

eV, $H_{pp} = -6.06$ eV, $H_{dd} = -14.0$ eV, $\zeta_{s,p} = 2.2$, $\zeta_{d1} = 5.95$, $\zeta_{d2} = 2.3$, $c_1 = 0.5933$, $c_2 = 0.5744$ respectively. To calculate average properties for the 1-D cases a 100-point k-point set was used.¹⁶ The geometries used for calculations were as follows: Cu-Cu-

(monomer), 2.35 Å; Cu-Cu(polymer), 2.26 Å; N-N, 1.34 Å; Cu-N, 2.03 Å; N-H, 1.0 Å; Cu-N-N, 122.5°; N-N-N, 115.0°; H-N-N, 118.0°.

Registry No. [Cu(tolylN(N)N(N)Ntolyl)]₃, 96129-16-7; [Cu₃(tolylN(N)N(N)Ntolyl)₄]⁻, 114326-40-8; [Cu(tolylN(N)N(N)N(N)Ntolyl)]₄, 114350-60-6.

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Preparation and Properties of the Mo₂X₄(PMe₃)₄ Compounds with X = NCS and NCO

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The Mo₂X₄(PMe₃)₄ compounds where X = NCO and NCS are formed in a high-yield, one-pot reaction from Mo₂(O₂CCH₃)₄ and (CH₃)₃SiX in the presence of the phosphine. Both compounds crystallize in the tetragonal space group *P*4₂,₂ with the following unit cell dimensions. X = NCO: $a = b = 11.990$ (2) Å, $c = 20.271$ (2) Å, $V = 2914$ (1) Å³, $Z = 4$. X = NCS: $a = b = 12.556$ (1) Å, $c = 21.033$ (4) Å, $V = 3316$ (1) Å³, $Z = 4$. Both molecules consist of quadruply bonded molybdenum atoms with trans phosphines and X groups as ligands. Electrochemical and spectroscopic properties of these compounds have been investigated and correlated with other compounds where X = Cl, Br, and I.

Introduction

Mo₂X₄L₄ complexes are among the most often studied multiple-bonded dimetal complexes. They have contributed much to the understanding of the nature of the multiple bonds between metal atoms.¹ In the past, conclusions have been drawn on some incomplete classes of these compounds. Recently the discovery of some new compounds, namely Mo₂I₄(PMe₃)₄² and Mo₂I₄(dppe)₂,³ has shed some new light on the subject. The Mo₂X₄(PMe₃)₄ (X = Cl, Br, I) set has received the most attention, because of the simplicity of the system, but two other classes, Mo₂X₄(dppe)₂ (X = Cl, Br, I) and Mo₂X₄(dppm)₂ (X = Cl, Br, I, NCS), have also been investigated and structurally characterized. In view of their theoretical importance, we decided to extend the Mo₂X₄(PMe₃)₄ series with some new compounds. As a part of our recent interest⁴ in the thiocyanate chemistry of M₂ species, we have prepared Mo₂(NCS)₄(PMe₃)₄. By the same synthetic route Mo₂(NCO)₄(PMe₃)₄ was also prepared. These two compounds, together with the Cl, Br, and I derivatives, form the largest known class of quadruply bonded, homologous compounds. In this study we report the preparation and molecular structures of these two new compounds, as well as their spectroscopic and electrochemical properties. The relationship between the energy of the δ - δ^* transition and the first reduction potential for the entire class has been examined.

Experimental Section

All reactions were done under anaerobic conditions. Me₃SiNCO and Me₃SiNCS were purchased from Aldrich Chemical Co. Trimethylphosphine was purchased from Strem Chemicals Inc.

Preparation of Mo₂(NCO)₄(PMe₃)₄ (1). A round-bottom flask was charged with 1.0 g (2.3 mmol) of Mo₂(O₂CCH₃)₄, 0.858 g (11 mmol) of PMe₃, 1.26 g (11 mmol) of Me₃SiNCO, and 50 mL of toluene. The reaction mixture was stirred at room temperature for 2 days and then evaporated to dryness. The solid residue was dissolved in hot toluene (about 150 mL), and the mixture was filtered hot through a short Celite column. The solution was refrigerated overnight to give well-formed crystals of the product, which were filtered out, washed with hexane, and vacuum-dried. The yield was 1.2 g (72% based on Mo) of blue-black

crystals. They are soluble in THF, benzene, and CH₂Cl₂ to give sky blue solutions. The compound can be handled in the air in the solid state but decomposes slowly in solution. UV-vis (CH₂Cl₂ solution): $\lambda = 617$ nm ($\epsilon = 8050$ M⁻¹ cm⁻¹), $\lambda = 460$ nm ($\epsilon = 430$ M⁻¹ cm⁻¹), $\lambda = 330$ nm ($\epsilon = 12370$ M⁻¹ cm⁻¹). The same λ_{max} values were recorded for the THF solution of the compound. IR (cm⁻¹): 2210 vs, 1380 m, 1345 m, 1305 m, 1290 m, 960 s, 865 w, 855 w, 750 m, 680 m, 620 m, 380 m. ³¹P NMR: -8.30 ppm (s).

