Attempts to isolate the dimer were unsuccessful.

The most probable mechanism for the spontaneous cis–trans isomerization of PtX_2L_2 therefore seems to be

$$2\,cis\text{- or }trans\text{-}PtX_2L_2 \rightleftarrows Pt_2X_4L_2 + 2L \qquad (5)$$

$$cis\text{- or }trans\text{-}PtX_2L_2 + L \underset{k_{-i}}{\overset{k_i}{\rightleftarrows}} trans\text{- or }cis\text{-}PtX_2L_2 + L \qquad (6)$$

Reaction 6 may proceed via either pseudorotation or consecutive displacement.[3] The observed reaction rate for the isomerization step (reaction 6) is thus a function of [L].[3] The induction period can be attributed to phosphine generation via reaction 5 and will exist until [L] reaches a stage where reaction 6 becomes much faster than reaction 5. Since phosphine acts as a catalyst, reaction 6 will be a pseudo-first-order reaction, and this explains why the semilog curves in Figure 1 become linear.

The rate law for reaction 6[3] (solvent = DMF, Me_2SO, CH_3CN) (see eq 7) predicts that the k_{obsd} values found for

$$k_{obsd} = (k_i + k_{-i})[L] \qquad (7)$$

the cis and trans substrates should be identical and that the rate should be first order in [complex]. From Tables II and III it can be seen that these k_{obsd} values are in fact comparable and independent of [complex]. For the solvents benzene and toluene $k_{-i} = 0$. Unfortunately [L] is not known, and the k_i values are thus not obtainable. The fact that reaction 6 is slower under an O_2 atmosphere can be attributed to free-phosphine oxygenation.

From the study of the photolysis of the cis–trans mixture of $PdCl_2(P\text{-}n\text{-}Pr_3)_2$,[6] it was not clear whether the isomerization results from the cis or trans isomer. Our present study requires that both isomers dimerize and that the cis isomer dimerizes faster than the trans isomer since the induction period for the trans substrate is longer. On the assumption that a two-step associative dimerization mechanism is operative, it can be shown that the trans dimer will be the product for both the cis and trans substrates.

The rate of the isomerization step (reaction 6) decreases with the polarity of the solvent (benzene > toluene > CH_3CN ~ Me_2SO > DMF) not only because this reaction is faster in nonpolar solvents but also most probably due to enhanced dimer formation and thus phosphine generation in nonpolar solvents, as is the case in the Ir(I)[7] and Rh(I)[8] systems.

Reaction 1 (X = I, L = PEt_3) in methanol exhibits no induction period.[3] This can be explained by the relative high polarity of the solvent preventing dimer formation.

Registry No. *cis*-$PtI_2(PEt_3)_2$, 35084-99-2; *trans*-$PtI_2(PEt_3)_2$, 15636-79-0; *cis*-$PtI_2(PMe_2Ph)_2$, 41119-52-2; *trans*-$PtI_2(PMe_2Ph)_2$, 41119-53-3; $[(cod)Ir(phen)]^+$, 48195-12-6.

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Synthesis and Characterization of Ni(II), Pd(II), and Pt(II) Complexes of $M'OS_3^{2-}$ (M' = Mo, W) and the Mixed-Ligand Compounds $[M(M'S_4)(S_2CNEt_2)]^-$

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A number of studies on the complexes formed by $M'X_4^{2-}$ ions (M' = Mo, W; X = O, S, Se, or a mixture of them) with first-row transition-metal ions have been published in the last few years.[1-3] As these materials involve three or four transition elements bound to each other through sulfur bridges, they have become interesting to groups studying metal–metal bonding and the effects of bridging ligands on such interactions, especially those between different transition metals.

