdenum chalcogenide clusters ($Mo_6Q_8$, Q = S, Se, Te) are the building blocks of the Chevrel phases[1] that are well-known for their superconductivity,[2] fast ionic conductivity,[3,4] thermoelectric properties[5–7] and catalytic activity.[8–11] Molecular $Mo_6S_8L_6$ clusters (L = $PEt_3$, nitrogen Lewis base ligands) were prepared independently by Saito and co-workers[12,13] and by McCarley *et al.*[14] to study their structural relation to the solid-state Chevrel phases and to use these molecular precursors to prepare Chevrel phases.[15,16] However, these two synthetic procedures are not ideal for further studies of the solution chemistry of the clusters. It is very hard to replace the $PEt_3$ ligand in Saito's synthetic product, $Mo_6S_8(PEt_3)_6$, and the direct product in McCarley's route, $Mo_6S_8$(pyridine)$_6$, is insoluble in most solvents. In addition, these reactions are plagued by poor yields.

Although tungsten analogues of the Chevrel phases have never been prepared, molecular $W_6S_8L_6$ clusters are available.[17–19] In the pursuit of network structures with $W_6S_8$ clusters as building blocks, we developed a high yield synthesis of $W_6S_8$(4-tbp)$_6$ (4-tbp = 4-*tert*-butylpyridine) starting from $(Bu_4N)_2W_6Cl_8Cl_6$,[20] a procedure that was modified from McCarley's $W_6S_8$(pyridine)$_6$ cluster synthetic route.[18] Due to the ease of its preparation on a large scale (10 g) and its amenable properties, $W_6S_8$(4-tbp)$_6$ has become the key intermediate molecule in our cluster research.[21] In this report, we extend this direct sulfidation synthesis to prepare more $W_6S_8L_6$ clusters and the new $Mo_6S_8$(4-tbp)$_6$ complex. The advantage of this $Mo_6S_8$(4-tbp)$_6$ preparation is illustrated with the synthesis and characterization of three $Mo_6S_8L_6$ (L = $PEt_3$, 4,4′-bipyridyl (4,4′-bipy) and $CH_3NH_2$) complexes. The properties of $Mo_6S_8L_6$ clusters, particularly in comparison with their tungsten analogues, are briefly discussed.

## Experimental

### General

$(Bu_4N)_2W_6Cl_8Cl_6$ and $(Bu_4N)_2Mo_6Cl_8Cl_6$ were prepared using $WCl_6$ and $MoCl_5$ based on the high yield syntheses developed by Messerle and co-workers[22,23] and were described previously.[20] The synthesis of KSH was also described previously.[20] All other reagents were of commercial origin. Morpholine and aniline were dried with potassium hydroxide, degassed and distilled under reduced pressure. Acetonitrile and 4-*tert*-butylpyridine were dried with 4 Å molecular sieves and were degassed and distilled under reduced pressure. THF, diethyl ether and benzene were treated with sodium wire and distilled under reduced pressure. All other reagents were used as received. Methylamine and $PEt_3$ solutions in THF were received sealed under dinitrogen from Aldrich. All reagents and products were stored in a glove box filled with argon. All operations were carried out in the glove box unless otherwise stated. The "reaction bomb" used below is a thick-walled glass vessel (id = 1 in, thickness = 1/8 in) equipped with a Teflon valve and a Teflon stir bar.

$^1H$ NMR spectra were obtained using an IBM/Bruker AF-300 or a Varian INOVA-400 spectrometer with no $^{31}P$ decoupling and were internally referenced to residual solvent resonance. $^{31}P$ NMR spectra were obtained using a Varian VXR-400 instrument at 162 MHz with 85% $H_3PO_4$ as external standard and with $^1H$ decoupling unless otherwise noted. Powder X-ray diffraction was done on a Scintag XDS2000 diffractometer. The thermogravimetric analyses (TGA) of the cluster complexes were done on a Seiko TG/DTA 220 thermal analyzer. The samples were loaded onto an aluminum pan and were heated from room temperature to 550 °C at the rate of 20 °C $min^{-1}$ under a flow of dinitrogen (60 mL $min^{-1}$).