Mo₂(NCS)₄(PMe₃)₄ (2). The experimental procedure is essentially the same as that described above. Isolated yields were typically 80% of a dark green crystalline solid. Solubility and stability are similar to those of the NCO derivative. UV-vis (CH₂Cl₂ solution): $\lambda = 670$ nm ($\epsilon = 6680$ M⁻¹ cm⁻¹), $\lambda = 497$ nm ($\epsilon = 380$ M⁻¹ cm⁻¹), $\lambda = 395$ nm ($\epsilon = 23100$ M⁻¹ cm⁻¹). IR (cm⁻¹): 2040 vs, 1380 m, 1310 m, 1290 m, 960 s, 870 m, 810 m, 805 m, 750 m, 745 m, 625 m, 490 m, 360 m. ³¹P NMR: -6.8 ppm (s). Anal. Calcd for Mo₂S₂P₄N₄C₁₆H₃₆: C, 26.40; H, 4.98; N, 7.69. Found: C, 26.65; H, 5.08; N, 7.54.

Mo₂(NCS)₄(PMe₃)₄ could also be prepared by an alternative procedure: Mo₂Cl₄(PMe₃)₄, 0.20 g (0.313 mmol), KSCN, 0.122 g (1.25 mmol), and 15 mL of MeOH were refluxed for 24 h. The reaction mixture turned from fluorescent red-blue to green during this time. It was cooled and filtered. The solid residue was washed with a small amount of MeOH and extracted with boiling toluene. The toluene solution was filtered hot through a Celite bed and refrigerated. Next day the crystalline product was filtered out and vacuum-dried. The yield was 0.144 g (53%). The spectroscopic (UV-vis, ³¹P NMR) and electrochemical properties were identical with those of the sample obtained by the Me₃SiNCS method.

We were unable to obtain Mo₂(NCO)₄(PMe₃)₄ by the similar ligand-exchange reaction.

Measurements. Elemental analyses were performed by Galbraith Laboratories Inc. IR spectra were recorded as Nujol mulls on KBr plates (4000-600 cm⁻¹) or CsI plates (600-300 cm⁻¹) with a Perkin-Elmer 785 spectrophotometer. The electronic spectra were recorded on dichloromethane solutions (Aldrich, HPLC grade) with a Cary 17D spectrophotometer. Electrochemical measurements were done with a BAS-100 electrochemical analyzer, employing 0.2 M tetra-*n*-butylammonium hexafluorophosphate solutions in THF or CH₂Cl₂. A three-electrode configuration was used with platinum working and auxiliary electrodes and a silver-silver chloride reference electrode. The potentials are corrected for the solution resistance. Under the experimental conditions, ferrocene is oxidized at $E_{1/2} = 0.510$ V in CH₂Cl₂ and $E_{1/2} = 0.595$ V in THF. ³¹P NMR samples were recorded on CDCl₃ solutions with a Varian XL 200 spectrometer and are referenced to 85% H₃PO₄.

X-ray Crystallography

Single crystals of compounds 1 and 2, obtained as described in the experimental section, were glued on top of glass fibers. Indexing revealed tetragonal cells, Laue class (*4/mmm*), and axial dimensions were con-

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Table I. Crystallographic Data for $\text{Mo}_2(\text{NCO})_4(\text{PMe}_3)_4$ (**1**) and $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$ (**2**)

formula	$\text{Mo}_2\text{P}_4\text{O}_4\text{N}_4\text{C}_{16}\text{H}_{36}$	$\text{Mo}_2\text{S}_4\text{P}_4\text{N}_4\text{C}_{16}\text{H}_{36}$
fw	664.27	728.52
space group	$P4_32_12$	$P4_32_12$
syst absences	0k0: $k \neq 2n$ 00l: $l \neq 4n$	0k0: $k \neq 2n$ 00l: $l \neq 4n$
a, Å	11.990 (1)	12.556 (1)
b, Å	11.990 (1)	12.556 (1)
c, Å	20.271 (4)	21.033 (4)
α , deg	90.0	90.0
β , deg	90.0	90.0
γ , deg	90.0	90.0
V, Å ³	2914 (1)	3316 (1)
Z	4	4
d_{calcd} , g/cm ³	1.514	1.459
cryst size, mm	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.4
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	10.819	11.834
data colln instrument	AFC5R	P3
radiation (monochromated in incident beam)	Mo K α ($\lambda_a = 0.71073$ Å)	
orientation refls: no.; range (2 θ), deg	25, 16 < 2 θ < 30	25, 20 < 2 θ < 30
temp, °C	22	20
scan method	ω	ω
data colln range, 2 θ , deg	4 < 2 θ < 55	4 < 2 θ < 45
total no. of unique data	2012	1299
no. of data for $F_o^2 > 3\sigma(F_o^2)$	1389	946
no. of parameters refined	136	188
trans factors: max, min		0.996, 0.938
R^a	0.0491	0.02618
R_w^b	0.0713	0.03249
quality-of-fit indicator ^c	1.505	0.669
largest shift/esd, final cycle	0.03	0.24
largest peak, e/Å ³	1.017	0.47