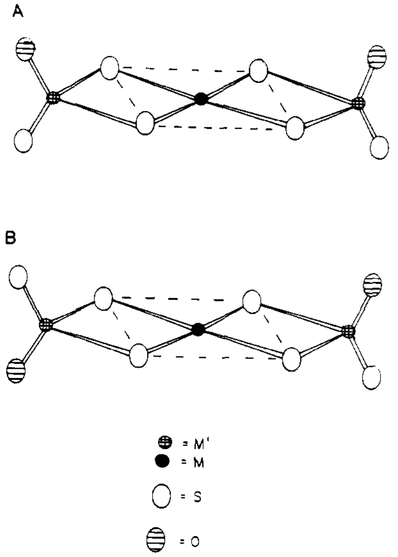

Figure 1. Possible structures of $M(M'OS_3)_2^{2-}$ complexes: A, cis isomer; B, trans isomer.

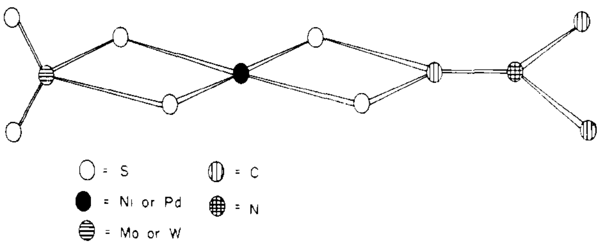

Figure 2. Proposed structure of $[M(S_2CNEt_2)(M'S_4)]^-$ complexes, where M = Ni or Pd and M' = Mo or W. Ethyl groups are represented by single carbon atoms.

We have previously reported a study of the Ni(II), Pd(II), and Pt(II) complexes of MoS_4^{2-} and WS_4^{2-}[4,5] and shown that their electrochemical behavior corresponds to sequential reduction localized at the central d^8 M(II) metal, with little influence on the part of the $M'S_4^{2-}$ ligands. Here we report the synthesis and characterization of the monooxo analogues of these species $M(M'OS_3)_2^{2-}$ and the mixed-ligand complexes $[M(M'S_4)(S_2CNEt_2)]^-$. The electrochemical properties of these materials will be discussed in a subsequent paper.[6]

Results and Discussion

I. Synthesis and Characterization of $M(M'OS_3)_2^{2-}$ Complexes. As earlier work had shown[4,5] a mixed CH_3CN–H_2O solvent system to be beneficial in the preparation of d^8 metal complexes of $M'S_4^{2-}$, we used this route to prepare the Ni(II) and Pd(II) complexes of the $M'OS_3^{2-}$ ions, as shown in eq 1.

$$M(II) + 2M'OS_3^{2-} \rightarrow M(M'OS_3)_2^{2-} \qquad (1)$$

The dianionic products were isolated as tetraalkylammonium

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Table I. Major Infrared Bands of $M(M'OS_3)_2^{2-}$ Complexes[a]

compd	$\nu(M'{=}S)$	$\nu(M'{-}S_{br})$	$\nu(M'{=}O)$
$Ni(MoOS_3)_2^{2-}$	507 (s)	460, 456, 448 (m)	905 (s)
$Ni(WOS_3)_2^{2-}$	496 (s)	454 (s)	913 (s)
$Pd(MoOS_3)_2^{2-}$	508 (s)	456, 440 (m)	900 (s)
$Pd(WOS_3)_2^{2-}$	497 (s)	444 (s)	917 (s)
$Pt(MoOS_3)_2^{2-}$	507 (s)	465 (m), 440 (w)	905 (s)
$Pt(WOS_3)_2^{2-}$	490 (s)	451, 442 (s)	915 (s)

[a] Nujol mulls.

salts; preparative details and analytical data are presented in the Experimental Section. As was found for the $M(M'S_4)_2^{2-}$ complexes, this solvent system led to no intractable byproducts, and product yields were >60% (Müller did not report the yield of $Ni(MoOS_3)_2^{2-}$ and $Ni(WOS_3)_2^{2-}$ from his aqueous route).[7,8] A mixed H_2O–Me_2SO solvent system was used to prepare the Pt(II) complexes of $M'OS_3^{2-}$, for the reaction rate was substantially greater in this mixture than in acetonitrile–water. For example, after equal reaction times a yield of 10% $Pt(WOS_3)_2^{2-}$ was obtained from CH_3CN–H_2O, while Me_2SO–H_2O afforded a 75% yield.

