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^{95}Mo NMR studies of five heterometallic trinuclear incomplete cubane-like clusters

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Abstract—^{95}Mo NMR data for five diamagnetic Mo^V compounds: three bimetallic trinuclear incomplete cubane-like clusters, a tetranuclear cubane-like cluster and their precursor, a $Mo_2S_4^{2+}$-containing compound having a d^1–d^1 configuration, are reported. The ^{95}Mo chemical shift was found to be correlated linearly with the average excitation energy, indicating that the shielding is dominated by the spectrochemical ΔE term of the local paramagnetic contribution. © 1997 Elsevier Science Ltd

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There is extensive interest in trinuclear, triangular metal clusters. Trimolybdenum and tritungsten clusters with the incomplete cubane-like core $[Mo_3S_4]^{4+}$ (M = Mo, W) have attracted special attention [1]. The $[Mo_3S_4]^{4+}$ ions have special stability and with three μ_2-S atoms they can react with many metals, such as Cu, Ag, Fe and Ni, to form cubane-like bimetallic clusters [2]. A series of such clusters has been synthesized in one of our laboratories (Fuzhou, China) over the last decade and the structures of many of them have been characterized by spectroscopic techniques and X-ray diffraction [3]. ^{95}Mo NMR is a useful technique for the study of such compounds. However, due to the usually low solubility and the short relaxation time, the observation of ^{95}Mo signals for bimetallic or bridged Mo compounds has been difficult and impossible for paramagnetic compounds Mo^V, Mo^{III} and Mo^I compounds. In this work, ^{95}Mo NMR data for a series of Mo^V compounds: three bimetallic trinuclear incomplete cubane-like clusters, a tetranuclear cubane-like cluster and their precursor, a $Mo_2S_4^{2+}$-containing compound, which are diamagnetic despite having a d^1 configuration, are reported.

1. EXPERIMENTAL

Materials and preparation

The compounds studied in this work are listed as follows: $[Et_4N]_2[Mo_2S_4(edt)_2]$ (**1**, where edt is ethane-1,2-dithiolato); $[Et_4N][Mo_2CuS_4(edt)_2(PPh_3)]$ (**2**); $[Et_4N][Mo_2AgS_4(edt)_2(PPh_3)]\cdot CH_2Cl_2$ (**3**), $[Et_4N]_2[Mo_2CuS_4(edt)_2(CN)]$ (**4**) and $[Mo_2Cu_2S_4(edt)_2(PPh_3)_2]$ (**5**).

The synthesis of **2**–**5** was made by unit construction methods with **1** as the building block [4]. The reaction scheme and the chemical diagram for each compound are shown in Fig. 1.

Compound **1** was synthesized according to the procedure of Pan *et al.* [5]. Compound **2** was prepared according to the procedures reported previously [6,7]. Compound **3** was synthesized according to the following procedure [8]: $[Et_4N]_2[Mo_2S_4(edt)_2]$ (0.385 g, 0.5 mmol) and $Ag(PPh_3)_3NO_3$ (0.048 g, 0.5 mmol) were dissolved in CH_2Cl_2 (40 cm^3). The resulting dark-red mixture was filtered. Dark crystals (0.26 g) were obtained from allowing Et_2O to diffuse slowly into the filtrate. All operations were carried out in a dinitrogen atmosphere.

