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APPLICATIONS OF ^{95}Mo NMR TO INORGANIC AND BIOINORGANIC CHEMISTRY

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Abstract—A variety of dinuclear Mo(V), Mo(IV), Mo(III) and Mo(I) complexes, and tri- and tetranuclear homo- and heterometallic complexes of molybdenum have been studied by ^{95}Mo NMR. The Mo(V) complexes, $Cp'_2Mo_2Y_2(\mu\text{-}X)_2$ (Y = O or S, X = S or Se, Cp′ = η^5-C_5Me_5), exhibit resonances in the −93 to 478 ppm region, the chemical shifts being sensitive to changes in the oxygen, sulfur and selenium content of the coordination spheres. The Mo(IV) complexes, $Cp'_2Mo_2(\mu\text{-}X)_2(\mu\text{-}X_2)$ (X = S or Se), and their derivatives exhibit resonances in the 382–790 ppm region: isomers of $Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ which differ in the arrangement of the bridging ligands were also detected. Dinuclear Mo(III) complexes of the form Mo_2L_6 (L = amido, alkoxy or alkyl ligand) exhibit very deshielded resonances (2430–3624 ppm). The complexes $Cp_2Mo_2\{\mu\text{-}S_2C_2(CF_3)_2\}_2$ and $Cp_2Mo_2(CO)_2\{\mu\text{-}S_2C_2(CF_3)_2\}_2$ (Cp = η^5-C_5H_5) exhibit resonances consistent with their formulation as distinct Mo(III) and mixed-valence Mo(IV–II) complexes, respectively. The Mo(I) complexes exhibit resonances which are very sensitive to the bond order of the Mo–Mo bond: the resonances of the $L_2Mo_2(CO)_6$ complexes (L = Cp, −1856 ppm; L = Cp′, −1701 ppm) are more than 1800 ppm more shielded than the triply metal–metal bonded complexes, $L_2Mo_2(CO)_4$ (L = Cp, 182 ppm; L = Cp′, 133 ppm). The molybdenum containing homo- and heterometallic complexes exhibit resonances in the −133 to −1619 ppm region. The Fe_2Mo_2 cubane complex, $Cp'_2Mo_2Fe_2(\mu_3\text{-}S)_4(CO)_4$, exhibits a resonance at −506 ppm. The ease of observation of the sulfurized complexes suggests that ^{95}Mo NMR may be a valuable technique for the study of hydrodesulfurization processes.

In recent years the characterization of coordination and organometallic complexes of molybdenum by ^{95}Mo NMR spectroscopy has developed rapidly. In general, the measurement of the spectra of Mo(VI), Mo(II) and Mo(0) complexes has become routine, and the chemical-shift ranges and halogen dependencies of such complexes are well-defined.[1] For these oxidation states the ability of ^{95}Mo NMR to monitor solution processes,[2,3] to distinguish diastereomers[4–6] and to aid solid–solution structure correlations[7] has also been demonstrated.

In contrast, the study of Mo(V), Mo(IV), Mo(III) and Mo(I) complexes has been limited or nonexistent. ^{95}Mo NMR investigations of Mo(V),

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Mo(III) and Mo(I) complexes are restricted to spin-paired $(Mo_2)_n$ species possessing the diamagnetism necessary for NMR observation. Mo(V) complexes possessing *syn*- and *anti*-$[Mo_2O_2(\mu\text{-}X)_2]^{2+}$ (X = O or S) structural cores exhibit resonances in the 320–982-ppm region,[3,8] the chemical shifts being sensitive to changes in the stereochemistry of the core, e.g. *syn*- and *anti*-$[Mo_2O_4L_2]^{2+}$ (L = 1,4,7-triazacyclononane) exhibit resonances at 586 and 342 ppm, respectively.[3] Dinuclear Mo(IV) complexes have not been studied by ^{95}Mo NMR, although an extensive study of complexes possessing the $[Mo_3O_4]^{4+}$ core has been reported.[8,9] Our recent investigation of mononuclear oxo-Mo(IV) complexes by ^{95}Mo NMR[10] has established an enormous range of chemical shifts (3180 to -1309[11] ppm)* and linewidths (80[11] to >5000 Hz) for mononuclear Mo(IV) complexes. To date, complexes of Mo(III) have not been studied by ^{95}Mo NMR, and only one Mo(I) complex, $Cp_2Mo_2(CO)_6$[12] (hereafter, Cp = η^5-C_5H_5, Cp′ = η^5-C_5Me_5), has been investigated by this technique.