The infrared spectra of the Ni(II) complexes of $MoOS_3^{2-}$ and WOS_3^{2-} synthesized by our mixed-solvent system are in agreement with those reported previously on materials prepared in water.[9,10] Intense bands at 905 and 913 cm^{-1} can be assigned to $\nu(M'{=}O)$, respectively, and $\nu(M'{=}S)$ is observed at 507 and 496 cm^{-1}. Vibrations assigned as $\nu(M'{-}S_{br})$ were observed at 444 and 454 cm^{-1}. The absence of IR absorptions just below 870 cm^{-1} indicated the absence of isomers in which the ligand oxygen occupies a bridging position and confirmed that the predominant mode of bonding of the $M'OS_3^{2-}$ ligand to Ni(II) is through two sulfur atoms. These observations do not, however, distinguish between the cis and trans forms of the idealized $M(M'OS_3)_2^{2-}$ structures possible (Figure 1).

The IR spectra of the Pd(II) and Pt(II) complexes of $M'OS_3^{2-}$ are similar to those of the Ni(II) species and indicate that the mode of coordination of the ligands is similar for all three d^8 metals. Major observed vibrational frequencies of the compounds and their assignments are presented in Table I.

II. Synthesis and Characterization of $[M(M'S_4)(S_2CNEt_2)]^-$ Complexes. A. Preparation. Different synthetic methods had to be used to prepare the mixed-ligand complexes of MoS_4^{2-} and WS_4^{2-}. In the latter case, the bis ligand complexes $M(WS_4)_2^{2-}$ are relatively stable and could be used as reactants with $M(S_2CNEt_2)_2$ to give the mixed-ligand species as shown in eq 2. This redistribution reaction occurred readily for M

$$M(WS_4)_2^{2-} + M(S_2CNEt_2)_2 \rightarrow 2[M(WS_4)(S_2CNEt_2)]^- \quad (2)$$

= Ni(II), requiring only 12 h at room temperature, while a significant yield of the Pd(II) analogue required 24-h reflux in aqueous acetonitrile. No evidence of redistribution according to eq 2 could be seen with M = Pt(II) under similar conditions. These observations are in agreement with previous studies[11] which established the relative rates of substitution reactions of these d^8 metals.

Owing to the thermal instability of the $M(MoS_4)_2^{2-}$ salts under the conditions necessary to effect ligand exchange according to eq 2, a different approach to the synthesis of the mixed-ligand complexes $[M(MoS_4)(S_2CNEt_2)]^-$ was necessary. Reaction of $M(S_2CNEt_2)_2$ with $(NH_4)_2MoS_4$ proved to be effective, although once again the kinetic stability of Pt(II) dominated so that this reaction, eq 3, was only effective

$$(NH_4)_2MoS_4 + M(S_2CNEt_2)_2 \rightarrow (NH_4)M(S_2CNEt_2)(MoS_4) + NH_4S_2CNEt_2 \quad (3)$$

for M = Ni(II) or Pd(II). No evidence for the potential byproduct $M(MoS_4)_2^{2-}$ was observed. This method could also be used to prepare the mixed-ligand complexes $[Ni(WS_4)(S_2CNEt_2)]^-$, and $[Pd(WS_4)(S_2CNEt_2)]^-$ complexes, but again the Pt(II) reactants did not give the desired product.

Table II. Conductivity Data on Mixed-Ligand Complexes[a]

compd	Λ_0, Ω^{-1} cm^2 equiv^{-1}	slope *A*
$[Ni(S_2CNEt_2)(MoS_4)]^-$	132 (4)	−323 (39)
$[Ni(S_2CNEt_2)(WS_4)]^-$	130 (2)	−309 (43)
$[Pd(S_2CNEt_2)(MoS_4)]^-$	135 (2)	−388 (35)
$[Pd(S_2CNEt_2)(WS_4)]^-$	136 (4)	−387 (33)

[a] Pr_4N^+ salts in CH_3CN solution; estimated standard deviations in parentheses.