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^cQuality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

firmed with oscillation photographs. The space group was determined to be $P4_32_12$ or its enantiomorph, $P4_32_12$, which differs in the sense of rotation about the 4-fold axis. For compound **1**, only the unique part of the data was collected up to 55° in 2 θ . In the case of compound **2** the data were collected as for the Laue class 4/m (0 → h, 0 → k, 0 → l) and later successfully averaged. Data processing was routine to our laboratory.⁵ Lorentz, polarization, and absorption corrections⁶ based on selected ψ scans were applied.

Mo₂(NCO)₄(PMe₃)₄ (1). The structure was solved with the Patterson interpretation provided by the SHELXS-86.⁷ Refinement proceeded routinely, but two of the carbon atoms could not be located from the difference Fourier map. At this point the enantiomorph was changed, and also the space group was changed to $P4_32_12$. A difference Fourier map now revealed the two missing atoms as top peaks. The isotropic refinement converged with the agreement factors $R = 0.06924$ and $R_w = 0.09654$. As a double check, the structure was taken back to the $P4_32_12$ space group and refined to give agreement factors $R = 0.07002$ and $R_w = 0.09691$. The refinement was then continued in $P4_32_12$. The structure was refined with all non-hydrogen atoms anisotropic. Hydrogen atoms were added at calculated distances⁸ with a common thermal parameter included in the refinement. Relevant crystallographic and procedural information is given in Table I. The cyanate groups were treated as N-bonded (for reasons given in the Discussion).

Mo₂(NCS)₄(PMe₃)₄ (2). The solution of the structure was initiated in the space group $P4_32_12$ with the position of the Mo atoms taken from the structure of **1**. Least-squares refinement and a difference Fourier map revealed all but two of the non-hydrogen atoms. These missing atoms could not be located in an additional difference Fourier map. At this point the enantiomorph and the space group was changed to $P4_32_12$ and, as before, the missing atoms were easily located in a difference Fourier map. The refinement converged to give $R = 0.02618$ and $R_w =$

Table II. Positional Parameters and Their Estimated Standard Deviations

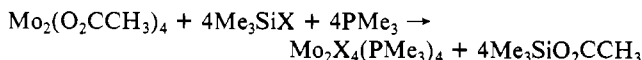
atom	x	y	z	B_i^a , Å ²
Mo₂(NCO)₄(PMe₃)₄				
Mo	0.92507 (7)	0.95852 (7)	0.77002 (4)	3.12 (2)
P(1)	1.0377 (2)	0.8655 (3)	0.8592 (1)	4.37 (6)
P(2)	0.7513 (2)	0.9913 (2)	0.7012 (1)	3.76 (6)
O(10)	0.9733 (9)	0.6227 (8)	0.6850 (6)	8.8 (3)
O(20)	0.754 (1)	1.106 (1)	0.9404 (4)	9.0 (3)
N(10)	0.9409 (8)	0.8068 (7)	0.7211 (5)	4.9 (2)
N(20)	0.8384 (7)	1.0338 (8)	0.8458 (4)	4.5 (2)
C(1)	1.094 (1)	0.948 (1)	0.9263 (5)	6.2 (3)
C(2)	0.948 (1)	0.768 (1)	0.8984 (7)	8.0 (4)
C(3)	1.150 (1)	0.7739 (9)	0.8374 (6)	5.6 (3)
C(4)	0.7547 (9)	0.956 (1)	0.6137 (4)	4.8 (3)
C(5)	0.683 (1)	1.125 (1)	0.7030 (6)	5.6 (3)
C(6)	0.648 (1)	0.892 (1)	0.7333 (7)	7.2 (4)
C(10)	0.956 (1)	0.718 (1)	0.7043 (6)	5.3 (3)
C(20)	0.7955 (9)	1.072 (1)	0.8951 (5)	4.7 (3)
Mo₂(NCS)₄(PMe₃)₄				
Mo	0.92786 (5)	0.96320 (5)	0.77140 (3)	3.39 (1)
S(10)	0.9745 (2)	0.6154 (2)	0.6766 (2)	7.21 (7)
S(20)	0.7292 (2)	1.1126 (3)	0.9455 (1)	7.26 (7)
P(1)	1.0367 (2)	0.8797 (2)	0.85989 (9)	4.40 (5)
P(2)	0.7573 (2)	0.9896 (2)	0.7080 (1)	4.77 (5)
N(10)	0.9456 (5)	0.8177 (5)	0.7248 (3)	4.1 (1)
N(20)	0.8503 (5)	1.0433 (6)	0.8442 (3)	4.9 (2)
C(1)	0.9451 (8)	0.7936 (9)	0.9039 (4)	7.1 (3)
C(2)	1.0944 (7)	0.9615 (9)	0.9220 (4)	6.4 (3)
C(3)	1.1446 (8)	0.7908 (7)	0.8399 (4)	6.2 (3)
C(4)	0.7577 (7)	0.9556 (9)	0.6254 (4)	6.2 (3)
C(5)	0.6578 (9)	0.8986 (8)	0.7417 (6)	7.7 (3)
C(6)	0.6921 (9)	1.1177 (9)	0.7113 (4)	7.7 (3)
C(10)	0.9553 (7)	0.7320 (7)	0.7047 (4)	4.5 (2)
C(20)	0.8006 (6)	1.0726 (7)	0.8873 (4)	4.4 (2)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