Here we report the ^{95}Mo NMR spectra of 22 dinuclear metal–metal bonded complexes of Mo(V), Mo(IV), Mo(III) and Mo(I). This work describes the first ^{95}Mo NMR data for dinuclear complexes of Mo(IV) and Mo(III) and expands upon the single previous result[12] for Mo(I). In addition, preliminary studies on several homo- and heterometallic molybdenum cluster compounds are presented. The compounds investigated are relevant to studies involving hydrodesulfurization and bioinorganic catalysis.

EXPERIMENTAL

Sample preparation

The complexes were prepared by literature methods or slight modifications thereof: a guide to the source of each complex is given in Table 1. Solutions of air-sensitive samples were prepared under anaerobic conditions using dried and deoxygenated solvents. Concentrations in the range 3–100 mM were employed.

Instrumentation

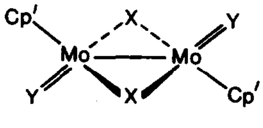
The ^{95}Mo NMR spectra were recorded on a Bruker WM250 spectrometer equipped with a 10-mm molybdenum probe and operating at 16.3 MHz. To reduce the effects of probe ringing[1] a Doty Scientific duplexer and pre-amplifier with a 16 MHz center was inserted between the probe and the Bruker broadband pre-amplifier. The duplexer was gated off during the pulse and for 5 μs thereafter. With this arrangement the pre-acquisition delay was reduced to 100 μs. The transmitter output was amplified with a Heathkit SB-201 (1-kW) linear amplifier. The input was attenuated to give a 26-μs 90° pulse. A 2 M $Na_2[MoO_4]$ solution in D_2O, effective pH 11, was used as external reference.

RESULTS AND DISCUSSION

The ^{95}Mo NMR data are summarized in Table 1, along with a guide to the structure and source of each complex. Structural formulae for the complexes are given in the appropriate sections.

Mo(V) complexes

Singly metal–metal bonded dinuclear Mo(V) complexes possessing the *anti*-$[Mo_2Y_2(\mu\text{-}X)_2]^{2+}$ core[13,14] exhibit resonances in the -93 to 478 ppm region. With the exception of $Cp'_2Mo_2S_2(\mu\text{-}S)_2$ (**2**),[14] these complexes are more shielded than previously studied dinuclear Mo(V) analogues.[3,8] The oxo complex, $Cp'_2Mo_2O_2(\mu\text{-}S)_2$ (**1**),[14] exhibits the most shielded resonance of the series at -93 ppm. Considerable deshielding of the ^{95}Mo nuclei occurs upon replacement of the Mo═O$_t$ (t = terminal) groups of **1** by Mo═S$_t$: the resonance of **2** (478 ppm) is deshielded by 571 ppm compared to the oxo complex **1**. The deshielding influence of the Mo═S$_t$ group has been previously observed in complexes such as $[MoX_4]^{2-}$ [15] and $MoX_2(R_2NO)_2^2$ (X = O or S): for these types of complexes, conversion of each Mo═O$_t$ group to Mo═S$_t$ results in a deshielding of *ca* 500 and 700 ppm, respectively. Similarly, a deshielding of *ca* 320 ppm results upon successive replacement of Mo═S$_t$ groups by Mo═Se$_t$ groups.[2,15(b)] However, comparison of **1** and $Cp'_2Mo_2O_2(\mu\text{-}Se)_2$ (**3**) reveals that replacement of the μ-S ligands by μ-Se ligands deshields the ^{95}Mo nuclei by only *ca* 230 ppm. A reduced deshielding effect of 203 ppm has also been observed upon replacement of the μ-O ligands of $[Mo_2O_4(\text{L-cysteinate})_2]^{2-}$ by μ-S ligands.[8] These trends show that the substitution of bridging vs terminal atoms can be readily distinguished by ^{95}Mo NMR.



X=S, Y=O (**1**)
X=S, Y=S (**2**)
X=Se, Y=O (**3**)

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* The values given in Ref. 11 are for $[Mo(CN)_8]^{4-}$.