Table III. Infrared Spectra (520–300 cm^{-1}) of $[M(S_2CNEt_2)(M'S_4)]^-$ Complexes and Their Bis Ligand Analogues[a]

	absorption bands and assignts			
compd	$\nu(M'{=}S)$	$\nu(M'{-}S)$	$\nu(M{-}S{-}M')$	$\nu(M{-}S{-}C)$
$[Ni(S_2CNEt_2)(MoS_4)]^-$	508 vs, 500 vs	468 vs, 445 s	322 w	384 m
$[Ni(S_2CNEt_2)(WS_4)]^-$	492 vs, 486 vs	455 vs, 448 vs	*b*	396 s
$Ni(MoS_4)_2^{2-}$	515 vs, 499 vs	454 s, 439 s	*b*	
$Ni(WS_4)_2^{2-}$	497 vs, 494 vs	453 vs	330 m	
$Ni(S_2CNEt_2)_2$				392 w
$[Pd(S_2CNEt_2)(MoS_4)]^-$	510 vs, 503 vs	458 s, 437 s	313 s	373 s
$[Pd(S_2CNEt_2)(WS_4)]^-$	495 vs	449 vs, 443 vs	309 s	373 s
$Pd(MoS_4)_2^{2-}$	509 vs, 494 vs	450 s, 435 s	330 w	
$Pd(WS_4)_2^{2-}$	502 vs, 496 vs	447 vs	340 vs	
$Pd(S_2CNEt_2)_2$				359 s

[a] All values in cm^{-1}. Key: vs, very strong; s, strong; m, medium; w, weak. Spectra measured as Nujol mulls (Pr_4N^+ salts of all anions). [b] Too weak to observe or obscured by other bands.

B. Conductivity Studies. In order to completely characterize the products of these reactions, we measured the conductivities of these mixed-ligand complexes to confirm their formulation as monomers; some analogous sulfur-coordinated complexes have been shown to be dimers.[12,13] In order to discern between the 1:1 and 2:1 electrolyte formulations, R[MLL′] and $R_2[M_2L_2L'_2]$, it was necessary to use a method which would indicate the degree of polymerization, not just the empirical formula. With use of the Onsager limiting law, eq 4, from

$$\Lambda_0 - \Lambda_e = (a\Lambda_0 - b)c^{1/2} = Ac^{1/2} \quad (4)$$

a plot of the equivalent conductivity Λ_e vs. the square root of the equivalent concentration $c^{1/2}$, the equivalent conductivity at infinite dilution, Λ_0, is obtained as the intercept. The slope of this plot, *A*, is the more important parameter, as its value differs for 1:1 and 2:1 electrolytes. All four $[M(M'S_4)(S_2CNEt_2)]^-$ complexes behaved as 1:1 electrolytes, exhibiting *A* values close to that expected[14] (−320) for an ideal

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Table IV. Electronic Spectra[a]

compd	λ_{max} (ϵ)
$Ni(MoS_4)_2^{2-}$	30.3, 35.6, 40.3 sh, 46.1[b]
$[Ni(S_2CNEt_2)(MoS_4)]^-$	18.9 (5), 29.4 (24), 32.3 (42), 45.5 (56)
$Ni(S_2CNEt_2)_2$[c]	15.8, 21.2, 23.4, 25.8, 30.6[b]
$Pd(MoS_4)_2^{2-}$	21.4 (12), 26.3 sh, 28.7 (15), 32.0 (24), 36.5 sh, 37.3 (34)
$[Pd(S_2CNEt_2)(MoS_4)]^-$	20.8 (7), 29.0 (16), 33.1 (47), 48.8 (74)
$Pd(S_2CNEt_2)_2$	22.2, 28.8[b]
$Ni(WS_4)_2^{2-}$	14.3, 19.0, 23.5, 26.7, 30.3, 34.5, 38.2, 40.5, 47.6[b]
$[Ni(S_2CNEt_2)(WS_4)]^-$	14.9 (0.1), 22.7 (4), 32.3 (40), 43.5 (30), 48.8 (450)
$Pd(WS_4)_2^{2-}$	25.3 (21), 27.4 (21), 32.2 (21), 35.0 sh, 39.7 (20), 44.4[b]
$[Pd(S_2CNEt_2)(WS_4)]^-$	19.4 (0.2), 25.0 (8), 29.0 (14), 32.3 (33), 36.4 (30), 40.0 (23)

[a] Absorption maxima in cm^{-1}, extinction coefficients (ϵ) in L mol^{-1} cm^{-1}, CH_3CN solvent, anions measured as Pr_4N^+ salts. [b] Extinction coefficient(s) not determined. [c] $CHCl_3$ solution.

electrolyte in CH_3CN solution. *A* values of 2:1 electrolytes in the same solvent are reported to be ca. −760.[13] Values of these conductivity parameters for the mixed-ligand complexes are presented in Table II.

