Metallodithiolato ligands as bridges in multiply bonded dimolybdenum complexes†

Stephen P. Jeffery, Jonghyuk Lee and Marcetta Y. Darensbourg*

For the first time, a NiN_2S_2 metallothiolate ligand is used as a bidentate bridging ligand for a multiply bonded dimetal unit.

The *cis*-dithiolates derived from structurally reinforced diazacycles as in Ni(bme-daco), Ni-**1** (1,5-bis(mercaptoethyl)-1,5-diazacyclooctane)nickel) and Ni(bme-dach), Ni-**1′** (1,4-bis(mercaptoethyl)-1,4-diazacycloheptane)nickel), have proven exceptional as metallodithiolate ligands which nucleate a broad scope of cluster complexes. Along with other NiN_2S_2 complexes, the donor abilities of Ni-**1** and Ni-**1′** have been addressed *via* analysis of $\nu(CO)$ vibrational spectroscopy of NiN_2S_2 derivatives of $W(CO)_4$.[1] The thermally stable complexes have been subjected to X-ray diffraction studies for determination of solid state structures. In solution facile chelate ring opening produces the $(\eta^1$-$NiN_2S_2)W(CO)_5$ in the presence of added CO. Such studies have established that the NiN_2S_2 metallodithiolate ligands are hemilabile and that they bind to low valent metals with electron donor abilities comparable to amines, diphosphines and diimines.

Seen in Fig. 1 is a structural overlay of Ni-**1*** {[1,5-bis(2-mercapto-2-methylpropyl)-1,5-diazacyclooctane]nickel} and (*o*-phen)$W(CO)_4$. The square planarity of the nickel dithiolates, coupled with the hinge associated with the lone pairs of sulfur in bridging dithiolates, engenders a stereoorientational effect not seen in either the typically bulky diphosphines or the flat diimines. This unique steric character is responsible for the profusion of paddlewheel-type clusters formed as Zn, Cu, Ag, and Pd
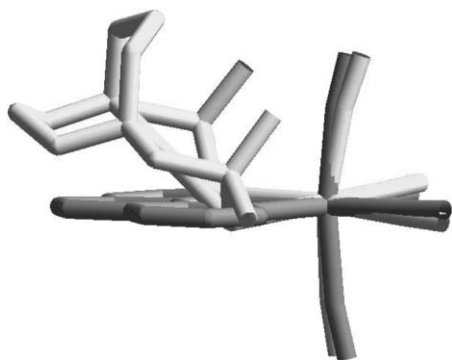
derivatives.[2–5] Fig. 2 lists formulations of such clusters in which M–M distances > 4 Å result from tetrahedral S_3X donor environments about Zn^{II} and Cu^I; planar S_4 or S_3 donor environments about Pd^{II} and Ag^I in the C_4 and C_3 paddlewheels, respectively, engender non-bonded M–M distances of around 3 Å. As the NiN_2S_2 ligands also serve as bidentate ligands to a single metal, a reasonable goal is the isolation of dinuclear multiply-bonded M_2^{n+} units. The latter are typically found as carboxylate and formamidinate derivatives which have been extensively chronicled in explorations of metal–metal bonds in the Cotton laboratories.[6] Thus, in order to determine whether the steric and donor characteristics of NiN_2S_2 ligands perform similarly to those of traditional bidentate bridging ligands of multiply-bonded dinuclear compounds, two complexes containing quadruply-bonded dimolybdenum (Mo_2^{4+}) units were prepared and characterized *via* X-ray crystallography, cyclic voltammetry, and electron spray ionization mass spectroscopy.‡

Complexes **1** and **2** crystallize as MeCN solvates, **1**·6MeCN and **2**·4MeCN, in the monoclinic space group $P2_1/n$. Shown in Fig. 3 are the molecular structures of the Mo_2Ni_4 cations. There are two molecular cations in the unit cell with the four charge-balancing BF_4 anions residing within the lattice interstices. The central methylene carbons [C(4) and C(7)] on one of the diazacycles of compound **1** is disordered between two positions 70% of the time, reflecting the ease of interconverting chair/boat forms of the nickel–diazacycle hexane rings.