The procedure for the preparation of **4**: 50 cm^3 of CH_3CN was added to the mixture of $[Et_4N]_2[Mo_2$

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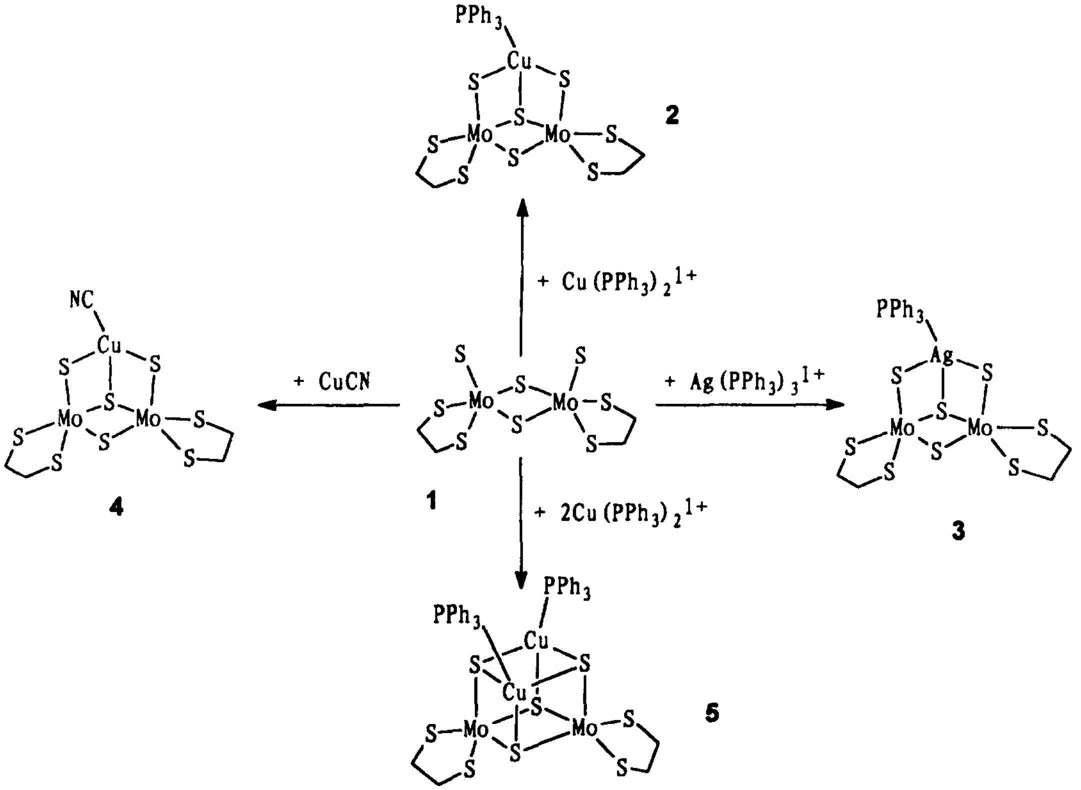

Fig. 1. The reaction scheme and the chemical diagrams for **2**–**5**.

$S_4(edt)_2]$ (0.385 g, 0.5 mmol) and CuCN (0.045 g, 0.5 mmol). The suspension was stirred for 24 h and then filtered. Dark-red crystals (0.14 g) were achieved by allowing Et_2O to diffuse slowly into the filtrate. All operations were carried out in a dinitrogen atmosphere.

The procedure for the preparation of **5** [9]: To a solution of $Cu(PPh_3)_3(dtp)$ [where dtp = $S_2P(OCH_2CH_3)_2^-$; 0.51 g, 0.66 mmol] in CH_2Cl_2 (10 cm^3) was added a solution of $[Et_4N]_2[Mo_2S_4(edt)_2]$ (0.255 g, 0.33 mmol) in CH_3CN (30 cm^3) in air. The resultant mixture was filtered. Dark-red crystals (0.18 g) were obtained by allowing the dark-red filtrate to stand in air for 1 day.

^{95}*Mo NMR spectroscopy*

All NMR work was carried out on a Bruker AMX-500 spectrometer, operating at 32.6 MHz for ^{95}Mo. A version of the anti-(acoustic) ringing pulse sequence [10] was used for the experiment. A broad-band 10 mm probe was used, with the pulse width at 14 μs, corresponding to $\sim 35°$ flip angle. Typically, a spectral width of 100 KHz and 2 K points were used, yielding a digital resolution of 50 Hz. The samples were made of saturated solution of the compounds in dimethylsulfoxide (DMSO)-d_6. The temperature of the sample was 50°C. All ^{95}Mo chemical shifts were referenced to external 2 M Na_2MoO_4 in D_2O at pH 11. 64 K scans were accumulated for **1** with a total accumulation time of ~ 35 min and 200–300 K scans for **2**–**5**, with accumulation times between 2 to 3 hours per spectrum.

