dimensions of the analogous cores in isostructural $[(WS_4)_2Fe_2S_2]^{4-}$ are very similar to those in $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.[13] The average of the terminal Mo–O distances shown in Figure 1 (1.78 Å) is the same as the Mo–O distance in Cs_2MoOS_3.[14] The unit cell of $(Ph_4P)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ contains chains of anions (cf. Figure 2 (supplementary material)). These chains are linked by water molecules which are hydrogen-bonded to terminal oxygen atoms, O1 and O2 of the anion. The longer Mo–O1 distance could be the result of an extra water molecule that is within hydrogen-bonding distance of O1. This pattern of hydrogen bonding suggests that solvation of the terminal oxygen atoms may help stabilize $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ in water.

The electronic absorption spectrum of $(Ph_4As)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ in acetonitrile shows three principal bands [λ_{max}, nm (ϵ, $mM^{-1}\ cm^{-1}$): 290 (23.1), 372 (14.6), 526 (12.2). Absorption and resonance Raman spectra of the analogous "linear" cluster $[(WS_4)_2Fe_2S_2]^{4-}$ suggest that the lowest energy absorption band involves transitions within the Fe_2S_6 portion of the anion.[1a,15] The ^{57}Fe Mössbauer spectrum of a frozen solution of $(Ph_4As)_4[(MoO_2S_2)_2Fe_2S_2]\cdot 6H_2O$ in acetonitrile shows a single quadrupole doublet at both 200 and 4.2 K. Parameters of the doublet at 4.2 K are $\delta = 0.42$ mm/s and $\Delta E_Q = 1.04$ mm/s vs. metallic iron at 300 K. No significant changes in these parameters occur upon application of a 2.2-kG magnetic field. These data are consistent with the expected antiferromagnetic coupling between iron atoms.[2c,11,12] Using the empirical relationship between Mössbauer isomer shift and mean oxidation state, s, developed by Christou et al.[16] for clusters containing tetrahedral FeS_4 sites gives $s = 2.4$ for each iron atom in $[(MoO_2S_2)_2Fe_2S_2]^{4-}$. Thus, while the anion formally contains Fe(II) and Mo(VI), this calculation indicates considerable delocalization of electron density from Fe onto Mo, and a mean oxidation state of Fe approximately midway between Fe(II) and Fe(III). $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ appears to be the first example of a cluster containing an $[Fe_2S_2]^{1+}$ core without trapped valence Fe(II) and Fe(III).

The spectral time courses for reactions of Fe^{2+} with $MoO_{4-x}S_x^{2-}$ ($x = 2$–4) at pH 12 shown in Figure 3 demonstrate that the same product, namely $[(MoO_2S_2)_2Fe_2S_2]^{4-}$ (indicated by the dashed spectra with λ_{max} at 510, ~350 sh, and 290 nm), is obtained in each case.[17] However, the rate of formation of this product decreases monotonically with increasing numbers of sulfido vs. oxo ligands in the starting $MoO_{4-x}S_x^{2-}$. This trend in rates is the same as that observed for hydrolyses of $MoO_{4-x}S_x^{2-}$ at basic pHs.[18] In the absence of Fe^{2+} the half-time for hydrolysis of MoS_4^{2-} under these conditions is ~170 h at 25 °C. Thus, Figure 3C shows that Fe^{2+} accelerates the hydrolysis of MoS_4^{2-} by at least a factor of 100. Similar acceleration is observed for $MoOS_3^{2-}$ in Figure 3B. The even more rapid reaction of $MoO_2S_2^{2-}$ shown in Figure 3A together with the trend in rates discussed above strongly suggests that some complete hydrolysis to MoO_4^{2-} occurs in all cases during formation of $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.

Our results imply that the MoFe cofactor of nitrogenase is *not* constructed by a combination of "free" Fe^{2+} and performed MoS_4^{2-} in an aqueous environment, since this combination would likely result ultimately in MoO_4^{2-} and FeS. This statement applies only in the absence of thiol. In the presence of 2-mercaptoethanol at pH 9, the combination of MoS_4^{2-} and Fe^{2+} in water results in assembly of the "double-cubane" cluster $[Fe_6S_8Mo_2(SCH_2CH_2OH)_9]^{3-}$,[19] which we have isolated in 60% yield as its n-Bu_4N^+ salt.[20]

Acknowledgment. We thank J. T. Sage and P. G. Debrunner of the Department of Physics, University of Illinois, for obtaining the Mössbauer spectra. This research was supported by the National Science Foundation (D.M.K., Grant DMB-8216447) and by the Office of Basic Energy Sciences Division of the U.S. Department of Energy. Ames Laboratory is operated for the USDOE by Iowa State University under Contact No. W-7405-ENG-82.

