Supplementary Material (ESI) for Chemical Communications

Metallodithiolato Ligands as Bridges in Multiply Bonded Dimolybdenum Complexes

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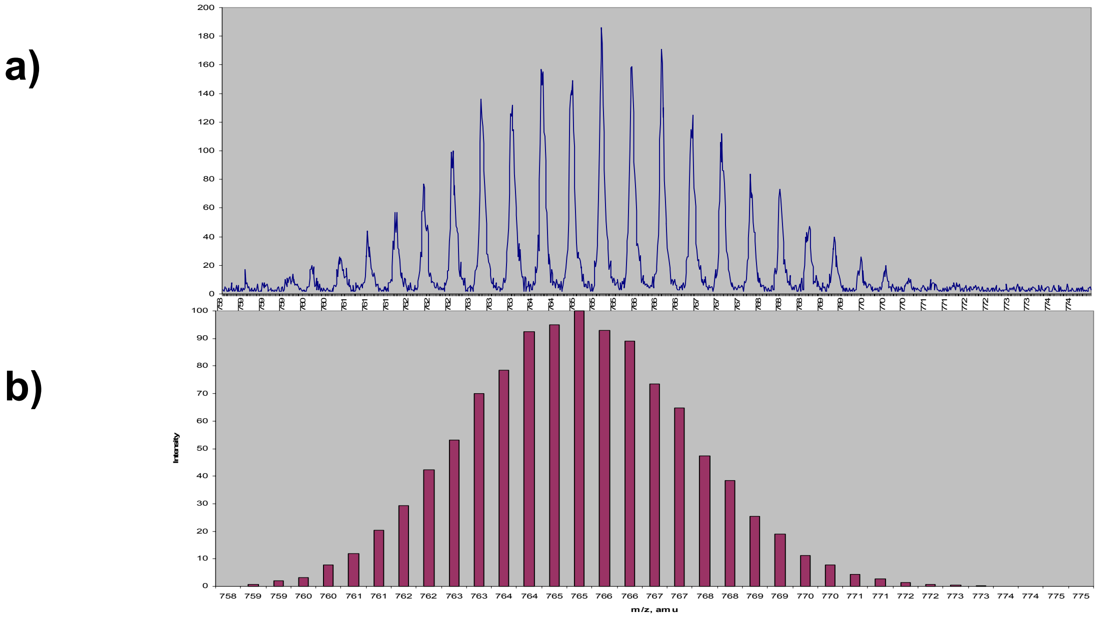
Preparation of $[\mathrm{Mo_2}(\mathbf{Ni\text{-}1})_4][\mathrm{BF_4}]_4\cdot 6\mathrm{MeCN}$ (1)