2. RESULTS AND DISCUSSION

Mononuclear Mo^V complexes have a d^1 electron configuration and are paramagnetic. Therefore, they are not amenable to ^{95}Mo NMR studies. Most of the few Mo^V complexes studied to date by ^{95}Mo NMR are diamagnetic binuclear complexes with a Mo—Mo σ bond [11,12]. From the oxidation state dependence of ^{95}Mo chemical shifts, it can be interpolated an imputed value of ~ 1185 ppm as the "center" of the range of chemical shifts for Mo^V [13]. The ^{95}Mo chemical shift range determined for the present series of compounds, 1465–2002 ppm (Table 1), is thus on the low-field side in this expected Mo^V range of chemical shifts. The presence of five sulphur ligands is expected to shift δ substantially downfield. For example, the $\delta(^{95}Mo)$ generally found in MoS_4 units for (Mo^{VI})) is in the 2000 ppm range (~ 2200 ppm for MoS_4^{2-}) [14,15].

It is usually assumed that the shielding for the nuclei of heavy atoms, such as Mo, is dominated by the paramagnetic term of the Ramsey equation [11,16]. As shown in Fig. 2, a trend between the ^{95}Mo chemical shifts of this series of compounds and the longest

Table 1. ^{95}Mo NMR parameters and λ_{max} in the visible spectrum for compounds **1–5**

Compound	$\delta(^{95}Mo)$ (ppm)[a]	$\Delta\nu$ (Hz)[b]	λ_{max}/nm
1	1465 ± 3	1300	445
2	1800 ± 5	2100	482
3	1656 ± 5	1600	460
4	1924 ± 10	> 3000[c]	485
5	2002 ± 10	> 3000[c]	510

[a] Referenced from 2 M Na_2MoO_4 in D_2O at pH 11.

[b] Full width at half-height.

[c] The linewidth cannot be measured precisely because the line is too broad.

wavelength of the electronic absorption of these compounds in the visible range was observed (the correlation coefficient for the linear regression is 0.95). Thus, it confirms that the spectrochemical ΔE term of the local paramagnetic contribution to the Mo shielding is dominant. Within this series of structurally similar compounds, the average excitation energy [17,18], as approximated by the energy of the lowest excitation, is the major factor that determines the ^{95}Mo chemical shift. Good correlations between ^{95}Mo chemical shifts and the average excitation energy have been found in some Mo complexes, e.g. in the $[MO_{4-n}S_n]^{2-}$ (M = Mo, W ; n = 0–4) series [19] and in the $Mo(CO)_4LL'$ compounds [20]. Similarly, Casewit *et al.* also demonstrated that the variation of the ^{95}Mo chemical shift correlated well with the electronic spectra in a series of sulphur-bridged cyclopentadienyl molybdenum compounds [21]. On the other hand, some other series of compounds, such as the six-coordinate complexes containing the *cis*-$\{Mo(NO)_2\}^{2+}$ unit [22], showed small variations in ΔE that are not correlated with changes in the ^{95}Mo chemical shift. Instead, the nephelauxetic effect [18], i.e. the changes in the $\langle r^{-3}\rangle_{np}$ and $\langle r^{-3}\rangle_{nd}$, was found to be the main contribution to the variation in the chemical shift. The normal halogen dependence of $\delta(Mo^{95})$, i.e. the shielding of ^{95}Mo follows the $I^- > Br^- > Cl^-$ order, is a result of the dominance of the nephelauxetic effect in the paramagnetic shielding term, as illustrated in the $[Mo(CO)_5X^-]$ series, where X is a halide or a pseudohalide [23]. The patterns of influence of the spectrochemical and nephelauxetic effects on ^{95}Mo chemical shifts have been discussed previously for many ligands and for different oxidation states of Mo [11,24]. Not much was mentioned for Mo^V, however.