Supplementary Material Available: Figure 2 (which contains a view of the unit cell) and listings of atomic positional and thermal parameters and bond and dihedral angles for the anion (9 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Synthesis, Molecular Structure, and Physicochemical Properties of $M_2(form)_4$ (M = Ni, Pd; form = *N,N'*-Di-*p*-tolylformamidinato). Attempts To Generate a Palladium(III) Dimer

Sir:

Many dinuclear compounds of platinum(III) containing four bidentate bridging ligands and a metal–metal interaction through an electron-rich single bond of electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ are known.[1,2] A few dinuclear compounds with the Pt atoms in the 2.5 average oxidation state and a formal bond order of 0.5 between the two metals have also been prepared.[3,4] On the other hand, analogous compounds for nickel and palladium have never been reported. Only one Ni_2^{5+} compound, $Ni_2(S_2CCH_3)_4I$, has been described.[5]

Since many dinuclear, quadruply bridged compounds of nickel(II) and palladium(II) are known, we thought that we might have a chance to generate oxidized species from these provided we could find the right combination of ligands and oxidizing material. We decided to test the *N,N'*-di-*p*-tolylformamidinato (form) ligand for the following reasons. First, the nitrogen donors are expected to increase the electronic charge on the metal atoms as compared, for example, to that obtained with carboxylato ligands, thereby decreasing the oxidation potential. Such a trend has been well established for compounds of the Rh_2^{4+} core.[6]

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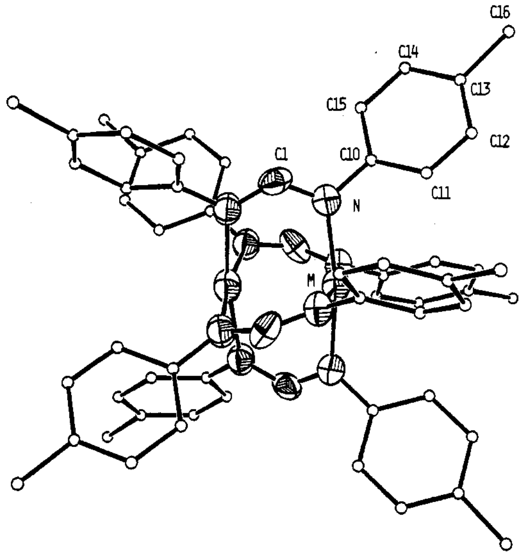

Figure 1. ORTEP view of the $M_2(form)_4$ (M = Ni, Pd) molecule. Distances: M–M = 2.485 (2) Å (Ni), 2.622 (3) Å (Pd); M–N = 1.904 (5) Å (Ni), 2.06 (1) Å (Pd). Torsional N–M–M′–N′ angle: 16.82° (Ni), 15.1° (Pd).

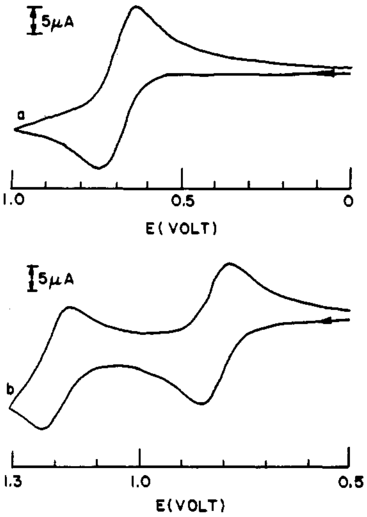

Figure 2. Cyclic voltammograms of $M_2(form)_4$ in CH_2Cl_2 (ca. 0.1 M $n\text{-}Bu_4N^+PF_6^-$) at a platinum electrode: (a) M = Ni; (b) M = Pd. Reference electrode: Ag/AgCl. Scan speed = 200 $mV{\cdot}s^{-1}$. The $FeCp_2/FeCp_2^+$ couple had $E_{1/2}$ = +0.49 V under the same conditions.

Second, the geometry and the steric bulkiness of the ligand should favor the bridging dinuclear structure over the possible mononuclear or oligonuclear structures that are known to be formed with other bidentate ligands.[7] Finally, $Rh_2(form)_4$[6c] and $Ir_2(form)_4$,[8] which are isoelectronic with a hypothetical Pd_2^{6+} compound, have been recently described.