0.03249. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map, assigned a common thermal parameter, and refined.

Results and Discussion

Synthesis. The route utilized here has been shown to be of a great synthetic value in preparing molybdenum halophosphine complexes.⁹⁻¹³ It has also found some use for other elements like Ru, Os, and Rh. The reaction scheme is outlined as follows:



The driving force of the reaction is the formation of a very stable Si-O bond. Some Si-X bond energies¹⁴ are as follows (kJ/mol): Si-O, 466; Si-Cl, 400; Si-Br, 330; Si-N, 333; Si-C, 307; Si-F, 597. This indicates that from a thermodynamic point of view almost any group (with the notable exception of F) can be introduced by means of this reaction. The byproduct, Me_3SiOAc , is a volatile liquid that can be easily removed from the reaction mixture. Although this type of reaction has been known for a number of years, there has been previously little use of the Me_3SiX reagents with X other than halogen. In this study we have shown for the first time that this route has a more general utility and that NCS^- and NCO^- groups can be introduced via the appro-

(5) Calculations were done on a MicroVax II with SDP Plus package software.

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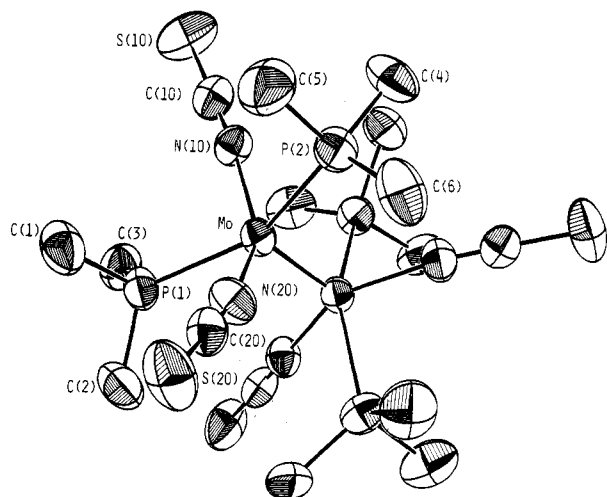


Figure 1. ORTEP drawing of the Mo₂(NCS)₄(PMe₃)₄ molecule, including the atom-labeling scheme, drawn at the 50% probability level.

Table III. Bond Distances (Å) and Bond Angles (deg) for Mo₂(NCO)₄(PMe₃)₄^a

Distances			
Mo-Mo	2.134 (1)	O(10)-C(10)	1.22 (2)
Mo-P(1)	2.517 (3)	O(20)-C(20)	1.12 (1)
Mo-P(2)	2.538 (3)	N(10)-C(10)	1.13 (2)
Mo-N(10)	2.081 (9)	N(20)-C(20)	1.21 (1)
Mo-N(20)	2.063 (9)		
Angles			
Mo-Mo-P(1)	102.24 (8)	P(2)-Mo-N(10)	87.0 (3)
Mo-Mo-P(2)	103.10 (7)	P(2)-Mo-N(20)	85.9 (2)
Mo-Mo-N(10)	109.3 (3)	N(10)-Mo-N(20)	141.6 (4)
Mo-Mo-N(20)	109.1 (3)	Mo-N(10)-C(10)	169 (1)
P(1)-Mo-P(2)	154.7 (1)	Mo-N(20)-C(20)	172.7 (8)
P(1)-Mo-N(10)	84.6 (3)	O(20)-C(20)-N(20)	179 (1)
P(1)-Mo-N(20)	86.0 (3)	O(10)-C(10)-N(10)	179 (1)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

appropriate Me₃SiX reagent. The reactions proceed in excellent yield, and the products can be easily isolated. The Mo₂(NCS)₄(PMe₃)₄ compound can also be prepared by a ligand-exchange reaction from Mo₂Cl₄(PMe₃)₄ and KSCN in refluxing methanol as solvent. This route has previously been employed by Walton¹⁵ and co-workers to prepare Mo₂(NCS)₄(PEt₃)₄. We are currently investigating the reactivity of other Me₃SiX (among others X = N₃, CN) reagents.

