

It is not clear that this mechanism can rationalize the observed results exactly.

The results of initial kinetic studies based on spectrophotometric monitoring have shown that the mechanism of water oxidation is complex kinetically and may involve more than one pathway and at least one discernible intermediate. Additional studies will be required before distinctions can be drawn among the various mechanistic possibilities.

Comparison to Photosynthesis. The ruthenium complex may or may not serve as a model for the oxygen-evolving complex (OEC) of photosystem II. Only one oxygen-labeling study has addressed directly the question of the source of the oxygen atoms that are coupled to the production of dioxygen in photosynthesis.⁵ In the study, chloroplasts in the S_1 state were equilibrated with ^{18}O -labeled or unlabeled water for several minutes at 11 °C, and were preflashed once or twice to achieve the S_2 or S_3 states. The samples were then diluted with unlabeled water for approximately 1 min and flashed sequentially, with the isotopic yield of dioxygen determined mass spectrometrically. Only unlabeled dioxygen was observed in all cases. On the basis of these results, either (1) the OEC in S_1 chloroplasts does not exchange water at all in several minutes, (2) the S_2 and S_3 chloroplasts exchange completely with water in 1 min, or (3) the oxidation of water by the OEC does not involve bound water. Although the results for the OEC appear to differ considerably from those obtained for the ruthenium complex, the mechanisms could be the same. The difference between the two could lie in differences in available exchange pathways rather than in a difference in oxidation mechanism.

Acknowledgments are made to the National Institutes of Health under Grant No. 5-RO1-GM32296-06 and the National Science Foundation under Grant No. CHE-8806664 for support of this research.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Novel Ambidentate and Chelate Complexes of Ruthenium with Methylenebis(1,3,2-dithiaphospholane) and (Methylimino)bis(1,3,2-dithiaphospholane) as Ligands

Sangha Kim, Marie Pontier Johnson, and D. Max Roundhill*

Received October 30, 1989

Diphosphorus compounds having either a single methylene group or an amino group between the two phosphorus nuclei have been variously used as chelating and bridging ligands to transition-metal centers.¹ A research area of growing importance is the use of these complexes in photochemical reactions and catalysis.² A potential drawback to such applications is the possibility that either the ground or excited state of the complex can undergo irreversible cyclometalation with functional groups at the ligand periphery.³ A plausible approach to the use of diphosphorus ligands in these complexes, while minimizing the likelihood of cyclometalation side reactions, is to employ small rings as peripheral substituents at phosphorus. In this note, we report the synthesis of several new ligands of this type and show how, in complexation with ruthenium(II), chelation via phosphorus and a ring heteroatom can occur to circumvent ring strain.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. The compounds $\text{CH}_2(\text{PCl}_2)_2$, $\text{CH}_3\text{N}(\text{PCl}_2)_2$, and $\text{RuCl}_2(\text{PPh}_3)_3$ were synthesized according to the literature procedures.⁴ All solvents were dried and distilled under nitrogen. Ethylene glycol was purified by distillation and catechol by sublimation. Ethanedithiol and DABCO were used as received from Aldrich. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a Bruker AC200 spectrometer. The NMR simulation for $\text{RuCl}_2(\text{pcps})_2$ was performed by using the PANIC software routine.⁵ Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Methylenebis(1,3,2-dioxaphospholane), $\text{CH}_2(\text{POCH}_2\text{CH}_2\text{O})_2$. To a stirred solution of $\text{CH}_2(\text{PCl}_2)_2$ (0.15 mL, 1 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of ethylene glycol (0.14 mL, 2 mmol) in dichloromethane (10 mL) at 0 °C. After being stirred for 10 min, the solution was filtered to remove the white precipitate of DABCO-HCl. The solution volume was reduced to 10 mL and *n*-hexane (30 mL) added. Additional DABCO-HCl precipitated, and it was removed by filtration. The filtrate was kept under vacuum for 24 h to give the product as a pale yellow liquid. Yield: 0.078 g (40%).

(Methylimino)bis(1,3,2-dioxaphospholane), $\text{CH}_3\text{N}(\text{POCH}_2\text{CH}_2\text{O})_2$. Using a similar procedure as for $\text{CH}_2(\text{POCH}_2\text{CH}_2\text{O})_2$ with $\text{CH}_3\text{N}(\text{PCl}_2)_2$ (0.14 mL, 1 mmol) and the other reagents in the same stoichiometric ratios gave the compound as a pale yellow liquid. Yield: 0.084 g (40%).