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† Electronic supplementary information (ESI) available: powder X-ray diffraction patterns of $W_6S_8$(morpholine)$_6$ and $Mo_6S_8(CH_3NH_2)_6$. Thermogravimetric traces of $Mo_6S_8$(4-*tert*-butylpyridine)$_6$, $Mo_6S_8(PEt_3)_6$, $Mo_6S_8$(4,4′-bipy)$_6$ and $Mo_6S_8(CH_3NH_2)_6$ compounds. See http://www.rsc.org/suppdata/dt/b2/b202246j/

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### Synthesis of $Mo_6S_8$(4-*tert*-butylpyridine)$_6$

A 50 mL Schlenk flask was charged with $(Bu_4N)_2Mo_6Cl_8Cl_6$ (0.805 g, 0.517 mmol), DMF (8 g), 4-*tert*-butylpyridine (0.836 g, 6.18 mmol) and finally KSH (0.345 g, 4.78 mmol) to form a yellow slurry. Upon addition of potassium *tert*-butoxide (0.233 g, 2.08 mmol), the mixture turned brownish black. The flask was sealed and heated at 100 °C with stirring for 4 days outside of the glove box. After the solvent was removed in dynamic vacuum, the resulting dark tacky residue was broken up by agitation and more 4-*tert*-butylpyridine (3 g) was added. The flask was then sealed and heated at 100 °C while stirring for another 4 days. The resulting suspension mixture of fine light-brown particles was allowed to cool and settle before it was filtered through an "E" frit (ACE Glass Inc.). The solid remaining on the frit was washed first with acetonitrile (15 mL) until the filtrate was colorless, then with deoxygenated water (about 80 mL) until the filtrate gave no precipitate with $AgNO_3$ solution, then with a copious amount of acetonitrile again, and finally with diethyl ether (25 mL). After drying *in vacuo*, the fine brown powder product weighed 0.590 g (70% yield).

$Mo_6S_8$(4-tbp)$_6$ is quite soluble in benzene and THF. $^1H$ NMR in $C_6D_6$: $\delta$ 9.74 (d, 2, $J$ = 7 Hz, α-H), 6.64 (d, 2, $J$ = 7 Hz, β-H), 0.80 (s, 9, Me). Single crystals of this complex were grown by layering diethyl ether on top of a benzene solution of the compound.

### Direct syntheses of some other known $W_6S_8L_6$ complexes

**$W_6S_8(PEt_3)_6$.** A reaction bomb was charged with $(Bu_4N)_2W_6Cl_8Cl_6$ (1.00 g, 0.479 mmol), DMF (8 g), 1 M solution of $PEt_3$ in THF (5.7 ml, 5.7 mmol) and KSH (0.291 g, 4.04 mmol) to form a yellow slurry, which turned dark brown upon addition of $^t$BuOK (0.233 g, 2.37 mmol). After the sealed reaction bomb was heated at 100 °C with stirring for 4 days, some red crystals and white particles were visible in the reaction mixture. After cooling, the reaction mixture was filtered through an "E" glass frit (ACE Glass Inc.) and the resulting solid was washed with acetonitrile until the filtrate was colorless. This was followed by washing with deoxygenated water (about 50 mL) until the filtrate gave no precipitate with $AgNO_3$ solution, then with a large amount of acetonitrile again. After a quick wash with 5 mL of cold THF and finally 25 mL of diethyl ether, the solid was dried, yielding a fine red–brown powder weighing 0.716 g (72 % yield).

**$W_6S_8$(morpholine)$_6$.** Similar procedures were carried out with the following reagents $(Bu_4N)_2W_6Cl_8Cl_6$ (0.400 g, 0.192 mmol), DMF (4.5 g), morpholine (1.68 g, 19.3 mmol, 1 : 100 equiv.), KSH (0.118 g, 1.64 mmol) and $^t$BuOK (0.098 g, 0.875 mmol) producing a dark suspension mixture after heating and finally a brownish green powder that weighed 0.195 g (54% yield). PXRD available in ESI. CHN analysis found (calculated): C 15.48% (15.31%), H 3.01% (2.89%), N 4.18% (4.46%).

### Syntheses of other $Mo_6S_8L_6$ complexes from $Mo_6S_8$(4-tbp)$_6$

Most other complexes can be prepared from $Mo_6S_8$(4-tbp)$_6$ using ligand exchange reactions similar to those described for the tungsten analogues[21] but at lower reaction temperatures (50–80 °C). A detailed description is included only for $Mo_6S_8$(4,4′-bipy)$_6$ as its tungsten analogue was not reported.