Table 1. ^{95}Mo NMR data[a]

Complex	Chemical shift (ppm)	Linewidth (Hz)	Reference (synthesis)
Mo(V)			
$Cp'_2Mo_2O_2(\mu\text{-}S)_2$ (1)	−93	90	14
$Cp'_2Mo_2S_2(\mu\text{-}S)_2$ (2)	478	260	14
$Cp'_2Mo_2O_2(\mu\text{-}Se)_2$ (3)	131	90	17
Mo(IV)			
$Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (4)	440	110	16
$Cp'_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}Se_2)$ (5)	770	110	17
$Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ (6)	714, 728	40, 50 (2:1)	18
$Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SMe)_2$ (7)	790	70	20
$[Cp'_2Mo_2(\mu\text{-}S)(\mu\text{-}SMe)(\mu\text{-}S_2)]I$ (8)	382	110	18
$Cp'_2Mo_2S_2(\mu\text{-}S_2)$ (9)	756	20	16
$Cp'_2Mo_2OS(\mu\text{-}S_2)$ (10)	−54, 699	100, 100	16
Mo(III)[b]			
$Mo_2(NMe_2)_6$ (11)	2430	1320	21
$Mo_2(OCHMe_2)_6$ (12)	2444	350	22
$Mo_2(OCH_2CMe_3)_6$ (13)	2447	600	22
$Mo_2(OCMe_3)_6$ (14)	2645	120	22
$Mo_2(CH_2SiMe_3)_6$ (15)	3624	500	23
$Cp_2Mo_2\{\mu\text{-}S_2C_2(CF_3)_2\}_2$ (16)	2301	37	25
$Cp_2Mo_2(CO)_2\{\mu\text{-}S_2C_2(CF_3)_2\}_2$ (17)	−789	190	25
Mo(I)			
$Cp_2Mo_2(CO)_6$ (18)	−1856	180	28, 29
$Cp'_2Mo_2(CO)_6$ (19)	−1701	180	29
$Cp_2Mo_2(CO)_4$ (20)	182	160	28
$Cp'_2Mo_2(CO)_4$ (21)	133	150	31
$Cp'_2Mo_2(CO)_3\{P(OMe)_3\}$ (22)[c]	d 373, $J = 416$ Hz	150	32
	s 154	150	
"Cubanes"			
$Cp'_2Mo_4(\mu_3\text{-}S)_4(CO)_6$ (23)	−558, −1256	15, 74	33
$Cp'_2Mo_2Cr_2(\mu_3\text{-}S)_3(\mu_3\text{-}O)(CO)_6$ (24)	−265, −471	20, 20	20
$Cp_2Cp'_2Mo_4(\mu_3\text{-}S)_4$ (25)	−1444, −1619	64, 230	34
$Cp'_2Mo_2Fe_2(\mu_3\text{-}S)_4(CO)_4$ (26)	−506	25	33
$Cp'_2Mo_2(\mu_2\text{-}S_2CO)(\mu_3\text{-}S)_2Fe(CO)_2$ (27)	−133	70	33

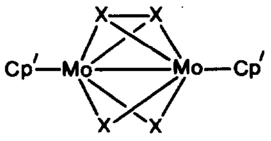
[a] At ambient temperature in CH_2Cl_2 solvent unless otherwise specified.

[b] All Mo(III) complexes, except 16 and 17, were studied in toluene.

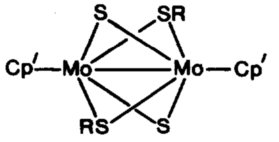
[c] d = doublet, s = singlet.

Mo(IV) complexes

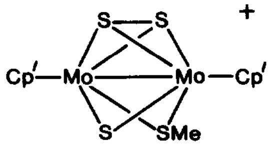
The $Cp'_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ complex (4)[16] exhibits a resonance at 440 ppm whereas the selenium analogue, $Cp'_2Mo_2(\mu\text{-}Se)_2(\mu\text{-}Se_2)$ (5),[17] exhibits a relatively deshielded resonance at 770 ppm. The 330-ppm deshielding observed upon complete replacement of μ-S ligands by μ-Se ligands is also small compared to that expected for the exchange of a similar number and type of terminal ligands (cf. 1 and 3). Hydrogenation of **4** results in an isomeric mixture of **6**,[18] which exhibits two resonances at 714 and 728 ppm. This is consistent with the previous detection, by ^{1}H NMR, of two isomers in the analogous