Methylenebis(benzo-1,3,2-dioxaphospholane), $\text{CH}_2(\text{POC}_6\text{H}_4\text{O})_2$. To a stirred solution of $\text{CH}_2(\text{PCl}_2)_2$ (0.15 mL, 1 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of catechol (0.22 g, 2 mmol) in dichloromethane (10 mL) at 0 °C. After being stirred for 10 min, the solution was filtered to remove the white precipitate of DABCO-HCl. The solution volume was reduced to 10 mL and *n*-hexane (30 mL) added. The solvent was removed from the filtrate under vacuum to give the product as a pale yellow liquid. Yield: 0.158 g (54%).

(Methylimino)bis(benzo-1,3,2-dioxaphospholane), $\text{CH}_3\text{N}(\text{POC}_6\text{H}_4\text{O})_2$. Using a similar procedure as for $\text{CH}_2(\text{POC}_6\text{H}_4\text{O})_2$ with $\text{CH}_3\text{N}(\text{PCl}_2)_2$ (0.14 mL, 1 mmol) and the other reagents in the same stoichiometric ratios gave the compound as a pale yellow liquid. Yield: 0.184 g (60%).

Methylenebis(1,3,2-dithiaphospholane), $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$. To a stirred solution of 1,2-ethanedithiol (0.17 mL, 2 mmol) was added dropwise a solution of $\text{CH}_2(\text{PCl}_2)_2$ (0.15 mL, 1 mmol) in dichloromethane (10 mL) at ambient temperature. After the mixture was stirred for 2 h, the volume of solvent was reduced to 20 mL under vacuum and methanol (40 mL) added. The colorless crystals were filtered immediately and washed with a small portion of cold methanol. The compound (pcps) was recrystallized from dichloromethane and *n*-hexane as a solvate containing half of a molecule of dichloromethane. Yield 0.195 g (75%). mp 63–64°, Anal. Calcd for $\text{C}_5\text{H}_{11}\text{ClP}_2\text{S}_2$: C, 21.8; H, 3.66. Found: C, 21.3; H, 3.99.

(Methylimino)bis(1,3,2-dithiaphospholane), $\text{CH}_3\text{N}(\text{PSCH}_2\text{CH}_2\text{S})_2$. To a stirred solution of 1,2-ethanedithiol (0.17 mL, 2 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of $\text{CH}_3\text{N}(\text{PCl}_2)_2$ (0.14 mL, 1 mmol) in dichloromethane (10 mL) at 0 °C. The solution was stirred for 2 h while it was allowed to warm to ambient temperature. The white precipitate of DABCO-HCl was filtered, and the solution volume was reduced under vacuum to 20 mL. Methanol (40 mL) was added, and the colorless crystals were filtered immediately and washed with a small portion of cold methanol. The compound (pnps) was recrystallized from dichloromethane and *n*-hexane. Yield: 0.192 g (70%). Mp: 142–145 °C. Anal. Calcd for $\text{C}_5\text{H}_{11}\text{NP}_2\text{S}_2$: C, 21.8; H, 4.03; N, 5.09. Found: C, 21.7; H, 4.07; N, 5.05.

trans-Dichlorobis(methylenebis(1,3,2-dithiaphospholane))ruthenium(II), $\text{RuCl}_2(\text{pcps})_2$. To a stirred solution of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.18 g, 0.2 mmol) in dichloromethane (20 mL) was added dropwise a solution of pcps (0.1 g, 0.4 mmol) in dichloromethane (10 mL). The color of the solution changed from brown to yellow. The solution was stirred for 30 min, and the volume of the solution changed from brown to yellow. The solution was stirred for 30 min, the volume of the solution reduced to 15 mL under vacuum, and *n*-hexane (40 mL) added to give a yellow precipitate. The yellow complex was filtered, recrystallized from dichloromethane and *n*-hexane, and dried in vacuo. Yield: 0.093 g (82%). Anal.

(1) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191–243. Puddephatt, R. *Chem. Soc. Rev.* **1983**, *12*, 99–127.
(2) Roundhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55–61.
(3) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73–86. Constable, E. C. *Polyhedron* **1984**, *3*, 1037–1057.