Molecular Structures. Compounds **1** and **2** are isotopic. Fractional coordinates for both are listed in Table II, and the molecular structure and atom-numbering scheme for the thiocyanate are shown in Figure 1. The molecular structure of the cyanate is very similar, and the atom numbering is the same except for O(10) and O(20) replacing S(10) and S(20). Selected bond distances and angles are given in Tables III and IV.

The Mo-Mo distances refined to the same value, namely, 2.134 (1) Å, which is similar to those found in numerous other complexes of Mo₂⁴⁺ that have no bridging ligands.¹ The Mo-P distances, similar in the two compounds, are in the range 2.517 (3)-2.544 (3) Å, which is typical for Mo₂X₄(PMe₃)₄ molecules in general. The Mo-N-C-X chains are all approximately linear, as can be seen in Tables III and IV. It is clear that in the thiocyanato compound the ions are N-bonded, as in all previous cases where thiocyanate ions serve as ligands to quadruply bonded Mo₂⁴⁺ and Re₂⁶⁺ units.

In the cyanato compounds, because of the very similar sizes and scattering factors for N and O, a decision between N- and O-bonding was not so straightforward. We have decided in favor of N-bonding on the basis of the following considerations.

Table IV. Bond Distances (Å) and Bond Angles (deg) for Mo₂(NCS)₄(PMe₃)₄^a

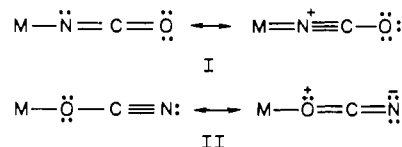
Distances			
Mo-Mo	2.134 (1)	S(10)-C(10)	1.597 (9)
Mo-P(1)	2.536 (2)	S(20)-C(20)	1.599 (8)
Mo-P(2)	2.544 (2)	N(10)-C(10)	1.16 (1)
Mo-N(10)	2.085 (6)	N(20)-C(20)	1.16 (1)
Mo-N(20)	2.074 (6)		
Angles			
Mo-Mo-P(1)	103.26 (6)	P(2)-Mo-N(10)	87.6 (2)
Mo-Mo-P(2)	103.60 (6)	P(2)-Mo-N(20)	85.9 (2)
Mo-Mo-N(10)	107.2 (2)	N(10)-Mo-N(20)	145.3 (3)
Mo-Mo-N(20)	107.5 (2)	Mo-N(10)-C(10)	173.3 (6)
P(1)-Mo-P(2)	153.11 (8)	Mo-N(20)-C(20)	169.3 (7)
P(1)-Mo-N(10)	85.7 (2)	S(10)-C(10)-N(10)	177.3 (8)
P(1)-Mo-N(20)	84.9 (2)	S(20)-C(20)-N(20)	178.4 (7)

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

(1) Both the N- and O-bonded models were refined to convergence, and the former gave significantly lower residuals, viz., $R = 0.0446$ and $R_w = 0.0605$ as against $R = 0.0468$ and $R_w = 0.0641$.

(2) When the O-bonded model was refined, the relative values of the thermal displacement parameters were unreasonable, with the inner atom (assigned as O) having a larger parameter than the outer atom (assigned as N). On the other hand, with the Mo-N-C-O model, the thermal ellipsoid of O was larger than that for N, as would be expected. The results for the O-bonded model indicate that too much electron density is being assigned to the inner atom and too little to the outer one, leading to thermal parameters that tend to compensate for this.

(3) The near linearity of the Mo-N-C-O chains is more consistent with the N-bonded model. For the resonance hybrid I linearity seems more credible than for II.



(4) The bond distances are consistent with the Mo-N-C-O arrangement (though not necessarily inconsistent with the O-bonded model). The Mo-N distances are not significantly different from those in the Mo-NCS groups. The N-C and C-O distances show so much scatter as to be inconclusive, although the average of the N-C distances, 1.17 [4] Å, is about equal to that, 1.16 [1] Å, in the thiocyanate.

This is not the first time that the question of the bonding mode in a cyanate complex has been difficult to answer.¹⁶ The case of (C₅H₅)₂Ti(NCO)₂¹⁷ is, perhaps, even more inconclusive than the present one.