X=S (**4**) or Se (**5**)



R=H (**6**) or Me (**7**)



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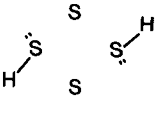
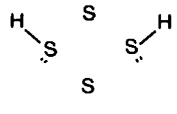
$(MeCp)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}SH)_2$ complex.[19] For the *trans* isomer[19] two arrangements of the bridging SH ligands are possible (*anti* and *syn* below). The bis-μ-



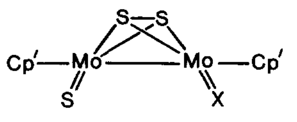
anti



syn

methylthiolate complex (**7**), having a chemical shift of 790 ppm, has been crystallographically characterized as the *anti* isomer.[20] The reaction of **4** with methyl iodide results in the methylation of one μ-S group:[18] the resulting cationic complex, **8**, exhibits a slightly shielded resonance at 382 ppm. The chemical shifts of **6** and **7** reflect the opening of the μ-S_2^{2-} ligand to form two deshielding μ-S^{2-} ligands.

Complex **4** is converted, at 45°C in toluene, to $Cp'_2Mo_2S_2(\mu\text{-}S_2)$ (**9**):[16] the transformation of the

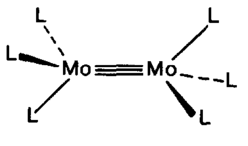


X=S (**9**) or O (**10**)

two μ-S^{2-} ligands into two terminal S^{2-} ligands leads to a deshielding of the ^{95}Mo nuclei and the observation of a resonance at 756 ppm for **9**. A by-product of this reaction, the unsymmetrical complex $Cp'_2Mo_2OS(\mu\text{-}S_2)$ (**10**),[16] provides a nice example of the deshielding influence of the Mo$=$S$_t$ group relative to Mo$=$O$_t$. For **10**, the two resonances at -54 and 699 ppm may be readily assigned to the Mo$=$O$_t$ and Mo$=$S$_t$ centers, respectively. The 753-ppm shielding difference observed here is similar in magnitude to that observed elsewhere.[2]

Mo(III) complexes

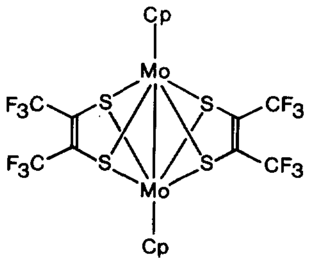
A wide variety of diamagnetic Mo(III) dimers having general formulae Mo_2L_6 ($L = NR_2^-, OR^-$ or R^-) have been reported by Chisholm[21,22] and Wilkinson:[23] we have initiated a study of these complexes, their derivatives and their tungsten analogues. The complexes Mo_2L_6 [$L = NMe_2^-$ (**11**), $OCHMe_2^-$(**12**), $OCH_2CMe_3^-$ (**13**), $OCMe_3^-$ (**14**) or $CH_2SiMe_3^-$ (**15**)] exhibit resonances over the chemical-shift range 2430–3624 ppm, a very deshielded portion of the known chemical-shift



L=NMe_2^- (**11**), $OCHMe_2^-$ (**12**), $OCH_2CMe_3^-$ (**13**), $OCMe_3^-$ (**14**) and $CH_2SiMe_3^-$ (**15**)

range.[1] Only one other class of metal–metal-bonded complex, quadruply bonded Mo(II) dimers, possesses more deshielded resonances (3227–4148 ppm).[1] The shielding of the ^{95}Mo nuclei increases in the order alkyl < 3°-alkoxide < 1°- and 2°-alkoxide < dialkylamide. The *N*- and *O*-donor ligand complexes exhibit a narrow range of chemical shifts while the chemical shift of the silyl derivative **15**[23] is quite disparate.* Accounting for such observations will provide a critical test for developing theoretical treatments of ^{95}Mo chemical-shift data. The linewidths of the Mo(III) resonances range from 120 to 1320 Hz, contrasting with the generally broad resonances of Mo(II) dimers.[1]

The μ-dithiolene complexes **16** and **17** exhibit readily observable resonances. The singly metal–metal bonded **16** [Mo—Mo = 2.584(1) Å[25]] exhibits a deshielded resonance at 2301 ppm ($W_{1/2} = 37$ Hz). The relatively shielded position compared to the triply metal–metal bonded M_2L_6 complexes is consistent with a similar trend found in the Mo(I)