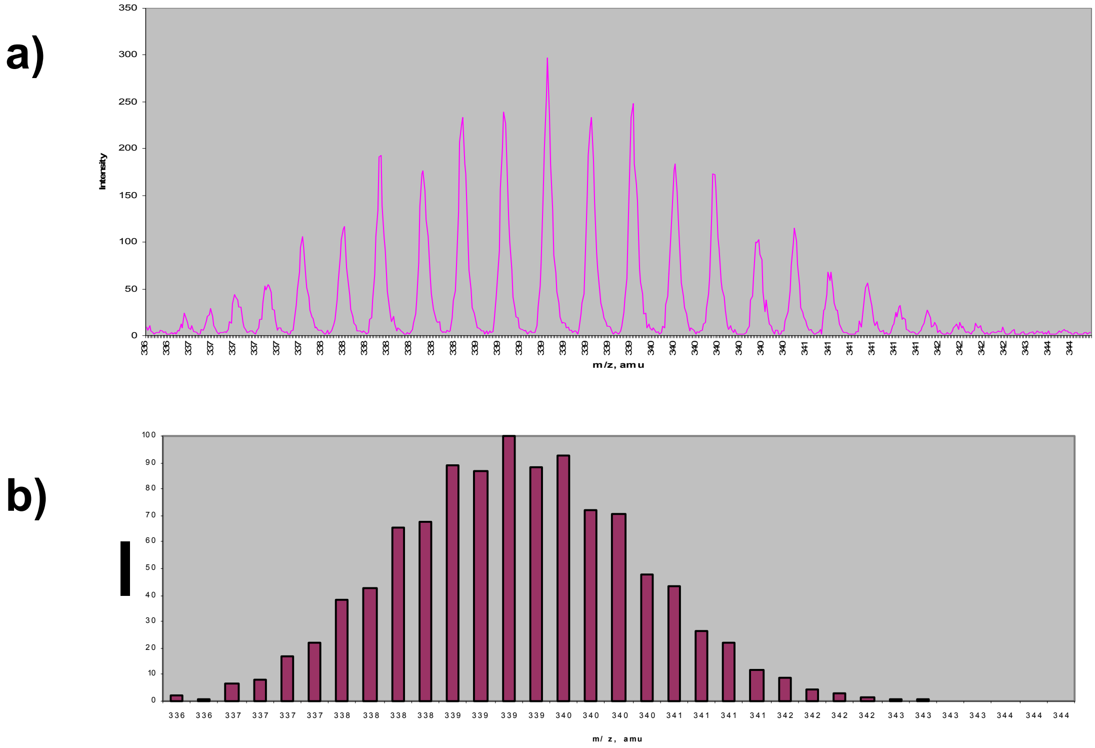
To a Schlenk flask containing 15 mL of MeCN, $[\mathrm{Mo_2(MeCN)_{10}}][\mathrm{BF_4}]_4$ (0.10 g, 1.0 mmol) and **Ni-1** (0.1160 g, 3.9 mmol) were added. The solution immediately turned dark red brown. The solution was stirred for 2.5 h at ambient temperature. The solution was then transferred to a test tube and layered with $\mathrm{Et_2O}$. Reddish-brown crystals formed in approximately one week, giving 45.1% yield (0.080 g). UV-Vis: λ_{max}: MeCN, nm (ε) = 226 (11248), 272 (10691), 316 (4067), 440 (852), 530 (497). Anal. Calcd (Found) for $\mathrm{C_{52}H_{98}B_4F_{16}Mo_2N_{14}Ni_4S_8}$: C, 28.2 (28.4); H, 4.73 (4.74) ; N, 6.58 (6.87). ESI-MS (MeCN, *m/z*) $\{(\mathbf{Ni\text{-}1})_2\mathrm{Ni}^{2+}\}$ 320 (100), $\{\mathrm{N_2S_2H})^+\}$ 233 (64.6), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1})_4]^{4+}\}$ 339 (7.68), $\{[(\mathbf{Ni\text{-}1})_2\mathrm{Ni}]^{2+}\}$ 727 (4.65), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1})_4](\mathrm{BF_4})_2{}^{2+}\}$ 765 (4.81),

$[\mathrm{Mo_2}(\mathbf{Ni\text{-}1'})_4][\mathrm{BF_4}]_4\cdot 4\mathrm{MeCN}$ (2)

In an identical manner, the **Ni-1'** derivative was isolated in 73.3% yield (0.142 g) UV-Vis: λ_{max}: MeCN, nm (ε) = 226 (10252), 270 (7485), 306 (4322), 408 (1156), 536 (523). Anal. Calcd (Found) for $\mathrm{C_{44}H_{84}B_4F_{16}Mo_2N_{12}Ni_4S_8}$: C, 25.8 (25.4); H, 4.32 (4.77); N, 6.87 (6.16). ESI-MS (MeCN, *m/z*) $\{[\mathbf{Ni\text{-}1'}]^+\}$ 276 (100), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1'})_2(\mathrm{MeCN})_{3.5}](\mathrm{BF_4})_2{}^{2+}\}$ 531 (50.8), $\{[(\mathbf{Ni\text{-}1'})_2\mathrm{Ni}]^{2+}\}$ 306 (40.5), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1'})_4]^{4+}\}$ 325 (23.8), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1'})_2(\mathrm{MeCN})_3](\mathrm{BF_4})_2{}^{2+}\}$ 520 (11.8), $\{[\mathrm{Mo_2}(\mathbf{Ni\text{-}1'})_4](\mathrm{BF_4})_2{}^{2+}\}$ 737 (8.67).



Electron spray ionization mass spectrum of $\{[Mo_2(\mathbf{Ni\text{-}1})_4][BF_4]_2\}^{2+}$ a) experimental observation b) simulation of isotopic envelope.



Electron spray ionization mass spectrum of $\{[Mo_2(\mathbf{Ni\text{-}1})_4]\}^{4+}$ a) experimental observation b) simulation of isotopic envelope.