$Ni_2(form)_4$ has been obtained by interaction of anhydrous $NiBr_2$ with Li^+form^-, the latter being obtained in situ from Hform and LiBu, in THF as solvent. It crystallizes as a dark green diaqua adduct from CH_2Cl_2/*n*-hexane when the crystallization is carried out in the air.[9] $Pd_2(form)_4{\cdot}2H_2O$ has been obtained as orange crystals by a similar procedure from $Pd_3(OAc)_6$ and Li^+form^-. Crystallization from dry THF gave $Pd_2(form)_4{\cdot}2THF$,[10] while $Pd_2(form)_4{\cdot}C_6H_5CH_3$ was obtained from toluene.[11]

The crystal structures of the H_2O adducts of both compounds have been determined by X-ray diffraction methods.[12] The two compounds are isostructural. The molecules (see Figure 1) have imposed D_4 symmetry and contain, as expected, two metal atoms bridged by four formamidinato ligands, with four nitrogen atoms around each metal atom in a square-planar configuration. The M-M distances [2.485 (2) Å (M = Ni); 2.622 (3) Å (M = Pd)] are comparable to, although a little longer than, those of $M_2(dpt)_4$ (dpt = 1,3-diphenyltriazine).[13]

The cyclic voltammograms of $M_2(form)_4$ are reported in Figure 2. Neither compound shows any reduction process, but both undergo interesting oxidation processes. $Ni_2(form)_4$ exhibits a reversible (ΔE_p = 78 mV at 200 $mV{\cdot}s^{-1}$) oxidation with $E_{1/2}$ = +0.73 V and a second irreversible oxidation with E_{pc} = ca. +1.25 V. $Pd_2(form)_4$ shows two reversible waves, the first one centered at $E_{1/2}$ = +0.81 V (ΔE_p = 61 mV at 200 $mV{\cdot}s^{-1}$) and the second one with $E_{1/2}$ = +1.19 V (ΔE_p = 55 mV at the same scan speed). These two waves have the same limiting current, and they are therefore associated with the same number of electrons. Controlled-potential coulometry carried out at +1.00 V for both $Pd_2(form)_4{\cdot}2THF$ and $Ni_2(form)_4{\cdot}2H_2O$ established the nature of the oxidized species as $[M_2(form)_4]^+$ (M = Ni, dark emerald green; M = Pd, dark brown). The amount of charge consumed in the processes was slightly higher than one electron per dimer, perhaps because of water present in the system. The $[M_2(form)_4]^+$ (M = Ni, Pd) ions are actually able to oxidize water with production of the neutral M(II) dimers, although such a reaction (monitored by visible spectroscopy) is quite slow in CH_2Cl_2. After the coulometric experiment, cyclic voltammetry on the resulting solutions confirmed the completion of the oxidation processes.

We tried to obtain salts of the oxidized species in crystalline form, but we have so far been unsuccessful: when the CH_2Cl_2 solutions from the bulk electrolysis are evaporated to dryness and the residues dissolved in acetonitrile, immediate formation of the neutral M(II) dimers occurs. The same behavior was observed when we tried to precipitate the cations from CH_2Cl_2 as the BPh_4^- salts (by using the CH_2Cl_2 soluble $n\text{-}Bu_4N^+BPh_4^-$).[14]

The solutions from bulk electrolysis were more fully characterized by EPR and visible spectroscopy. The EPR spectra are reported in supplemental Figure 3. The nickel species shows a spectrum consistent with axial symmetry, with $g_\perp$ = 2.210 and $g_\parallel$ = 2.038. The only other known Ni_2^{5+} compound of similar configuration, $Ni_2(S_2CCH_3)_4I$, is said to be EPR silent.[5] The palladium compound, on the other hand, shows only a symmetric line at liquid-nitrogen temperature. No other Pd_2^{5+} compound seems to have been described in the literature. A Pt_2^{5+} compound has been characterized by EPR, and it is reported to have a spectrum typical of axial symmetry with $g_\perp$ = 2.079 and $g_\parallel$ = 2.008.[4]

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(9) $Ni_2(form)_4{\cdot}2H_2O$. Anal. Calcd for $C_{60}H_{64}N_8Ni_2O_2$: C, 68.9; H, 6.2; Ni, 11.2. Found: C, 70.3; H, 6.4; Ni, 10.5. IR (Nujol mull/cm^{-1}): 1620 m, 1590 s, 1535 m, 1500 s, 1345 s, 1230 s, 970 m, 830 m, 820 m, 535 m, 525 m, 475 w, 465 m. Visible [CH_2Cl_2, λ_{max}/nm (ϵ/$mol^{-1}{\cdot}L{\cdot}cm^{-1}$)]: 630 (800), 482 (2700). ^1H NMR ($CDCl_3$, δ): 1.53 (s, H_2O, 4 H), 2.52 (s, CH_3, 24 H), 6.14 (s, N–CH–N, 4 H), 7.08 (m, aromatic, 32 H). The peak at δ 1.53 disappeared upon treatment with D_2O.