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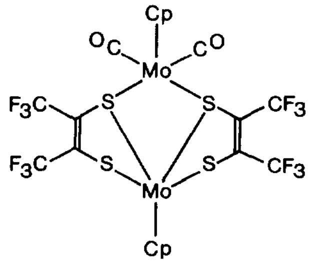

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* The similarly disparate ^{183}W NMR chemical shifts of $W(CXMe_3)(CH_2XMe_3)_3$ (X = C, 2867 ppm; X = Si, 3613 ppm) support a general deshielding influence for β-Si substitution.[24]

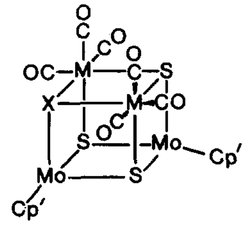
complexes below. A structure determination of **17** revealed two distinctly different molybdenum environments and a Mo...Mo interatomic distance of 3.256(1) Å,[25] indicative of a localized Class I mixed-valence complex in the Robin and Day classification.[26] The ^{95}Mo NMR spectrum of **17** is consistent with this formulation as only one peak at −789 ppm is observed. This peak is likely to be due to the CpMo(II)(CO)$_2$ moiety, while that due to the Mo(IV) fragment remains unobserved due to its rapid relaxation time.[10] Supporting this contention, the complexes

$$\mathrm{CpMo(CO)_2(S_2CNEt_2),\ CpMo(CO)_2(S_2COEt)}$$

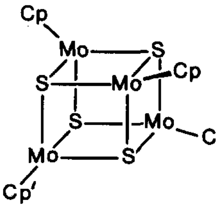
and

$$\mathrm{CpMo(CO)_2\{C(CF_3){=}C(CF_3)C(O)SMe\}}$$

resonate at −544, −559 and −845 ppm, respectively.[27]



M=Mo, X=S (**23**)
M=Cr, X=O (**24**)



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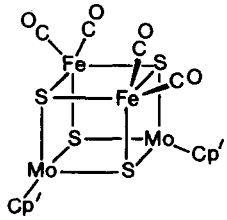

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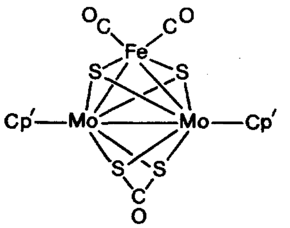

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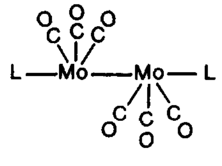
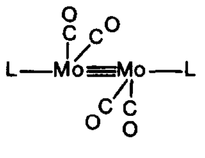
Mo(I) complexes

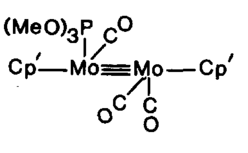
To date, the ^{95}Mo NMR spectrum of only one Mo(I) complex has been reported: the metal–metal singly bonded species Cp$_2$Mo$_2$(CO)$_6$ (**18**) exhibits a relatively shielded resonance at −1856 ppm.[12] In a similar spectral region, we have observed the resonance of Cp′$_2$Mo$_2$(CO)$_6$ (**19**)[29] at −1701 ppm. Remarkably, the metal–metal triply bonded complexes, **20** and **21**, exhibit resonances which are deshielded by over 1800 ppm compared to **18** and **19**: the tetracarbonyl complexes, **20**[28] and **21**,[30,31] exhibit resonances at 182 and 133 ppm, respectively. We have also studied the unsymmetrical triply bonded complex **22**,[32] which exhibits two resonances, a doublet ($J_{\mathrm{Mo-P}}$ = 412 Hz) at 373 ppm and a singlet at 154 ppm. The J value is *ca* 120 Hz higher than any previously observed value:[1] coupling of the ^{31}P nucleus to both Mo nuclei was not discerned.