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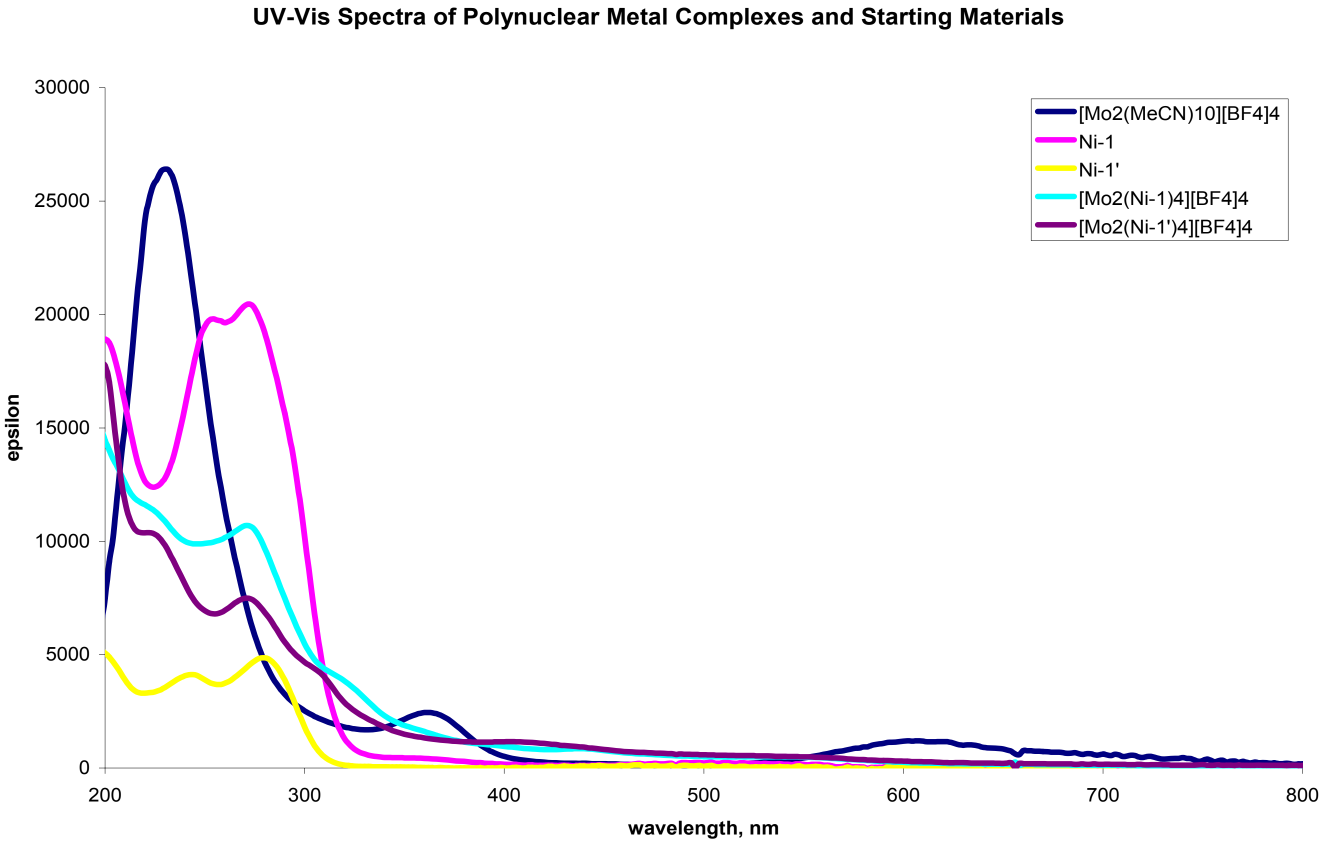


UV-Vis Spectrum of 10^{-4} M MeCN solutions of $[Mo_2(MeCN)_{10}][BF_4]_4$, **Ni-1**, **Ni-1'**, $[Mo_2($**Ni-1**$)_4][BF_4]_4$, and $[Mo_2($**Ni-1'**$)_4][BF_4]_4$.