C. Infrared Spectra. The IR spectra of these mixed-ligand complexes were all similar and could best be distinguished by differences in the 500–300-cm^{-1} region where the M′=S and M—S—M′ bridge vibrations, among others, occur. The most identifiable bands are ν(M′=S), as expected, which appear between 480 and 490 cm^{-1} (M′ = W) and 500 and 510 cm^{-1} (M′ = Mo). The vibration assigned to the stretch of the M′—S bridge at ca. 450 cm^{-1} was also readily identified. Important vibrations of these complexes observed below 500 cm^{-1} are presented in Table III, where comparison with values for the respective bis ligand complexes is also made. It can be seen that the spectra of the mixed-ligand complexes closely resemble the sum of the spectra of the two bis ligand analogues. The only significant change arises in the bands assigned to ν(M′—S—Pd) in the two mixed-ligand complexes, where the observed absorptions occur 20 cm^{-1} lower than those of the analogous $Pd(M'S_4)_2^{2-}$ compounds; such shifts are not seen when M = Ni.

D. UV–Visible Spectra. The electronic spectra of the new complexes are presented in Table IV, where they are also compared with those of the corresponding bis ligand complexes. The spectra of the mixed-ligand compounds cannot be derived by simple superimposition of the spectra of their bis ligand analogues. This observation is consistent with our formulation of these compounds as mixed-ligand species, $[MLL']^-$, rather than a mixture of the bis ligand components, ML_2 + $[ML'_2]^{2-}$.

Experimental Section

Materials. Common reactants and solvents were reagent grade products of reputable manufacturers and used without further purification. K_2PdCl_4 and K_2PtCl_4 were purchased from Matthey-Bishop or Engelhard Industries. $(NH_4)_2WS_4$ and $(NH_4)_2MoS_4$ were prepared according to literature methods,[15,16] as were $Ni(S_2CNEt_2)_2$[17] and $Pd(S_2CNEt_2)_2$.[18] Sodium diethyldithiocarbamate was purchased from Sigma, and the Ni- and $Pd(M'S_4)_2^{2-}$ complexes were synthesized by previously described methods.[4] Tetrapropylammonium bromide was purchased from Eastman. Special anhydrous methanol (MCB) was dried over CaH_2 prior to use, and Spectrograde CH_3CN (Aldrich or MCB) was used without further purification.

Methods. Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Infrared spectra (550–50 cm^{-1}) were recorded on Digilab FTS-14 or -15B Fourier transform interferometers as Nujol mulls between polyethylene plates, at 2.0-cm^{-1} resolution. Conductivities were measured in Spectrograde CH_3CN with a Radiometer conductivity meter equipped with a cylindrical platinum cell calibrated with aqueous KCl solutions. UV–visible spectra were recorded on a Cary 14 spectrophotometer using Spectrograde CH_3CN solutions and matched quartz cells.

Cs_2MoOS_3 and Cs_2WOS_3. These materials were prepared by Muller's method[19] and obtained in 80 and 75% yield, respectively. Anal. Calcd for Cs_2MoOS_3: S, 20.29. Found: S, 20.02. Calcd for Cs_2WOS_3: S, 17.12. Found: S, 17.20.