**$Mo_6S_8$(4,4′-bipy)$_6$.** A reaction bomb was charged with $Mo_6S_8$(4-tbp)$_6$ (0.200 g, 0.122 mmol) and 4,4′-bipyridyl (4,4′-bipy) (1.57 g, 10.1 mmol, 83 equiv.) along with 12 g of aniline. After heating at 50 °C for 2 days outside the glove box, the bloody red reaction mixture was filtered through a syringe filter in the glove box and layered with acetonitrile (25 mL) to precipitate the product. The resulting red powder was collected by filtration, washed with diethyl ether and weighed 0.147 g (54% yield). CHN analysis found (calculated): C 41.08% (40.73%), H 2.69% (2.73%), N 9.10% (9.50%). Block-shaped dark-red single crystals were grown by layering acetonitrile on a diluted aniline reaction solution.

**$Mo_6S_8(PEt_3)_6$.** This compound was prepared from $Mo_6S_8$(4-tbp)$_6$ in a similar fashion to its tungsten analogue[20] in almost quantitative yield. X-ray quality crystals were present but not analyzed, as the structure was previously investigated.[12,13] $^1H$ NMR in $C_6D_6$: $\delta$ 1.97 ("quintet", $J_{P\text{–}H} \approx J_{H\text{–}H}$ = 7 Hz, 2, $CH_2$), 1.20 ("quintet", $J_{P\text{–}H} \approx J_{H\text{–}H}$ = 7 Hz, 3, Me). $^{31}P\{^1H\}$ NMR: $\delta$ 19.26, no satellite peaks, but with a shoulder (width 5 Hz).

**$Mo_6S_8(CH_3NH_2)_6$.** This complex was prepared from $Mo_6S_8$(4-tbp)$_6$ in a similar fashion to its tungsten analogue[21] in a yield of 90%. It is insoluble in most solvents except aniline. Single crystals were grown by diffusion of diethyl ether into an aniline solution. PXRD are available in the ESI. †

### X-Ray structure determination

Single crystals suitable for X-ray crystallographic analysis were obtained for $Mo_6S_8$(4-tbp)$_6$, $Mo_6S_8$(4,4′-bipy)$_6$ and $Mo_6S_8(CH_3NH_2)_6$, as described in the synthesis section. Selected single crystals were mounted on a thin plastic loop using polybutene oil and were immediately placed in a cold dinitrogen stream. Single crystal X-ray diffraction data were collected on a Bruker SMART system with a CCD detector using Mo Kα radiation at 173 K. The cell constants were determined from more than 50 well-centered reflections. The data were integrated using SAINT software,[24] and empirical absorption corrections were applied using SADABS program (β revision).[25] The space groups were determined on the basis of systematic absences, intensity statistics, and the successful refinements of the structures. The structures were solved using SHELXS[26] with direct methods to reveal the positions of W and S atoms. Difference Fourier syntheses following the subsequent full-matrix least-squares refinements on $F_o^2$ with SHELXL software packages[26] revealed the ligand atoms. Hydrogen atoms were assigned to the ideal positions and refined using a riding model. There was some disorder in the *tert*-butyl groups of the ligand in the $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ cluster and the diethyl ether solvent molecules which was modeled successfully. All non-solvent non-hydrogen atoms were refined anisotropically. Final refinements converged and the residual electron densities were near the W atoms (typically within 1 Å). The crystallographic data are summarized in Table 1.

CCDC reference numbers 185879–185881.

See http://www.rsc.org/suppdata/dt/b2/b202246j/ for crystallographic data in CIF or other electronic format.

## Results and discussion

### Synthesis

The following factors have been determined to be important in the successful synthesis of $W_6S_8$(4-*tert*-butylpyridine)$_6$ by the sulfidation of the $\{W_6Cl_8\}^{4+}$ cluster (Scheme 1):[20] the use of

$$
\begin{array}{c}
(Bu_4N)_2M_6Cl_8Cl_6 + 8\ KSH + 4\ KO\mathit{t}\text{-}Bu + (6 + x)\ L \\
\text{DMF/other solvents}\ \Big\downarrow\ 100\ °C,\ 4\ d \\
M_6S_8L_6 + 12\ KCl + 2\ Bu_4NCl + 4\ \mathit{t}\text{-}BuOH + x\ L + 2\ H_2
\end{array}
$$