(4) Heitkamp, S.; Sommer, H.; Stelzer, O. *Inorg. Synth.* **1989**, *25*, 120–122. Nixon, J. F. *J. Chem. Soc., A* **1968**, 2689–2692. Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237–240.
(5) PANIC 83.3004. *Aspect 3000 NMR Software Manual*; Bruker Spectrospin: Karlsruhe, Germany, 1985.

Table I. Data for Crystal Structure Analysis of $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$

formula	$\text{C}_5\text{P}_2\text{S}_4\text{H}_{10}$
mol wt	260.23
crystal dimens, mm	$0.33 \times 0.23 \times 0.17$
cryst syst:	monoclinic
space group:	$P2_1/n$
cell dimens:	
<i>a</i> , Å	10.495 (2)
<i>b</i> , Å	10.386 (2)
<i>c</i> , Å	10.959 (2)
β, deg	113.89 (2)
<i>V</i> , Å ³	1092.19
<i>Z</i>	4
ρ(calcd), g cm ⁻³	1.58
radiation	Mo Kα ($\lambda_1 = 0.70930$ Å)
2θ range, deg	1.0–44
scan type	Ω/2θ
scan angle	$0.8 + 2 \tan \theta$
scan speed, deg min ⁻¹	4
total no. of data colld	1524
no. of unique data	1344
no. of obsd data with $I_0 > 3\sigma_I$	1162
μ, cm ⁻¹	10.71
transm coeff	0.9994–0.9183
<i>F</i> (000)	536
<i>R</i> _w ^a , %	4.4
<i>R</i> _w ^b , %	3.7

$$^a R = \sum(F_o - F_c) / \sum F_o \quad ^b R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}, w = 1/\sigma F_o$$

Table II. Table of Positional Parameters and Their Estimated Standard Deviations

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
S1	0.3161 (1)	0.0596 (2)	0.8891 (1)	5.76 (4)
S2	0.2193 (2)	0.0526 (2)	0.5835 (1)	5.38 (4)
S3	0.6082 (2)	0.4288 (2)	0.6497 (2)	5.99 (4)
S4	0.6007 (2)	0.1460 (2)	0.5659 (1)	5.64 (4)
P1	0.4088 (1)	0.0559 (2)	0.7520 (1)	4.62 (4)
P2	0.4656 (1)	0.2777 (2)	0.5948 (1)	4.68 (4)
C1	0.1606 (5)	0.1555 (7)	0.7903 (5)	7.0 (2)
C2	0.1126 (6)	0.1432 (8)	0.6510 (6)	9.5 (2)
C3	0.7620 (6)	0.3357 (6)	0.7370 (6)	6.2 (2)
C4	0.7715 (5)	0.2238 (7)	0.6627 (6)	7.4 (2)
C5	0.4626 (5)	0.2257 (6)	0.7540 (5)	5.0 (2)

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

Calcd for $\text{C}_{10}\text{H}_{20}\text{Cl}_2\text{P}_4\text{RuS}_8$: C, 17.3; H, 2.91. Found: C, 18.2, 16.6; H, 3.09, 2.38.

trans-Dichlorobis((methylimino)bis(1,3,2-dithiaphospholane))ruthenium(II), $\text{RuCl}_2(\text{pnps})_2$. To a stirred solution of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.18 g, 0.2 mmol) in dichloromethane was added dropwise a solution of pnps (0.11 g, 0.4 mmol) in dichloromethane (10 mL). The solution was stirred for 2 h, filtered, and passed through a 10-cm silica column. The yellow complex was isolated by adding *n*-hexane, followed by filtration and drying in vacuo. Yield: 0.045 g (38%). Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{Cl}_2\text{N}_2\text{P}_4\text{RuS}_8$: C, 16.6; H, 3.07. Found: C, 16.6; H, 2.84.

X-Ray Crystallographic Studies. The crystallographic data set was collected on an Enraf-Nonius CAD 4 diffractometer at 297 K by using Ω/2θ scan mode and Mo Kα radiation. The crystal was mounted on the end of a glass fiber. Crystal data and details for data collection and refinement are shown in Table I. The intensities of three check reflections were monitored during data collection and showed 30% decay during the data collection period. The intensities for all reflections were corrected for this linear decay. An empirical absorption correction was applied to all data based on ψ scans. The structure was solved by direct methods using the Enraf-Nonius SDP programs and was refined by using full-matrix least-squares techniques. The hydrogen atoms were placed in a combination of observed and calculated positions with their positions riding on the carbon atoms to which they are bonded. The parameters were fixed isotropically except where noted. Final coordinates and average temperature factors of the atoms are shown in Table II.