One final point concerning the structures has to do with the fact that these two compounds form chiral crystals ($P4_32_12$) despite the fact that the molecules are perfectly capable of adopting centrosymmetric (eclipsed) conformations. Instead, however, they have only C₂ symmetry, with the C₂ axis being a perpendicular bisector of the Mo-Mo bond, and show slight torsional twists, of 0.45° in **1** and 1.45° in **2**, about that bond.

Spectroscopic and Electrochemical Properties. Some spectroscopic results have already been cited in the Experimental Section. The ³¹P NMR spectra show only singlets. The results to be discussed here, along with those previously reported for the Mo₂X₄(PMe₃)₄ compounds with X = Cl, Br, and I, are collected in Table V. The UV-visible spectrum of Mo₂(NCS)₄(PMe₃)₄, shown in Figure 2, resembles closely that of Mo₂(NCS)₄(PEt₃)₄.¹⁵ It consists of two main absorption bands as well as some weaker ones. The two main bands may be assigned in accord with previous

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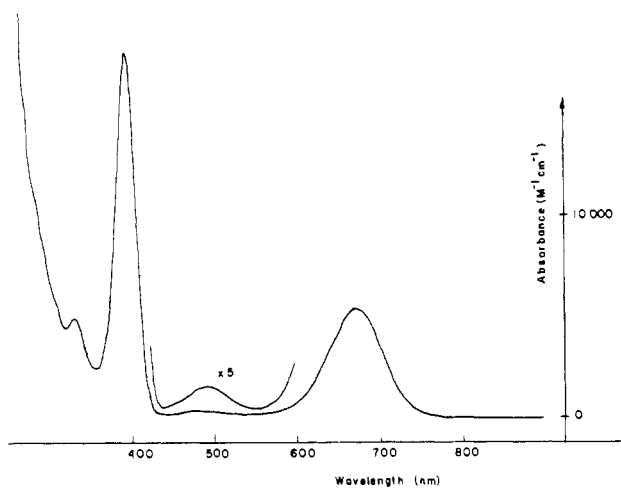
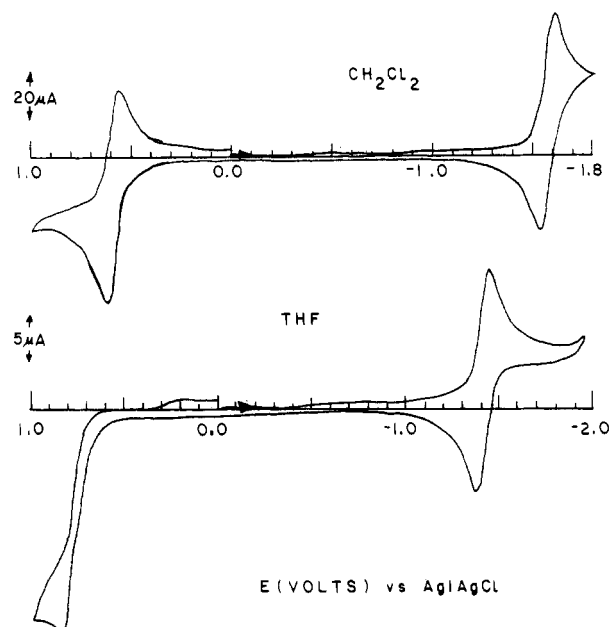
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Table V. Selected Properties of $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$ Compounds