L=Cp (**18**) or Cp′ (**19**)



L=Cp (**20**) or Cp′ (**21**)



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Homo- and heterometallic cubanes and related complexes

We have recently undertaken an NMR investigation of new homo- and heterometallic complexes of molybdenum and catalytically or biologically relevant co-metals such as cobalt, nickel (hydrodesulfurization) and iron (nitrogenase). Complexes **23**–**27** exhibit narrow, readily observable ^{95}Mo NMR resonances in the shielded portion of the chemical-shift range. Complexes **23**–**25** possess two environments for molybdenum and each exhibits two resonances of equal intensity: these have been assigned as described below. The shielded resonances of other carbonylmolybdenum(0) complexes[1] permits the assignment of the −1256 ppm resonance of **23**[33] to the Mo(CO)$_3$ moieties of this complex. The resonance at −558 ppm is therefore due to the Cp′Mo moieties. The μ_3-O ligand in **24**[20] is expected to shield the Mo center to which it is bound (relative to μ_3-S) and thus the −265 and −471 ppm resonances of this complex are assigned to μ_3-S-Mo and μ_3-O-Mo centers, respectively (compare **9** and **10**). The presence of a *ca* −500 ppm resonance attributable to μ_3-S-coordinated Mo in complexes **23** and **26** raises the possibility that the −471-ppm resonance of **24** is due to the μ_3-S-coordinated Mo center. This latter assignment is contrary to all previously observed shielding trends for Mo$=$X$_t$ and μ-X (X = O or S) ligand complexes[2,8,15] and, therefore, seems unlikely. Definitive assignment of the resonances of **24** awaits data for complexes such as Cp′$_2$Mo$_2$Cr$_2$(μ_3-X)$_4$(CO)$_6$ (X = O or S). A shielding effect of Cp relative to Cp′ is observed in resonances in the shielded portion of the chemical shift range (e.g. **18** and **19**) and on this basis the resonances of **25**[34] at −1444 and −1619 ppm are ascribed to Cp′- and Cp-bearing Mo atoms, respectively.

The paramagnetism of most Fe–Mo–S cubane and double-cubane cluster complexes has prevented their study by ^{95}Mo NMR. The diamagnetism of Fe–Mo–S clusters derived from **4** and $Fe_2(CO)_9$ make them attractive candidates for assessing the NMR properties of more biologically pertinent centers. Complex **26**[33] exhibits a single sharp resonance at −506 ppm, 946 ppm more shielded than the precursor **4**. The data for **26** provide evidence that μ_3-S ligands shield the molybdenum nuclei compared to μ-S and S_t ligands. The resonance of **27**[33] at −133 ppm is also shielded due to conversion of the μ-S ligands into μ_3-S ligands.

CONCLUSION

The ability of terminal X^{2-} (X = O or S) ligands to effect predictable changes in the chemical shifts of ^{95}Mo NMR resonances has been confirmed in this study. Moreover, new deshielding trends may be discerned from the data presented herein, e.g. the deshielding ability of bridging ligands involved in this study increase in the order μ-S_2^{2-} < μ-SH < μ-SMe < μ-S < μ-Se and μ_3-O < μ_3-S.

There also appears to be a deshielding effect upon increasing the bond order of the metal–metal bond. While changes in the coordination sphere accompany such reactions, the concomitant change in chemical shift is often not accounted for by these changes alone. The most dramatic example of this effect involves the pairs **18**–**20** and **19**–**21** where singly and triply bonded species differ in chemical shift by over 1800 ppm.

The ready detection and differentiation of sulfidomolybdenum complexes by ^{95}Mo NMR provides encouragement for the application of this technique to the study of hydrodesulfurization catalysis. The hydrodesulfurization reaction is an important catalytic process for the purification of petroleum products.[35] The reaction, exemplified by the equation below, involves the

$$RSH + H_2 \rightarrow RH + H_2S$$

hydrogenolysis of organosulfur compounds, and is most often effected by heterogeneous catalysts containing sulfided Mo and Co species supported on alumina. Both metal and sulfide ions have been proposed as active sites in the hydrodesulfurization reaction: the ability of sulfide ligands to react with hydrogen and other small molecules is exemplified by complexes such as **6**–**8** and **26** and **27**. Species such as **6**–**8** are important model complexes for reactivity and mechanistic studies of hydrodesulfurization.[19] Due to their narrow linewidths, the resonances of these species are readily detected even at concentrations of ^{95}Mo as low as 0.5 mM. Thus ^{95}Mo NMR may prove valuable in the characterization of solution species and intermediates, and for monitoring the course of homogeneous hydrodesulfurization systems.

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