	1·6MeCN	**2**·4MeCN
formula	$C_{52}H_{98}B_4F_{16}Mo_2N_{14}Ni_4S_8$	$C_{44}H_{84}B_4F_{16}Mo_2N_{12}Ni_4S_8$
formula weight	1949.88	1811.67
temperature (°C)	-163.15	-163.15
wavelength (Å)	0.71073	0.71073
Z	2	2
D_{calcd} (g/cm^3)	1.751	1.773
μ (cm^{-1})	1.64	1.779
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell		
a (Å)	11.319 (5)	12.693 (4)
b (Å)	23.770 (10)	20.039 (5)
c (Å)	13.822 (6)	14.166 (4)
b (°)	96.057 (8)	109.659 (4)
volume (Å^3)	3698 (3)	3393.3 (16)
GOF	1.048	1.055
R_1[b], wR_2[c](%) [$I > 2\sigma(I)$]	7.69, 16.45	6.18, 15.59
R_1[b], wR_2[c](%) all data	11.83, 18.46	5.84, 15.15

[a] Obtained using graphite-monochromatized Mo Kα radiation (l = 0.71073 Å) at 110K.

[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$.

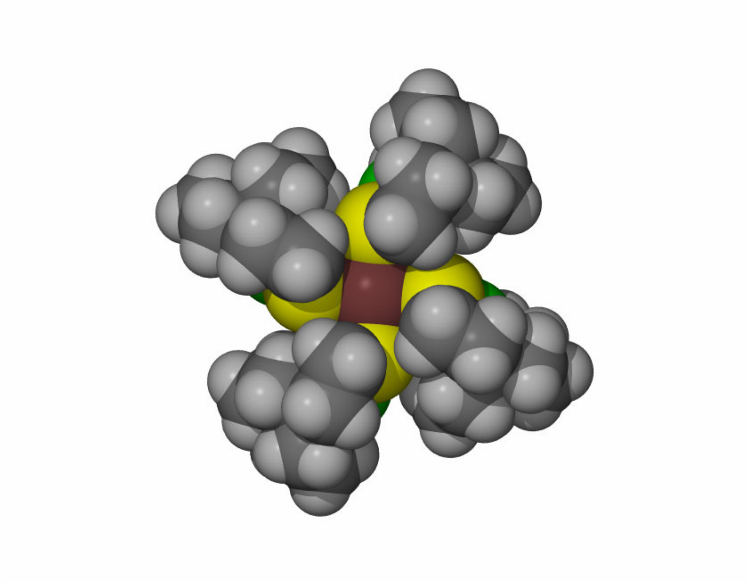
[c] $wR_2 = [\Sigma[\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$.

X-ray Structure Analysis: The x-ray data were obtained from the Crystal and Molecular Structure Laboratory Center for Chemical Characterization and Analysis at Texas A&M University. The crystals were mounted on a nylon loop with a small amount of oil and attached to a goniometer head. X-ray data were obtained on a SMART 1000 diffractometer. Low temperature (110K) x-ray diffraction data were collected on a Bruker SMART CCD-based diffractometer (Mo-Kα radiation, λ = 0.71073 Å) and covered a hemisphere of space upon combining three sets of exposures. The space groups were determined based on systematic absences and intensity statistics using the SMART program for data collection and cell refinement. Raw data frame integration was performed with SAINT+. The structures were solved by direct methods. Hydrogen atoms were added at idealized positions and refined with fixed isotropic displacement parameters equal to 1.2 times the isotropic displacement parameters of the atoms to which they were attached. The largest residual electron density is located at 0.05 Å from molybdenum Anisotropic displacement parameters were determined for all non-hydrogen atoms. Programs used for data collection and cell refinement, Bruker XSCANS; data reduction, SHELXTL; absorption correction, SADABS; structure solution, SHELXS-97 (Sheldrick); structure refinement, SHELX-97 (Sheldrick), and molecular graphics and preparation of material for publication, SHELXTL-Plus, version 5.1 or later (Bruker).