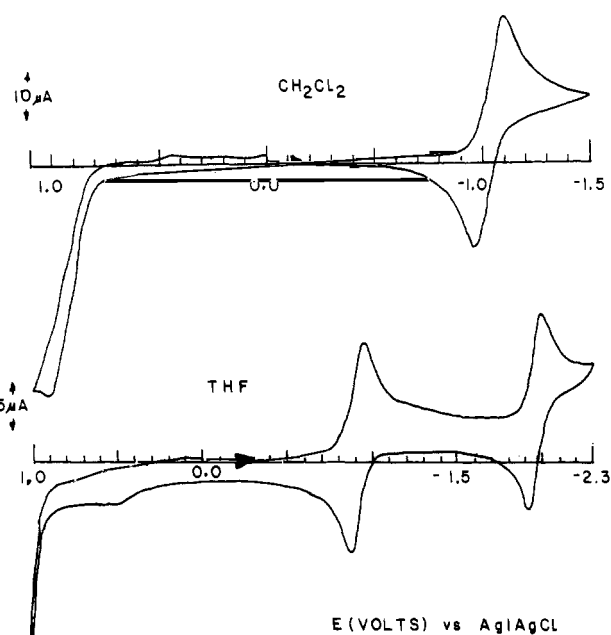
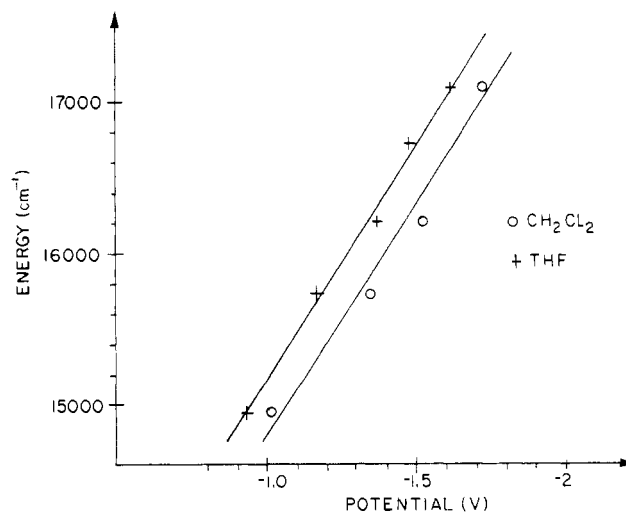
	$\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$	$\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4^a$	$\text{Mo}_2\text{I}_4(\text{PMe}_3)_4$	$\text{Mo}_2(\text{NCO})_4(\text{PMe}_3)_4$	$\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$	
THF	$E_{1/2}(\text{red}), \text{V}$	-1.62	-1.48	-1.17	-1.42	-0.93
	$E_{1/2}(\text{red}), \text{V}$					-1.95
	$E_{1/2}(\text{ox}), \text{V}$	+0.77	+0.87	+0.96	+0.83 ^b	+1.0 ^b
CH_2Cl_2	$E_{1/2}(\text{red}), \text{V}$	-1.72		-1.35	-1.57	-1.01
	$E_{1/2}(\text{ox}), \text{V}$	+0.50	+0.59	+0.73	+0.60	+1.0 ^b
$\delta \rightarrow \delta^*$, cm^{-1}	17240	16720	15800	16210	14930	
full width at half-height, cm^{-1}	1770		1720	1730	1785	
ϵ , $\text{M}^{-1} \text{cm}^{-1}$	3100	4060	5210	8050	6680	
LMCT, cm^{-1}	30860	28980	25320	30300	25320	
full-width at half height, cm^{-1}	2600	2030	1480	3130	1870	
ϵ , $\text{M}^{-1} \text{cm}^{-1}$	3700	6650	11000	12370	23100	
M-M dist, Å	2.130 (0)	2.125 (1)	2.127 (1)	2.134 (1)	2.134 (1)	

^aData taken from ref 2. ^bIrreversible electrochemical process.

Figure 2. UV-vis spectrum of $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$.Figure 3. Cyclic voltammograms of $\text{Mo}_2(\text{NCO})_4(\text{PMe}_3)_4$.

assignments: the one at 670 nm is due to the $\delta \rightarrow \delta^*$ transition while the one at 330 nm is caused by a ligand-to-metal charge-transfer transition.

We turn now to the electrochemical behavior. It is important to note that there is considerable dependence upon the solvent used, as can be seen in Figures 3 and 4. $\text{Mo}_2(\text{NCO})_4(\text{PMe}_3)_4$ (Figure 3) has a reversible oxidation and a reversible reduction in CH_2Cl_2 ; when the solvent is changed to THF, both potentials are shifted (ca. 0.1 V) to more positive values and the oxidation becomes

Figure 4. Cyclic voltammograms of $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$.Figure 5. Relationship between $\delta \rightarrow \delta^*$ transition energy and reduction potential for $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCO}, \text{NCS}$).

irreversible. For $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$ (Figure 4) in THF, there are two reversible reduction waves, but in CH_2Cl_2 the one at the most negative potential lies beyond the reduction potential of the solvent and cannot be observed. For $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ and $\text{Mo}_2\text{I}_4(\text{PMe}_3)_4$ we remeasured the cyclic voltammograms, since the compounds were on hand. Our results agreed well with those reported in the literature.¹⁸ See also ref 19 for electrochemistry

of additional dimolybdenum thiocyanato compounds.

In Figure 5 we present a plot of the $\delta \rightarrow \delta^*$ transition energies versus the first reduction potentials (not available for $\text{Mo}_2\text{Br}_4(\text{PMe}_3)_4$ in CH_2Cl_2). There is a good linear relationship, especially for the reductions measured in THF. Because of the ease of reduction of $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$, we are exploring the possibility that a compound containing the $[\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4]^-$ ion may be obtainable.