The Mo_2^{4+} coordination environments of the Mo_2Ni_4 clusters are C_4 paddlewheels containing a Mo–Mo axis and eight sulfurs derived from four NiN_2S_2 bidentate bridging paddles. The Ni-**1** and Ni-**1′** moieties are in their common configurations with Ni–N and Ni–S distances essentially unchanged from their unbound forms.[7] A plane of symmetry perpendicular to the Mo–Mo C_4
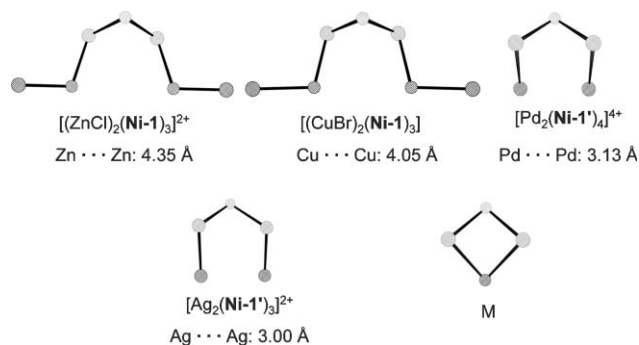

Fig. 1 Structural overlay of $W(CO)_4$ derivatives of Ni-**1*** and *o*-phenanthroline, matching the tungsten and (S/N) donor atoms.

Fig. 2 Range of metal–metal distances afforded by NiN_2S_2 ligands; see text for description of structures.
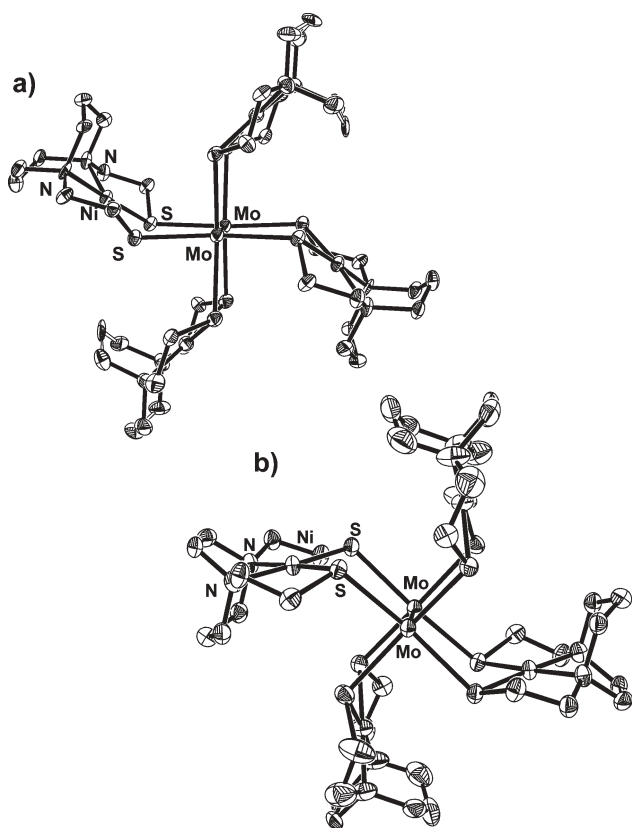
Fig. 3 Thermal ellipsoid plots of cations (a) complex **1**, $[Mo_2(Ni-\mathbf{1})_4]^{4+}$ and (b) complex **2**, $[Mo_2(Ni-\mathbf{1}')_4]^{4+}$.