M = W, Mo; L = 4-*tert*-butylpyridine, $PEt_3$, morpholine *etc.*

Scheme 1

**Table 1** Crystallographic data for $Mo_6S_8$(4-*tert*-butylpyridine)$_6$·$2Et_2O$, $Mo_6S_8$(4,4′-bipy)$_6$·5 aniline and $Mo_6S_8(CH_3NH_2)_6$

| | $Mo_6S_8$(4-tbp)$_6$·$2Et_2O$ | $Mo_6S_8$(4,4′-bipy)$_6$·5 aniline | $Mo_6S_8(CH_3NH_2)_6$ |
|---|---|---|---|
| Chemical formula | $C_{62}H_{98}N_6O_2S_8Mo_6$ | $C_{90}H_{83}N_{17}S_8Mo_6$ | $C_6H_{30}N_6S_8Mo_6$ |
| Formula weight | 1791.58 | 2234.85 | 1018.48 |
| Space group | $C2/c$ (no. 15) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$/Å | 30.192(3) | 9.3457(9) | 9.0965(10) |
| $b$/Å | 9.3346(8) | 15.7644(16) | 9.1746(10) |
| $c$/Å | 27.803(2) | 15.7752(16) | 9.5609(13) |
| $\alpha$/° | 90 | 99.506(3) | 116.812(2) |
| $\beta$/° | 103.450(3) | 98.305(3) | 103.418(2) |
| $\gamma$/° | 90 | 96.087(3) | 106.402(2) |
| $V$/Å$^3$ | 7620.7(11) | 2248.0(4) | 619.97(12) |
| $Z$ | 4 | 1 | 1 |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.562 | 1.651 | 2.728 |
| Reflections measured | 27811 | 14629 | 6962 |
| Independent reflections | 6478 ($R_{int} = 0.0516$) | 6007 ($R_{int} = 0.0523$) | 2882 ($R_{int} = 0.0331$) |
| $\mu$/cm$^{-1}$ | 12.18 | 10.53 | 36.23 |
| $R_1{}^b$ ($I > 2\sigma$/all) | 0.0451/0.0674 | 0.0435/0.0872 | 0.0401/0.0553 |
| w$R_2{}^c$ ($I > 2\sigma$/all) | 0.0920/0.0975 | 0.0787/0.0905 | 0.1023/0.1092 |

[a] $\lambda = 0.71073$ Å at 173 K. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

crystalline $(Bu_4N)_2W_6Cl_8Cl_6$ and pure KSH as reagents, the choice of 4-*tert*-butylpyridine as the axial ligand for the sulfide cluster, and a convenient workup procedure based on the solubility and other properties of the $W_6S_8$(4-*tert*-butylpyridine)$_6$ product. The mechanism of the sulfidation reaction is not fully understood, but there are speculations that basic conditions activate the inner ligands and that $^t$BuOK, in particular, acts as a deprotonation agent.[27] It is reasonable that this reaction scheme can be expanded to other ligands (L) and to the analogous molybdenum clusters (M = Mo) if these issues are properly addressed.

### Direct syntheses of some other known $W_6S_8L_6$ complexes

Although most other $W_6S_8L_6$ clusters can be prepared by ligand exchange reactions with $W_6S_8$(4-*tert*-butylpyridine)$_6$,[21] direct synthesis from the tungsten chloride cluster is more efficient when large quantities are needed. This should be relatively easy as most of the aforementioned factors remain unchanged. It is necessary to ensure, however, that the solubility properties of the targeted $W_6S_8L_6$ clusters allow simple workup procedures and that their stability can withstand the brief workup in air. The synthetic procedure would not be practical if tedious and scale-limiting chromatography or complete Schlenk operations had to be used for the separation and purification of the products. For these reasons, direct synthesis of the $W_6S_8L_6$ clusters where L are less strongly bound ligands to the $W_6S_8$ cluster,[21] such as $W_6S_8$(*n*-butylamine)$_6$,[28] was not possible even after repeated attempts in different solvent systems. On the other hand, the direct synthesis of $W_6S_8(PEt_3)_6$ works very well since $PEt_3$ is very strongly bound on the $W_6S_8$ cluster[21] and $W_6S_8(PEt_3)_6$ in the solid state is stable in air for months as determined by NMR. The solubility of $W_6S_8(PEt_3)_6$ is very much like that of $W_6S_8$(4-tbp)$_6$ so the workup procedures are identical. Only the solvent system for the reaction was changed from pure DMF to a 1 : 2 (v/v) mixture of THF/DMF. As $W_6S_8(PEt_3)_6$ is insoluble in DMF, the slight solubility of $W_6S_8(PEt_3)_6$ in THF allows a crystalline precipitate. The identity and purity of the product was confirmed by comparing the $^1$H NMR and $^{31}$P NMR with the compounds prepared *via* ligand exchange.[20] Morpholine is considered a slightly less strongly bound ligand than 4-*tert*-butylpyridine,[21] but $W_6S_8$(morpholine)$_6$ was also directly prepared from $(Bu_4N)_2W_6Cl_8Cl_6$ in a solvent mixture of morpholine/DMF in a similar manner. Perhaps the general insolubility of the $W_6S_8$(morpholine)$_6$ product provides some extra air stability and convenience. The product of this direct synthesis was verified by CHN analysis and PXRD, since it is insoluble in common NMR solvents.