(10) $Pd_2(form)_4{\cdot}2THF$. IR (Nujol mull/cm^{-1}): 1620 m, 1585 s, 1540 m, 1500 s, 1345 s, 1230 s, 1070 m, 965 m, 835 sh, 820 m, 545 w, 520 m, 450 m. Visible [CH_2Cl_2, λ_{max}/nm (ϵ/$mol^{-1}{\cdot}L{\cdot}cm^{-1}$)]: 492 (2600). ^1H NMR ($CDCl_3$, δ): 1.84 (m, THF, 8 H), 2.24 (s, CH_3, 24 H), 3.74 (m, THF, 8 H), 6.87 (m, aromatic, 32 H), 7.05 (s, N–CH–N, 4 H).

(11) $Pd_2(form)_4{\cdot}C_6H_5CH_3$. The IR (Nujol mull) spectrum was identical with that of $Pd_2(form)_4{\cdot}2THF$, with the exception of the band at 1070 cm^{-1}, not present in the toluene adduct. ^1H NMR ($CDCl_3$, δ): 2.25 (s, CH_3, 24 H), 2.35 [s, CH_3 (toluene), 3 H], 6.88 (m, aromatic, 32 H), 7.05 (s, N–CH–N, 4 H), 7.19 [m, aromatic (toluene), 5 H].

(12) Crystal data: Cubic, space group $Pn\bar{3}n$; a = 20.841 (5) Å (Ni), 21.067 (4) Å (Pd); V = 9052 (5) $Å^3$ (Ni), 9350 (5) $Å^3$ (Pd); Z = 6; R = 0.0492 (Ni), 0.0520 (Pd) [R_w = 0.0620 (Ni), 0.0649 (Pd)] for 521 (Ni) or 401 (Pd) data having $F_o^2 > 3\sigma(F_o^2)$.

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(14) Note added in Proof: Both $[M_2(form)_4]^+$ cations have now been isolated in salts and structurally characterized.

Both $[M_2(\text{form})_4]^+$ (M = Ni, Pd) solutions have strong absorptions in the near-infrared. The spectra are reported in supplementary Figure 4 and contrasted with those of the corresponding neutral species. An assignment of such bands will be presented following a molecular orbital study under way.

A bulk electrolysis was attempted for the palladium species at +1.35 V in order to electrogenerate the $[Pd_2(\text{form})_4]^{2+}$ species, but more than two electrons per molecule were consumed in the process and a following cyclic voltammetric experiment showed that most of the electroactive species had been destroyed. We attribute this instability to a slow process that follows the generation of the $[Pd_2(\text{form})_4]^{2+}$ species, since the peak separation and the peak currents in the process centered at $E_{1/2} = +1.19$ V in the cyclic voltammogram of $Pd_2(\text{form})_4$ (see Figure 2b) do not show any significant deviation from reversibility. Such a slow process may involve either the solvent or the formamidinato ligand.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Tables of crystallographic data, atomic fractional coordinates, bond distances and angles, and temperature factors for $Ni_2(\text{form})_4 \cdot 2H_2O$ and $Pd_2(\text{form})_4 \cdot 2H_2O$ and figures showing EPR spectra of $M_2(\text{form})_4{}^+PF_6{}^-$ (Figure 3) and visible spectra of $[M_2(\text{form})_4]^{n+}$ (Figure 4) (10 pages). Ordering information is given on any current masthead page.