$(Pr_4N)_2Ni(MoOS_3)_2$. To 30 mL of 1:1 (v/v) H_2O–CH_3CN was added 0.153 g (0.53 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.5 g of Pr_4NBr. The resulting solution was added dropwise to a suspension of Cs_2MoOS_3 in 40 mL of 1:1 H_2O–CH_3CN. A brown precipitate formed immediately. After addition of the Ni solution was complete, the brown solid was filtered off and washed with absolute methanol, water, absolute methanol, and anhydrous ether and vacuum-dried overnight. The yield was 75%. Anal. Calcd for $C_{24}H_{56}NiO_2S_6Mo_2$: C, 34.01; H, 6.66; N, 3.30; S, 22.69; Ni, 6.93; Mo, 22.64. Found: C, 33.47; H, 6.86; N, 3.46; S, 22.04; Ni, 7.14; Mo, 21.85.

$(Pr_4N)_2Ni(WOS_3)_2$. To a suspension of 0.842 g (1.49 mmol) of Cs_2WOS_3 in 10 mL of H_2O and 30 mL of CH_3CN was added dropwise a solution of 0.215 g (0.75 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$ in 10 mL of H_2O and 30 mL of CH_3CN. The resulting reaction mixture gradually changed from yellow to brown and was filtered after the addition was complete. A solution of 0.6 g of Pr_4NBr in 25 mL of H_2O was added to the filtrate, and the yellow-brown precipitate which formed was collected and recrystallized from nitromethane. The yield was 85%. Anal. Calcd for $C_{24}H_{56}N_2NiO_2S_6W_2$: C, 28.17: H, 5.52; N, 2.74; S, 18.80; Ni, 5.74; W, 35.93. Found: C, 28.19; H, 5.71; N, 2.88; S, 19.78; Ni, 6.64; W, 36.27.

$(Pr_4N)_2Pd(MoOS_3)_2$. A solution of 0.258 g (0.79 mmol) of K_2PdCl_4 in 10 mL of H_2O and 30 mL of CH_3CN was added dropwise to a stirred suspension of 0.75 g (1.59 mmol) of Cs_2MoOS_3 in 40 mL of 1:3 H_2O–CH_3CN. A deep purple solution resulted after a 10-min reaction period, and the solution was filtered after being stirred for 2 h to remove a small amount of black solid. A solution of 0.8 g of Pr_4NBr in 15 mL of CH_3CN was added dropwise to the filtrate, and the resulting solution was evaporated until a precipitate appeared and then stored at 0 °C overnight. The resulting purple-red crystals were filtered off and washed with anhydrous ethanol and ether. The yield was 61%. Anal. Calcd for $C_{24}H_{56}N_2PdO_2S_6Mo_2$: C, 32.20; H, 6.30; N, 3.13; S, 21.48; Pd, 11.88; Mo, 21.43. Found: C, 32.28; H, 6.52; N, 3.19; S, 21.13; Pd, 11.74; Mo, 20.91.

$(Pr_4N)_2Pd(WOS_3)_2$. This compound was prepared in a similar fashion to the one above. The red crystalline product was obtained in 84% yield. Anal. Calcd for $C_{24}H_{56}N_2PdO_2S_6W_2$: C, 26.91; H, 5.27; N, 2.61; S, 17.96; Pd, 9.93;, W, 34.33. Found: C, 26.98; H, 5.47; N, 2.88; S, 18.13; Pd, 10.00; W, 34.90.

$(Pr_4N)_2Pt(MoOS_3)_2$. A mixture of 0.307 g (0.74 mmol) of K_2PtCl_4 in 20 mL of 1:1 H_2O–Me_2SO was added dropwise to a stirring solution of Cs_2MoOS_3 (0.700 g, 1.48 mmol) in 40 mL of 1:3 H_2O–Me_2SO. The resulting deep purple mixture was stirred for 2 h before the addition of a solution of 1.0 g of Pr_4NBr in 20 mL of H_2O. The resulting red-orange precipitate was recrystallized from nitromethane and gave purple crystals in 72% yield. Anal. Calcd for $C_{24}H_{56}N_2PtO_2S_6Mo_2$: C, 29.30; H, 5.74; N, 2.85; S, 19.55; Pt, 19.83; Mo, 19.50. Found: C, 28.99; H, 5.94; N, 2.90; S, 19.20; Pt, 19.46; Mo, 19.80.