Results and Discussion

We have synthesized heterocyclic diphosphorus compounds by

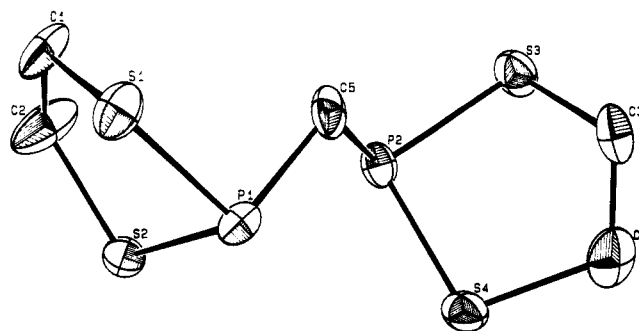
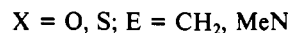
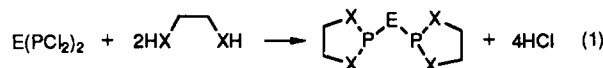


Figure 1. Thermal ellipsoid plot of the structure of $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$. Relevant distances (Å): S1–P1 = 2.096 (2), S1–C1 = 1.844 (6), S2–P1 = 2.096 (2), S2–C2 = 1.833 (8), S3–P2 = 2.082 (2), S3–C3 = 1.791 (6), S4–P2 = 2.086 (2), S4–C4 = 1.858 (6), P1–C5 = 1.852 (6), P2–C5 = 1.839 (6), C1–C2 = 1.407 (8), C3–C4 = 1.446 (1). Relevant angles (deg): P1–S1–C1 = 98.4 (2), P1–S2–C2 = 98.8 (2), P2–S3–C3 = 97.7 (2), P2–S4–C4 = 100.7 (2), S1–P1–S2 = 94.68 (8), S1–P1–C5 = 101.6 (2), S2–P1–C5 = 101.7 (2), S3–P2–S4 = 94.91 (9), S3–P2–C5 = 103.5 (2), S4–P2–C5 = 103.0 (2), S1–C1–C2 = 115.5 (5), S2–C2–C1 = 118.4 (5), S3–C3–C4 = 112.7 (4), S4–C4–C3 = 113.6 (4), P1–C5–P2 = 113.1 (3).

treating $\text{CH}_2(\text{PCl}_2)_2$ and $\text{CH}_3\text{N}(\text{PCl}_2)_2$ with ethylene glycol and 1,2-ethanedithiol. These reactions are shown in eq 1. The



procedure for the preparation of the stable ligands from 1,2-ethanedithiol involves stirring solutions of $\text{CH}_2(\text{PCl}_2)_2$ or $\text{CH}_3\text{N}(\text{PCl}_2)_2$ and $(\text{CH}_2\text{SH})_2$ in dichloromethane solvent for 2–3 h at 0 °C, followed by precipitation of the product with methanol. The precipitate is quickly filtered and washed with *n*-hexane. In the procedure for the synthesis of $\text{CH}_3\text{N}(\text{PSCH}_2\text{CH}_2\text{S})_2$, the base DABCO is added to the reaction mixture. The analogous phosphinite compounds from ethylene glycol are thermally unstable to decomposition and have not been isolated from solution in a pure state. The successful isolation of $\text{CH}_3\text{N}(\text{POCH}_2\text{CH}_2\text{O})_2$ from two other synthetic routes has been reported, but other analogues have not been reported.⁶ The ³¹P {¹H} NMR spectral data for all these compounds are as follows: $\text{CH}_2(\text{POCH}_2\text{CH}_2\text{O})_2$, δ 136.4 t (²J(PH): 8.5 Hz); $\text{CH}_3\text{N}(\text{POCH}_2\text{CH}_2\text{O})_2$, δ 140.2 s; $\text{CH}_2(\text{POCH}_2\text{CH}_2\text{O})_2$, δ 136.4 t (²J(PH) = 9.6 Hz); $\text{CH}_3\text{N}(\text{POCH}_2\text{CH}_2\text{O})_2$, δ 175.0 s. The hydrolytically unstable compounds $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$ (pcps) and $\text{CH}_3\text{N}(\text{PSCH}_2\text{CH}_2\text{S})_2$ (pnps) have been prepared as colorless crystalline compounds. The spectroscopic data for pcps and pnps are as follows (peak areas in parentheses): for $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$, ¹H NMR δ 2.2 t (2) (²J(PH) = 9.9 Hz), 3.3 s (8); ¹³C {¹H} NMR δ 43.6 t (1) (¹J(PC) = 58.6 Hz), 40.5 s (4); ³¹P {¹H} NMR δ 43.9 s; for $\text{CH}_3\text{N}(\text{PSCH}_2\text{CH}_2\text{S})_2$, ¹H NMR δ 2.6 t (2) (CH_3 , ³J(PH) = 4 Hz), 3.2 mult (4), 3.5 mult (4); ³¹P {¹H} NMR δ 105.5 s. No other compounds are formed in significant amounts. These spectroscopic data do not distinguish between alternate cyclic structures that have 5- or 7-membered rings. The single crystal X-ray structure of $\text{CH}_2(\text{PSCH}_2\text{CH}_2\text{S})_2$ confirms that this particular compound has two 5-membered rings (Figure 1). The distances and angles are normal, which suggests no significant strain within the rings. Because of the different heteroatoms (O and S), we cannot unambiguously deduce from this particular crystal structure whether the ethylene glycol and catechol derivatives have 5- or 7-membered rings.