### Synthesis of $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ from the chloride cluster

The extension of reaction Scheme 1 to the $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ synthesis became considerably easier after the experience with the tungsten clusters. First, an equally high yield synthesis of $(Bu_4N)_2Mo_6Cl_8Cl_6$ was achieved through a facile preparation of $[H_3O]_2[Mo_6Cl_8Cl_6]$·$y$$H_2O$ from $MoCl_5$[22] and subsequent metathesis to replace $H_3O^+$ by $Bu_4N^+$. The simple imitation of the $W_6S_8$(4-tbp)$_6$ reaction conditions with $(Bu_4N)_2Mo_6Cl_8Cl_6$ led to a thick dark brown suspension that was very hard to filter. Surprisingly, the solid captured after prolonged filtration was found by PXRD to contain KCl, and an NMR spectrum showed no organic component. However, $^1$H NMR resonances reminiscent of those observed for $W_6S_8$(4-tbp)$_6$[20] were observed among other peaks for the tacky filtrate, showing that the proposed reaction did proceed but that the desired $Mo_6S_8$(4-tbp)$_6$ product is quite soluble in DMF so that it does not precipitate out like its tungsten analogue. Different reaction solvents, including $CH_3CN$ (does not dissolve the product), THF (good solvent for the product) and DMF, and combinations of them, were explored, and various workup procedures were carried out, only to prove that they were not more convenient than DMF as the solvent. They all suffered from low yields (< 35%) and *very slow* filtration during the excessively prolonged (compared with the tungsten case[20]) $CH_3CN$ wash during the workup. It was then found that this unidentified tacky $CH_3CN$-soluble substance seemed to greatly diminish to a normal amount (compared with the tungsten version[20]) if the dried residue was reacted again with additional neat 4-*tert*-butylpyridine. Furthermore, since $Mo_6S_8$(4-tbp)$_6$ is only slightly soluble in neat 4-*tert*-butylpyridine (just like $W_6S_8$(4-tbp)$_6$ in DMF[20]), the distinct crystalline product is easily collected by filtration. The workup can be performed almost identically to the tungsten workup[20] after this additional round of heating with 4-*tert*-butylpyridine and the yield increased to 70%. We speculate that the reaction as depicted in Scheme 1 does not go to completion for molybdenum and some ligand-deficient species may exist. Heating in neat 4-*tert*-butylpyridine likely forces the full substitution of the axial ligands. We do not know what causes this difference between the tungsten and molybdenum reactions, but once such difference is taken into account, a convenient, scalable, high yield (70%) synthesis can also be achieved for $Mo_6S_8$(4-*tert*-butylpyridine)$_6$.

The examples discussed above make it clear that the reaction Scheme 1 is rather general and can be applied to many $M_6S_8L_6$ cluster syntheses. In fact, other $Mo_6S_8L_6$ clusters, such as $Mo_6S_8$(morpholine)$_6$, can be directly prepared from $(Bu_4N)_2Mo_6Cl_8Cl_6$. Such obvious extensions are omitted for brevity.