Fig. 4 Cyclic and square wave voltammograms of 1.0 mM solution of **2** in 0.1 M n-Bu$_4$NBF$_4$ with a glassy carbon electrode at a scan rate of 200 mV s^{-1}. Square-wave voltammogram shown in the bottom of the figure is initiated in the negative direction; square-wave voltammogram amplitude = 25 mV; frequency = 15 Hz; E_{step} = 4 mV. All potentials scaled to NHE *via* the Fc/Fc$^+$ reference couple.[10] E_{pc1} = -0.70, E_{pc2} = -1.18, E_{pc3} = -1.32, E_{pc4} = -1.43, E_{pc5} = -1.81, E_{pc6} = -2.11 V.

rotation axis includes the four nickel ions and the central methylene carbons in the four diazacyclohexane rings of $[Mo_2(Ni-\mathbf{1})_4]^{4+}$; a similar plane of symmetry exists in the contracted diazacycle-ring derivative of $[Mo_2(Ni-\mathbf{1}')_4]^{4+}$. The two MoS$_4$ planes are largely eclipsed, displaying a maximum torsion of 1.5°. A much greater torsion angle has been observed in a (NiN$_2$S$_2$)$_4$Ni$_2$ structure.[8] Thus, neglecting the diazacycle frameworks of complexes **1** and **2**, the molecular cations are of C_{4h} symmetry.

Ni-**1** and Ni-**1**′ coordinate to the dimolybdenum unit *via* their sulfur atoms with average Mo–S distances of 2.526(3) and 2.517(14) Å, respectively. These distances are ≈0.1 Å longer than those in S-donor complexes, Mo$_2$(S$_2$CR)$_4$, and similar to those in Mo$_2$(S$_2$PEt$_2$)$_4$.[9] The Mo–Mo bond distances of 2.142(18) and 2.162(10) Å for **1** and **2**, respectively, are not significantly different from each other or from the Mo$_2$(S$_2$CR)$_4$ derivatives which represent quadruply-bonded Mo$_2$$^{4+}$ units in neutral S-ligated C_4 structures.[9] The crystal packing diagrams show no anion or solvent contacts within bonding distances.

The bidentate bridging ligands in **1** and **2** display S–Ni–S angles that are compressed by *ca.* 2° from their free ligand values of 89.5 and 95.4° for Ni-**1** and Ni-**1**′, respectively. The S···S distances within one ligand 'paddle' are at 3.0 Å largely the same as those in the Mo$_2$(S$_2$CR)$_4$ analogs.

The redox behavior of the two dimolybdenum compounds in MeCN was examined at room temperature by cyclic voltammetry. Fig. 4 displays the CV and associated square wave (SW) voltammogram of compound **2** in the cathodic potential region. Further details for compounds **1** and **2** are listed in Table S1.†
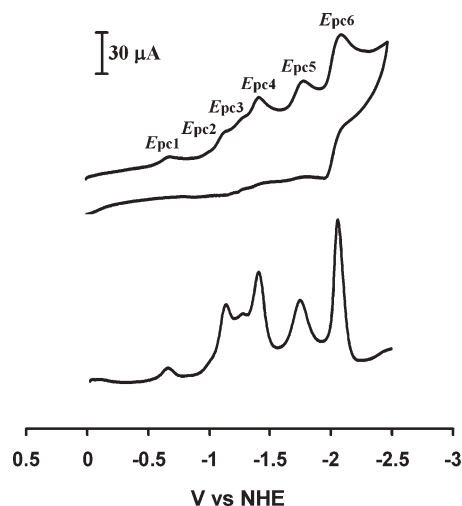
Consistent with earlier electrochemical studies of polynuclear compounds based on Ni-**1** and Ni-**1**′, the CVs of **1** and **2** show multiple and overlapping redox events.[11] In the case of **2**, the redox events commence at -0.70 V and, within the solvent window, finish with an apparently reversible wave at $E_{1/2}$ = -2.04 V. The SW amplifies and separates the electrochemical events indicating six reductive processes, four of which are quite distinct with two others, at -0.70 and -1.31 V, being weak and poorly defined.