It is clear from Table V that over the series of five $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$ compounds, the Mo-Mo distance is essentially constant, despite the large variation in $E_{1/2}$ and $\delta \rightarrow \delta^*$ values. The conclusion we draw from the combined data is that the changes in X have little influence on the energy of the HOMO (δ orbital)

but, rather, they change the energy of the LUMO (δ^*). Our observations also support and extend the work of Gray et al.,² who suggested that the $\delta \rightarrow \delta^*$ transition borrows intensity from the lowest LMCT band. Whether this relationship is capable of quantitative expression, however, remains uncertain. No doubt, experimental data on additional $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$ compounds would be informative, and we are trying to prepare several of them, especially the $\text{Mo}_2\text{F}_4(\text{PMe}_3)_4$ molecule, which may be the most important one to have.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Full listings of bond distances and angles, anisotropic thermal parameters, and positional parameters including those of hydrogen atoms for $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$, a cell packing diagram for $\text{Mo}_2(\text{NCS})_4(\text{PMe}_3)_4$, and a labeled PLUTO drawing for $\text{Mo}_2(\text{NCO})_4(\text{PMe}_3)_4$ (11 pages); listings of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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A New Sulfur-Bridged Ir(I)-Ir(I) Compound and Its Conversion to a Compound Containing a Metal-Metal Bond. Crystal Structures of $\text{Ir}_2(\text{SPh})_2(\text{COD})_2$ and $\text{Ir}_2\text{Cl}_2(\mu_2\text{-SPh})_2(\text{COD})_2$

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The thiolato-bridged dinuclear compound $\text{Ir}_2(\text{SPh})_2(\text{COD})_2$ (**1**) was obtained from the alkoxide-bridged analogue by ligand exchange. **1** crystallizes in the space group $P2_1/c$ with $a = 11.249$ (6) Å, $b = 11.564$ (5) Å, $c = 19.568$ (10) Å, $\beta = 100.28$ (5)°, and $Z = 4$. The dinuclear molecule consists of Ir atoms with square-planar coordination sharing a S-S edge. The Ir-Ir separation of 3.181 (1) Å agrees with the assumed absence of a bond. The dinuclear compound is nonrigid in solution. Upon oxidative addition of halogens (Br_2 , I_2), the dimeric M-M-bonded compounds of Ir(II), $\text{Ir}_2\text{X}_2(\mu_2\text{-SPh})_2(\text{COD})_2$, are obtained. Alternatively, the Br and I derivatives can be prepared by electrochemical reduction of $\text{Ir}_2(\mu_2\text{-X})_2\text{X}_2(\text{COD})_2$ (X = Br, I), followed by oxidative addition of PhSSPh. The chloro analogue, **2**, was prepared by oxidative addition of PhSSPh to $\text{Ir}_2\text{Cl}_2(\text{COD})_2$ and was structurally characterized. It crystallizes in the space group $P\bar{1}$ with $a = 8.370$ (2) Å, $b = 12.155$ (1) Å, $c = 13.184$ (2) Å, $\alpha = 94.33$ (1)°, $\beta = 97.63$ (2)°, $\gamma = 96.47$ (1)°, and $Z = 2$. The molecules are M-M-bonded dimers consisting of edge-sharing square pyramids. The Ir-Ir bond length is 2.800 (1) Å. The ¹³C and ¹H NMR spectra indicate that the solid-state structure is retained in solution. The phenyl rings of the thiolate bridges exhibit a syn relationship with respect to the four-membered [IrS]₂ core, and the mean planes of the phenyl rings are approximately perpendicular to the Ir-Ir vector. The average Ir-S bond length is 2.345 (2) Å. Other important bond lengths and angles are given in Table III.

Introduction

Diiridium(II) compounds containing iridium-iridium bonds are far fewer than the homologous dirhodium(II) compounds. Only a limited number of examples are known containing pyrazolate,¹ thiolato,² and other different bridging ligands.³ There is only one example reported of a diiridium(II) compound with no bridging ligand supporting the iridium-iridium bond.⁴

We have recently found⁵ that by reacting $\text{Ir}_2(\text{OMe})_2(\text{COD})_2$ with iodine a new Ir(II) complex, $\text{Ir}_2(\mu_2\text{-I})_2\text{I}_2(\text{COD})_2$, was obtained, which we used as starting material for the synthesis of cluster compounds.

We report here the preparation of several thiolato-bridged iridium compounds and the crystal structures of $\text{Ir}_2(\text{SPh})_2(\text{COD})_2$ and $\text{Ir}_2\text{Cl}_2(\mu_2\text{-SPh})_2(\text{COD})_2$.

Experimental Section

$\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Engelhard Industries and diphenyl disulfide from Aldrich Chemical Co. All manipulations were done under

dry nitrogen or argon. The solvents were of analytical grade and were distilled under nitrogen prior to use. $\text{Ir}_2\text{Cl}_2(\text{COD})_2$ ⁶ and $\text{Ir}_2(\text{OME})_2$

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