**Table 2** Selected bond lengths [Å] and angles [°] for $Mo_6S_8$(4-*tert*-butylpyridine)$_6$, $Mo_6S_8$(4,4′-bipy)$_6$ and $Mo_6S_8(CH_3NH_2)_6$ clusters[a]

| Clusters | $Mo_6S_8$(4-tbp)$_6$ | $Mo_6S_8$(4,4′-bipy)$_6$ | $Mo_6S_8(CH_3NH_2)_6$ |
|---|---|---|---|
| Mo–Mo | 2.6492(6)–2.6575(6) | 2.6464(8)–2.6509(8) | 2.6412(7)–2.6642(7) |
| mean[a] | 2.655(4) | 2.650(2) | 2.651(8) |
| $\delta_{\text{Mo–Mo}}$[b] | 0.008 | 0.0016 | 0.008 |
| Mo–S | 2.4381(13)–2.4601(15) | 2.4257(18)–2.4580(17) | 2.4329(15)–2.4693(15) |
| mean[a] | 2.450(6) | 2.442(9) | 2.454(13) |
| $\delta_{\text{Mo–s}}$[b] | 0.022 | 0.032 | 0.036 |
| Mo–Mo–Mo[c] | 89.73(2)–90.27(2) | 89.91(2)–90.09(2) | 89.89(2)–90.11(2) |
| $\delta_{\text{Mo–Mo–Mo}}$[b] | 0.54 | 0.18 | 0.22 |
| Mo–Mo–Mo[d] | 59.843(17)–60.226(17) | 59.90(2)–60.06(2) | 59.600(18)–60.353(18) |
| $\delta_{\text{Mo–Mo–Mo}}$[b] | 0.38 | 0.16 | 0.753 |
| Mo–N | 2.266(4), 2.276(4), 2.280(4) | 2.252(5), 2.263(5), 2.275(5) | 2.289(5), 2.293(5), 2.295(5) |
| Mean[a] | 2.274(6) | 2.263(9) | 2.292(5) |
| $\delta_{\text{Mo–N}}$[b] | 0.014 | 0.023 | 0.006 |

[a] Followed by standard deviations (σs) of the group of bond lengths in the parentheses. $\sigma = \{\Sigma(d_j - d_m)^2/n\}^{1/2}$. [b] Maximum deviations. [c] Within equatorial squares. The mean Mo–Mo–Mo angles within the equatorial squares are automatically 90° if the clusters have inversion centers. [d] Within triangular faces. The mean angles are 60° by geometry.

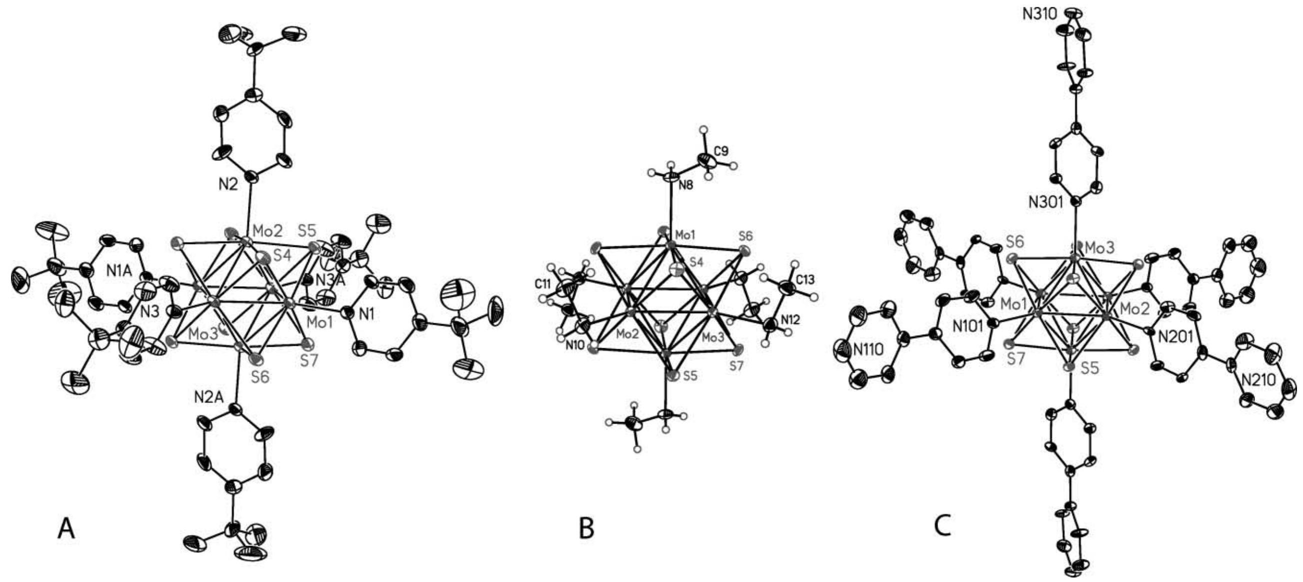

**Fig. 1** Molecular structures of (A) $Mo_6S_8$(4-*tert*-butylpyridine)$_6$, (B) $Mo_6S_8(CH_3NH_2)_6$ and (C) $Mo_6S_8$(4,4′-bipy)$_6$ clusters at 50% probability level with partial labeling scheme. H atoms for A and C were omitted for clarity.