$(Pr_4N)_2Pt(WOS_3)_2$. A solution of 0.359 g (0.62 mmol) of K_2PtCl_4 in 20 mL of 1:1 Me_2SO–H_2O was added dropwise to a stirring solution of 0.700 g (1.24 mmol) of Cs_2WOS_3 in 40 mL of 1:3 H_2O–Me_2SO. A ruby red color developed instantly. After 2 h a solution of 1 g of Pr_4NBr in 20 mL of H_2O was added, and the resulting orange precipitate was filtered and recrystallized from nitromethane. The yield was 71%. Anal. Calcd for $C_{24}H_{56}N_2PtO_2S_6W_2$: C, 24.86; H, 4.87; N, 2.42; S, 16.59; Pt, 16.82; W, 31.71. Found: C, 24.34; H, 5.11; N, 2.70; S, 16.60; Pt, 16.42; W, 32.13.

$(Pr_4N)Ni(S_2CNEt_2)(MoS_4)$. $Ni(S_2CNEt_2)_2$ (0.200 g, 0.563 mmol) was dissolved in 100 mL of acetone, and to this green solution was added dropwise a red solution of 0.147 g (0.563 mmol) of $(NH_4)_2MoS_4$

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dissolved in 40 mL of a 1:3 (v/v) mixture of water and acetone. The resulting mixture was stirred at room temperature for 24 h and filtered, and a solution of 3.0 g of Pr_4NBr in 30 mL of acetone was added to the resulting filtrate. After a further hour of stirring, the resulting mixture was evaporated to $^2/_3$ the original volume and stored at 0 °C for 24 h, after which unreacted starting materials and byproducts were filtered off. The resulting filtrate was again cooled at 0 °C while small ruby red crystals appeared. The product was filtered and washed with water, absolute ethanol, and anhydrous ether. The yield was 60% (mp 149–150 °C dec). Anal. Calcd for $C_{17}H_{38}N_2NiS_6W$: C, 33.60; H, 6.20; N, 3.54; Ni, 9.50; S, 31.15; Mo, 15.50. Found: C, 33.04; H, 6.20; N, 4.53; Ni, 8.39; S, 29.68; Mo, 14.13.

$(Pr_4N)Ni(S_2CNEt_2)(WS_4)$. $Ni(S_2CNEt_2)_2$ (0.067 g, 0.189 mmol) was dissolved in 20 mL of acetone, and $(Pr_4N)_2Ni(WS_4)_2$ (0.200 g, 0.189 mmol) was added to this solution, along with 20 mL of acetonitrile. The resulting red solution became golden brown after being stirred at room temperature for 12 h. The solution was evaporated to half its volume and cooled in a refrigerator for 8 h; a small amount of side product precipitated and was filtered off. Further evaporation of the reaction mixture to a volume of 10 mL resulted in the appearance of crystals upon standing at room temperature overnight. The brown crystals of product were filtered, recrystallized from CH_2Cl_2, and washed successively with water, absolute ethanol, and anhydrous ether. The yield was 70% (mp 172–173 °C dec). Anal. Calcd for $C_{17}H_{38}N_2NiS_6W$: C, 28.94; H, 5.42; N, 3.97; Ni, 8.32; S, 27.30; W, 26.06. Found: C, 28.83; H, 5.38; N, 3.86; Ni, 7.26; S, 25.43; W, 25.71.

$(Pr_4N)Pd(S_2CNEt_2)(MoS_4)$. $Pd(S_2CNEt_2)_2$ (0.408 g, 1.01 mmol) was suspended in 50 mL of acetone, and $(NH_4)_2MoS_4$ (0.264 g, 1.01 mmol) was partially dissolved in 40 mL of 1:3 (v/v) H_2O–acetone. The two suspensions were combined and stirred for 12 h at room temperature, and the resulting reaction mixture was evaporated to half its original volume. At this point any unreacted starting materials and some byproducts were removed by filtration. To the filtrate was added dropwise a solution of 2.0 g of Pr_4NBr in 40 mL of acetone, and the resulting solution was stored overnight at 0 °C. The small amount of solid that had collected was filtered off and discarded, and the filtrate was further evaporated until small red crystals began to appear. The product was filtered and washed with water, ethanol, and ether. The yield was 65% (mp 173–174 °C). Anal. Calcd for $C_{17}H_{38}N_2PdS_6Mo$: C, 30.69; H, 5.76; N, 4.21; Pd, 15.99; S, 28.91; Mo, 14.42. Found: C, 30.69; H, 5.63; N, 3.99; Pd, 15.24; S, 28.88; Mo, 13.78.