The C_3 paddlewheel based on zinc, $[(Ni-\mathbf{1})_3(ZnCl)_2][BF_4]_2$, showed three cathodic events,[2] which were assigned to successive reductions of Ni-**1** units. Thus a likely scenario for the C_4 paddlewheel compound **2** is that the four distinct reductions derive from the Ni-**1**′ units while the minor waves, E_{pc1} ($-.70$ V) and E_{pc3} (-1.32 V) are reasonably attributed to the dimolybdenum unit. The latter possibility is supported by the redox behavior of the starting material $[Mo_2(MeCN)_{10}][BF_4]_4$ which shows, under identical electrochemical conditions, a reversible reduction at $E_{1/2}$ = -0.21 V and an irreversible reduction at E_{pc} = -0.96 V. As the NiN$_2$S$_2$ ligands are better electron donors than MeCN,[1,12] the more negative reductions of compounds **1** and **2** are expected. The recently reported Mo$_2$(hpp)$_4$ (hpp = the anion of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine) also revealed two cathodic events of similar separation which were assigned to the dimolybdenum unit redox levels of Mo$_2$$^{6+/5+}$ and Mo$_2$$^{5+/4+}$.[13]

The electrochemical assignments have as their basic assumption that the hexanuclear cluster remains intact in MeCN solution. This assumption is challenged by the position of the most negative reduction wave, which is very similar to that of the free NiN$_2$S$_2$ ligand. The attempted 'spiking' of the electrochemical solution of compound **2** with Ni-**1**′ resulted in minor differences in the CV largely due to the insolubility of Ni-**1**′ in MeCN. For compound **1**, spiking with Ni-**1** produced some enhancement of the -2.1 V event and also a major anodic event wave at +0.17 V. As this oxidative event is characteristic of free NiN$_2$S$_2$ complexes and
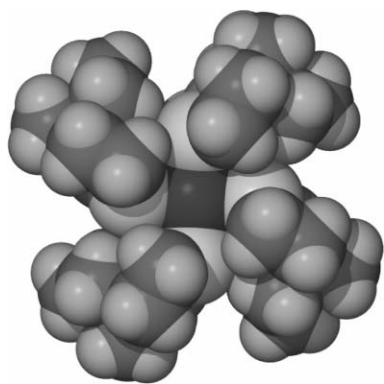
Fig. 5 Space filling model of the cation $[Mo_2(Ni\text{-}1')_4]^{4+}$ showing clefts between the NiN_2S_2 paddles.

Stephen P. Jeffery, Jonghyuk Lee and Marcetta Y. Darensbourg*

Texas A&M University, Department of Chemistry, College Station, Texas, USA. E-mail: marcetta@mail.chem.tamu.edu; Fax: (979) 845-0158; Tel: (979) 845-5417

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assigned to oxidation of thiolate to the thiyl radical,[14] we conclude that the absence of this oxidative wave in non-spiked **1** solutions is indicative of the lack of dissociation of Ni-**1** in solutions of compound **1**. Additional studies are required for definitive assignments and further development of the electrochemistry.

With this study we extend the range of metal to metal distances that are expressed in Fig. 2 by more than an angstrom; the new range of M⋯M distances spanned by nickel-*cis*-dithiolates is 2.14 to 4.35 Å. To our knowledge, no other bidentate bridging ligand can accomplish such structural diversity. This 'softness' or lack of directionality of the sulfur donor sites might be used to permit expansion or contraction of metal–metal distances arising from various redox levels in multiply-bonded M_2^{n+} units. Despite the apparent steric bulk of these ligands, the orientational possibilities of the square planar NiN_2S_2 ligand permit a structural meshing conducive to stable C_4 paddlewheel-type complexes. Indeed the space filling models, as shown in Fig. 5 show clefts between the paddles, exposing sulfur and nickel atoms.

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