### Properties of $Mo_6S_8L_6$ cluster complexes

Three more cluster complexes, $Mo_6S_8(PEt_3)_6$, $Mo_6S_8(CH_3NH_2)_6$, and $Mo_6S_8$(4,4′-bipy)$_6$ were synthesized *via* ligand exchange reactions with $Mo_6S_8$(4-tbp)$_6$ and were spectroscopically and/or crystallographically characterized. A large excess of free 4,4′-bipy is essential for preventing $Mo_6S_8$(4,4′-bipy)$_6$ from precipitating as possibly partially linked amorphous cluster oligomers. Since the $W_6S_8L_6$ complexes were systematically investigated,[21] these examples are sufficient to confirm that the ligand exchange reactions and ligand binding order on the $Mo_6S_8$ cluster are parallel to those observed for $W_6S_8L_6$ complexes.[21] It can be generally extrapolated that other desired $Mo_6S_8L_6$ complexes can be easily prepared by ligand exchange with $Mo_6S_8$(4-tbp)$_6$, if direct synthesis from $(Bu_4N)_2Mo_6Cl_8Cl_6$ is not successful. In terms of the comparison with the $W_6S_8L_6$ complexes, the molybdenum cluster complexes are generally more soluble than their tungsten analogues. The ligand exchange reactions proceed at lower temperatures. For example, we observed that 4-*tert*-butylpyridine in $Mo_6S_8$(4-*tert*-butylpyridine)$_6$ was fully replaced by $PEt_3$ at room temperature within several hours while heating is necessary for $W_6S_8$(4-tbp)$_6$.[21] The TGA traces (figures available in ESI) of $Mo_6S_8L_6$ show that the thermal deligation starts at 155 °C for L = 4-tbp, 190 °C for L = $PEt_3$, 190 °C for L = 4,4′-bipy and below 100 °C for L = $CH_3NH_2$ (not very clearly defined), consistently lower temperatures than their tungsten counterparts, 190 °C for L = 4-tbp, 250 °C for L = $PEt_3$, 220 °C for L = 4,4′-bipy and 160 °C for L = $CH_3NH_2$, respectively.[21] In summary, the $Mo_6S_8L_6$ cluster complexes are kinetically more labile, if not also thermodynamically less stable, than their tungsten counterparts.

### Crystal structures of $Mo_6S_8L_6$ complexes

Three crystal structures for the new $Mo_6S_8L_6$ clusters were determined (shown in Fig. 1). They share the same $Mo_6S_8$ core structure, which can be described as an octahedron of molybdenum atoms with its octahedral face capped by eight triply-bridging sulfur atoms. The selected bond lengths and angles summarized in Table 2 show that the $Mo_6S_8$ octahedra are quite regular as evidenced by the small variations of bond lengths and angles. Six donor ligands (L) coordinate to each of the six Mo atoms with average bond lengths (2.274(6) Å for L = 4-tbp, 2.263 Å for L = 4,4′-bipy and 2.292 Å for L = $CH_3NH_2$) comparable to those reported values (2.283 to 2.317 Å) for N-ligated $Mo_6S_8L_6$ clusters.[14] These Mo–N bond lengths are consistently shorter than those found in the tungsten counterparts.[21] This is probably mainly due to the smaller radius of Mo compared to W, instead of weaker M–N bonds, since the average Mo–Mo bond lengths found in the $Mo_6S_8L_6$ structures are all slightly but consistently shorter than those in the corresponding tungsten cases.[21] On the basis of Pauling's relation[29] and the single Mo–Mo bond length of 2.614 Å,[30] the bond orders of these Mo–Mo bonds are calculated to be 0.854, 0.871 and 0.868 for $Mo_6S_8(4\text{-tbp})_6$, $Mo_6S_8(4,4'\text{-bipy})_6$ and $Mo_6S_8(CH_3NH_2)_6$, respectively. Close to the expected bond order of 0.833 for 20 e clusters (20/24 = 0.833), these bond orders are slightly smaller than the corresponding tungsten values.[21]