The ^{95}Mo chemical of **3** is found to be ~150 ppm up field of that of **2**. The relative shift for these two compounds is opposite to that observed for the compounds $[Prn_4N]_2[CNMS_2MoS_2]$ (M = Cu, Ag) [14], where a replacement of Cu with Ag causes the ^{95}Mo chemical shift to move downfield by ~60 ppm. However, in both cases, the changes in the ^{95}Mo shifts are correlated with the changes in the λ_{max} in the visible spectrum of the respective compounds.

The linewidths of the ^{95}Mo signals for these compounds (Table 1) are very large and increase rapidly with the size of the molecules. The linewidth increases from about 1300 Hz for **1** to over 3 KHz for **3** and **5**, which is quite close to the limit of detection using a high resolution or liquid state NMR spectrometer. The linewidths of **3** and **5** are close to the largest linewidths reported in the literature to date (about 5 KHz) [25]. The extreme linewidth of any ^{95}Mo signal that may be present in these type of bimetallic com-

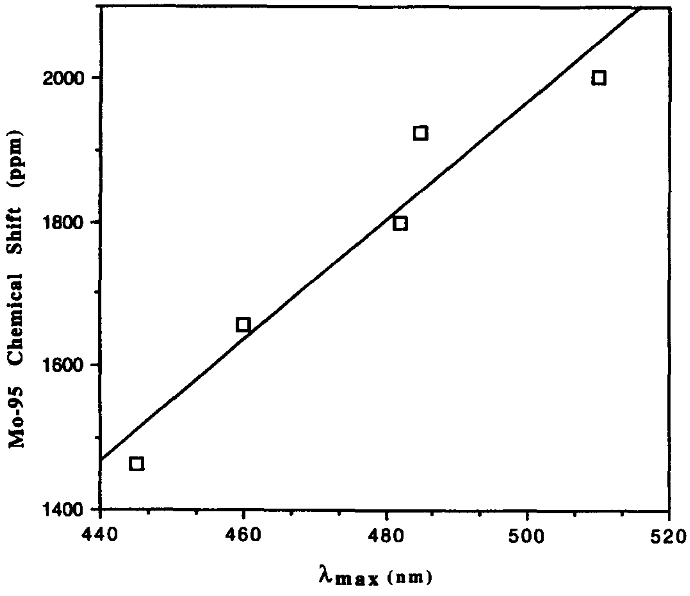

Fig. 2. Plot of $\delta(^{95}Mo)$ in ppm *vs* the wavelength (λ_{max}) in nm for compounds 1–5. The correlation coefficient of the linear fit is 0.95.

plexes is probably the reason why signals of some dinuclear Mo^V bridged compounds (such as imido compounds) remain undetectable [26]. The large linewidths are partly due to the lack of cubic symmetry (and thus large electric field gradient) at the sites of the five-coordinate Mo atoms. The high viscosity of the solvent (DMSO) used in this study probably contributes adversely to the linewidth problems. An increase in the relaxation of Mo may also have been caused by a rapidly relaxing neighbouring quadrupolar nucleus (or nuclei) [27], such as ^{63,65}Cu, in **2**, **4** and **5**. This may explain why the linewidth of the Ag-containing compound **3**, where Ag is a spin 1/2 nucleus and thus without a quadrupole moment, was found to have a narrower linewidth (1600 Hz) than that of the structurally similar Cu-containing compound **2** (2100 Hz). The same linewidth difference has been observed in other Ag- and Cu-containing Mo clusters [14].

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