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Comparison of Carbonate, Citrate, and Oxalate Chemical Routes to the High-T_c Metal Oxide Superconductors $La_{2-x}Sr_xCuO_4$

Sir:

It has been well over a decade since superconducting transition temperatures (T_c) reached a maximum of 23.7 K in the metal-alloy A-15 compounds such as Nb_3Ge.[1] Recently, Bednorz and Müller[2] observed superconductivity in oxygen-deficient compounds in the La–Ba–Cu–O (LBCO) system with overall composition $La_{5-x}Ba_xCu_5O_{5(3-y)}$. For various values of x, a three-phase mixture was present with an onset T_c of ~35 K and with zero resistance achieved at T ~ 13 K. Uchida et al.[3] and Takagi et al.[4] subsequently identified the superconducting phase in the LBCO system as having the composition $La_{2-x}Ba_xCuO_{4-y}$ (y unspecified) with the K_2NiF_4 layered-perovskite structure (tetragonal, space group *I*4/*mmm*). Onset T_c's in the 30 K range with zero-resistance temperatures of ~22 K were reported.[3,4] Simultaneously, Chu et al.[5] observed in samples with overall compositions of $La_{1-x}Ba_xCuO_{3-y}$ (x = 0.15–0.20, y unknown) onset T_c's of 32 K, which could be increased to 40.2 K and later to 52.5 K[5b] at a pressure of ~12 kbar. Shortly thereafter, Jorgensen et al.[6] reported the crystal structure of $La_{1.85}Ba_{0.15}CuO_4$ (confirmed K_2NiF_4 layered-perovskite, derived from powder neutron diffraction studies) with $T_c \simeq 33$ K. Cava et al.[7] and Capone et al.[8] then demonstrated that with the use of strontium in place of barium, materials of composition $La_{2-x}Sr_xCuO_4$ attained zero resistance at much higher temperatures, for example near 36 K for $La_{1.85}Sr_{0.15}CuO_4$.[7] Finally, reports[9] of large resistance decreases at T ~ 49 K and higher in LBCO materials suggested the possibility of much higher transition temperatures. A very recent report[10] shows that a T_c of 93 K occurs at ambient pressure in the Y–Ba–Cu–O system. In many of the cited studies bulk superconductivity was confirmed by Meissner effect measurements. Clearly, superconductivity at T_c's approximately quadruple that achieved previously has been observed, thereby opening a new frontier in research on superconducting materials.

Table I. Stoichiometric Ratios for $La_{2-x}Sr_xCuO_4$ Compounds Prepared from Different Chemical Routes

	La/Sr/Cu ratio for $La_{2-x}Sr_xCuO_4$[a]		
	$x = 0.10$	$x = 0.15$	$x = 0.20$
carbonate[b]	1.90/0.10/1.00	1.85/0.14/0.96	1.80/0.19/1.03
citrate	1.90/0.11/1.00	1.85/0.13/1.00	1.80/0.21/1.01
carbonate[c]	1.90/0.04/0.96	1.85/0.07/0.95	1.80/0.09/0.94
oxalate[c]	1.90/0.01/0.93		1.80/0.03/0.84

[a] Analysis accuracy is approximately 5% of each number. [b] With adjustment to pH 7–8. [c] Without pH adjustment.

The wide range of sample compositions reported thus far suggests that (i) considerable optimization of preparative conditions is required, and (ii) T_c varies with change in the alkaline-earth metal and its concentration. All reports (vide supra) suffer from the same major difficulties: incomplete synthesis conditions have been given and the reported compositions have been based only on initial reactant concentrations. As yet, no chemical analyses of the final products have been reported. Generally, the materials are prepared by repeated grinding and sintering of the parent oxides,[3–5,7] by co-precipitation reactions with oxalate[2,6,9] and carbonate,[8] or by a complexing reaction with citrate,[3] again followed by sample firing, grinding, and annealing. The main advantage of the solution techniques is that the final oxide products are more uniformly mixed than those prepared from binary oxides. In this communication we compare the carbonate, citrate, and oxalate solution techniques for the synthesis of the high-T_c compounds $La_{2-x}Sr_xCuO_4$.

Synthesis. Carbonate Route. A detailed procedure for the preparation of $La_{1.85}Sr_{0.15}CuO_4$ is given below. Samples of different metal compositions may be prepared by obvious changes in stoichiometry. Powdered samples (reagent grade) of $La(NO_3)_3 \cdot 6H_2O$ (8.25 g, 19.1 mmol), $Sr(NO_3)_2$ (0.33 g, 1.6 mmol), and $Cu(NO_3)_2 \cdot 3H_2O$ (2.50 g, 10.3 mmol) are dissolved together in 100 mL of distilled water. The nitrate solution is vigorously stirred and neutralized to pH 7–8, in order to suppress bicarbonate formation, by titration with a KOH solution (~19 mmol). A solution of K_2CO_3 (5.69 g, 41.2 mmol) in 60 mL of water is slowly added with stirring to the above mixture to give a thick, light blue precipitate. The precipitate is repeatedly washed and centrifuged

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