$(Pr_4N)Pd(S_2CNEt_2)(WS_4)$. $(Pr_4N)_2Pd(WS_4)_2$ (1.00 g, 0.906 mmol) was dissolved in 70 mL of CH_3CN, and a solution of $Pd(S_2CNEt_2)_2$ (0.365 g, 0.906 mmol) in 30 mL of $CHCl_3$ was added dropwise to it. The resulting mixture was heated to reflux for 24 h, evaporated to half its original volume, and stored at 0 °C for 4 days. After this time small red crystals began to appear. The product was collected by filtration, recrystallized from hot CH_3CN, and washed with water, ethanol, and ether. The yield was 65% (mp 184–185 °C). Anal. Calcd for $C_{17}H_{38}N_2PdS_6W$: C, 27.11; H, 5.08; N, 3.72; Pd, 14.1; S, 25.50; W, 24.41. Found: C, 26.83; H, 4.96; N, 3.68; Pd, 14.3; S, 25.35; W, 24.23.

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Registry No. $(Pr_4N)_2Ni(MoOS_3)_2$, 77121-85-8; $(Pr_4N)_2Ni(WOS_3)_2$, 77121-86-9; $(Pr_4N)_2Pd(MoOS_3)_2$, 77071-56-8; $(Pr_4N)_2Pd(WOS_3)_2$, 77071-58-0; $(Pr_4N)_2Pt(MoOS_3)_2$, 77071-60-4; $(Pr_4N)_2Pt(WOS_3)_2$, 77071-62-6; $(Pr_4N)Ni(S_2CNEt_2)(MoS_4)$, 77071-64-8; $(Pr_4N)Ni(S_2CNEt_2)(WS_4)$, 77079-67-5; $(Pr_4N)Pd(S_2CNEt_2)(MoS_4)$, 77079-69-7; $(Pr_4N)Pd(S_2CNEt_2)(WS_4)$, 77071-66-0; $(PrN)_2Ni(WS_4)_2$, 73952-50-8; $(Pr_4N)_2Pd(WS_4)_2$, 77071-67-1; $Ni(S_2CNEt_2)_2$, 14267-17-5; $Pd(S_2CNEt_2)_2$, 15170-78-2; $(Pr_4N)_2Ni(MoS_4)_2$, 73952-49-5; $(Pr_4N)_2Pd(MoS_4)_2$, 73952-52-0; Cs_2MoOS_3, 14348-14-2; Cs_2WOS_3, 14348-13-1; K_2PdCl_4, 10025-98-6; K_2PtCl_4, 10025-99-7; $(NH_4)_2MoS_4$, 15060-55-6.

Additions and Corrections

1980, Volume 19

Avi Bino, F. Albert Cotton,* Pascual Lahuerta, P. Puebla, and R. Usón: *o*-Phenylenebis(dimethylarsine)decacarbonyltriiron. Preparation and Structure of a Compound with Two Semibridging Carbonyl Ligands.

Pages 2357–2359. The unit cell constants were incorrectly stated, but all molecular dimensions were calculated from the correct ones and are accurate. The correct cell constants are as follows: a = 9.538 (2) Å, b = 11.404 (2) Å, c = 24.070 (3) Å, β = 99.84 (1)°, V = 2580 (1) Å^3.—F. Albert Cotton

1981, Volume 20

Masato Nishizawa and Peter C. Ford*: Long-Wavelength Excitation of Hexacyanocobaltate(III), $Co(CN)_6^{3-}$, in Aqueous Solution. Questions Regarding Intersystem-Crossing Efficiencies.

Page 294. An unfortunate error appears in the byline of this paper. The name of the first author should be correctly spelled as follows: Masato Nishizawa—Peter C. Ford.