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## References

1 R. Chevrel, M. Sergent and J. Prigent, *J. Solid State Chem.*, 1971, **3**, 515.
2 R. Chevrel and M. Sergent, *Top. Curr. Phys.*, eds. O. Fischer and M. B. Maple, Springer-Verlag, Heidelberg, 1982, vol. 32, pp. 25–86.
3 D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich and E. Levi, *Nature (London)*, 2000, **407**, 724.
4 P. J. Mulhern and R. R. Haering, *Can. J. Phys.*, 1984, **62**, 527.
5 T. Caillat, J. P. Fleurial and G. J. Snyder, *Solid State Sci.*, 1999, **1**, 535.
6 C. Roche, P. Pecheur, G. Toussaint, A. Jenny, H. Scherrer and S. Scherrer, *J. Phys.: Condens. Matter*, 1998, **10**, L333.
7 A. B. Kaiser, *Phys. Rev. B: Condens. Matter*, 1987, **35**, 4677.
8 R. K. Thompson, S. J. Hilsenbeck, T. J. Paskach, R. E. McCarley and G. L. Schrader, *J. Mol. Catal. A: Chem.*, 2000, **161**, 75.
9 S. J. Hilsenbeck, R. E. McCarley, R. K. Thompson, L. C. Flanagan and G. L. Schrader, *J. Mol. Catal. A: Chem.*, 1997, **122**, 13.
10 S. A. Kareem and R. Miranda, *J. Mol. Catal.*, 1989, **53**, 275.
11 K. F. McCarty, J. W. Anderegg and G. L. Schrader, *J. Catal.*, 1985, **93**, 375.
12 T. Saito, N. Yamamoto, T. Nagase, T. Tsuboi, K. Kobayashi, T. Yamagata, H. Imoto and K. Unoura, *Inorg. Chem.*, 1990, **29**, 764.
13 T. Saito, N. Yamamoto, T. Yamagata and H. Imoto, *J. Am. Chem. Soc.*, 1988, **110**, 1646.
14 S. J. Hilsenbeck, V. G. Young, Jr. and R. E. McCarley, *Inorg. Chem.*, 1994, **33**, 1822.
15 S. J. Hilsenbeck, R. E. McCarley and A. I. Goldman, *Chem. Mater.*, 1995, **7**, 499.
16 R. E. McCarley, S. J. Hilsenbeck and X. Xie, *J. Solid State Chem.*, 1995, **117**, 269.
17 T. Saito, A. Yoshikawa and T. Yamagata, *Inorg. Chem.*, 1989, **28**, 3588.
18 X. Zhang and R. E. McCarley, *Inorg. Chem.*, 1995, **34**, 2678.
19 G. M. Ehrlich, C. J. Warren, D. A. Vennos, D. M. Ho, R. C. Haushalter and F. J. DiSalvo, *Inorg. Chem.*, 1995, **34**, 4454.
20 D. Venkataraman, L. L. Rayburn, L. I. Hill, S. Jin, A.-S. Malik, K. J. Turneau and F. J. DiSalvo, *Inorg. Chem.*, 1999, **38**, 828.
21 S. Jin, R. Zhou, E. M. Scheuer, J. Adamchuk, L. L. Rayburn and F. J. DiSalvo, *Inorg. Chem.*, 2001, **40**, 2666.
22 L. Messerle, D. N. T. Hay, P. J. Schebler, V. Kolesnichenko and J. J. Luci, *Book of Abstracts, 219th ACS National Meeting*, San Francisco, CA, March 26–30, 2000, published by the ACS, Washington, DC, 2000, and by private communication.
23 V. Kolesnichenko and L. Messerle, *Inorg. Chem.*, 1998, **37**, 3660.
24 SAINT Plus, Software for the CCD Detector System, Bruker Analytical X-ray System, Madison, WI, 1999.
25 G. M. Sheldrick, the computer program SADABS is used by Siemens CCD diffractometers, Institute für Anorganische Chemie der Universität Göttingen, 1999.
26 G. M. Sheldrick, SHELXL, 5.10, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1999.
27 N. Prokopuk and D. F. Shriver, *Adv. Inorg. Chem.*, 1998, **46**, 1.
28 S. Jin, D. Venkataraman and F. J. DiSalvo, *Inorg. Chem.*, 2000, **39**, 2747.
29 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, 1960.
30 W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley, 1972.