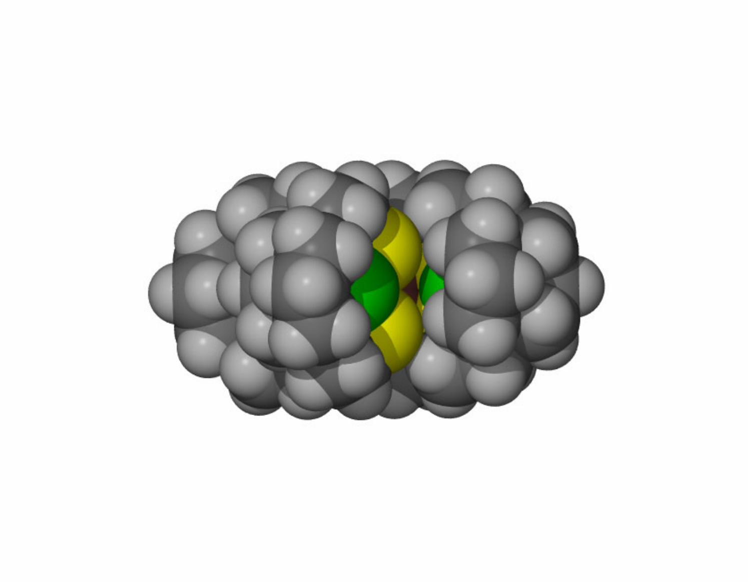
Reduction Potentials (V) for [Mo$_2$(**Ni-1**)$_4$][BF$_4$]$_4$and [Mo$_2$(**Ni-1'**)$_4$][BF$_4$]$_4$.[a]

Complex	(E_{pc1}	E_{pc2}	E_{pc3})[b]	E_{pc4}	E_{pc5}	E_{pc6}
[Mo$_2$(**Ni-1**)$_4$][BF$_4$]$_4$	(-0.71	-1.19	-1.33)	-1.43	-1.80	-2.11[c,e]
[Mo$_2$(**Ni-1'**)$_4$][BF$_4$]$_4$	(-0.70	-1.18	-1.32)	-1.43	-1.81	-2.11[d,e]

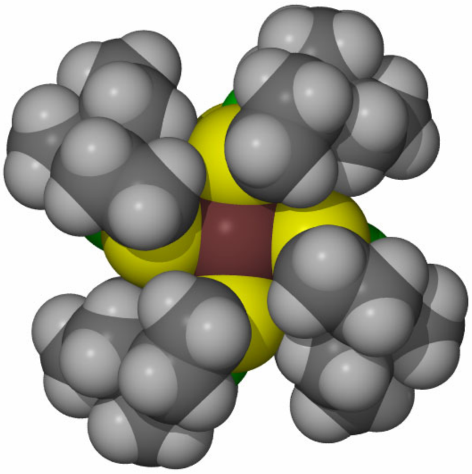
[a] All potentials are scaled to NHE and referenced to a Cp$_2$Fe/Cp$_2$Fe$^+$ standard ($E_{1/2}^{\mathrm{NHE}}$ = 0.40 V). The cyclic and square wave voltammograms were obtained in MeCN solutions of 0.1 M *n*-Bu$_4$NBF$_4$ electrolyte, with a glassy carbon working electrode, a Ag/AgNO$_3$ reference electrode, and a platinum coil auxiliary electrode at a scan rate of 200 mV/s. [b] These values were obtained from the square wave voltammogram due to the waves of the cyclic voltammogram being ill-defined. [c] This reduction peak is coupled to a return peak E_{pa} at –1.98 V ($E_{1/2}$ = -2.04 V, ΔE = 119 mV, i_{pa}/i_{pc} = 0.75). [d] This reduction peak is coupled to a return peak E_{pa} at –1.98 V ($E_{1/2}$ = -2.04 V, ΔE = 118 mV, i_{pa}/i_{pc} = 0.71). [e] Scanning at slower scan rates leads to loss of the anodic peak.



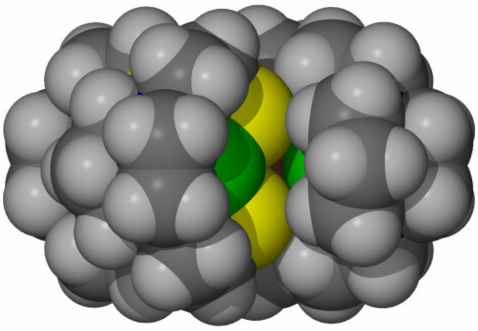
[Mo_2(**Ni-1**)$_4$][BF_4]$_4$: viewed down Mo-Mo axis



[Mo_2(**Ni-1**)$_4$][BF_4]$_4$: bisection of sulfur bridge (90° rotation from above)



$[Mo_2($**Ni-1'**$)_4][BF_4]_4$: viewed down Mo-Mo axis



$[Mo_2($**Ni-1'**$)_4][BF_4]_4$: bisection of sulfur bridge (90° rotation from above)