Treating $\text{RuCl}_2(\text{PPh}_3)_3$ with pcps or with pnps results in the substitution of triphenylphosphine to give two structurally different

(6) Pudovik, M. A.; Medvedeva, M. D.; Pudovik, A. N. *Zh. Obshch. Khim.* 1976, 46, 772–774. Mague, J. T.; Johnson, M. P. Manuscript in preparation.

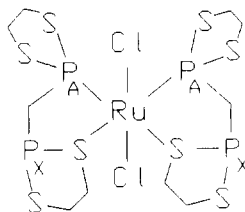
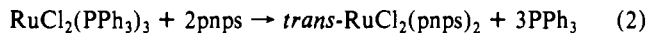


Figure 2. Structure of *trans*-RuCl₂(pcps)₂.

products. For the case of pnps the product is the P,P'-bonded chelate complex *trans*-RuCl₂(pnps)₂ (IR: $\nu(\text{RuCl})$ 330 cm⁻¹. ³¹P{¹H} NMR: δ 122.5 s) (eq 2).⁷ For the case of pcps, the



product RuCl₂(pcps)₂ shows a distinctly different ³¹P{¹H} NMR spectrum from that found for *trans*-RuCl₂(pnps)₂. The ³¹P{¹H} NMR spectrum of RuCl₂(pcps)₂ shows two groups of four lines of equal intensity centered at δ 60 and 140. Spectral simulation of this spectrum as an AA'XX' spin system gives good agreement with the experimental spectrum. The simulation uses the following values: ²J(P_AP_A) = 31 Hz; ²J(P_AP_X) = 32 Hz; ³J(P_{AX}) = 1 Hz; ⁴J(P_XP_X) = 0 Hz. The ³¹C{¹H} NMR spectrum shows the following equal intensity resonances: δ 52.9 d (¹J(PC) = 62.5 Hz), 43.1 s, 42.5 s, 40.6 s, 40.1 s. This complex RuCl₂(pcps)₂ is also formed upon the reaction of 2 equiv of pcps with RuCl₂(AsPh₃)₃. The complex RuCl₂(pcps)₂ in dichloromethane solution is a nonconductor of electricity.

These spectral data correspond to a chelate complex RuCl₂(pcps)₂ where each complexed pcps ligand is ambidentate by coordination through a phosphorus and a sulfur atom. Such a structure corresponds closely with that of the complex RuCl₂((tol)₂(DBT)P)₂ where DBT is a dibenzothiophene substituent on phosphorus. This complex also has P and S ligands coordinated to ruthenium(II) in a 5-membered chelate arrangement.⁸ In the complex, RuCl₂(pcps)₂ three fused 5-membered rings are formed with the coordinated phosphorus and sulfur atoms being common to each ring. The solution structure of RuCl₂(pcps)₂ is shown in Figure 2. All attempts to obtain single crystals of the complex have given powders. The ³¹P{¹H} NMR resonance at δ 60 is close to the value of δ 45 observed in free pcps, whereas the resonance at δ 140 is shifted downfield. We assign the resonance at δ 60 to the uncomplexed ring phosphorus P_X, and the resonance at δ 140 to the complexed phosphorus P_A. The need to use J(XX') = 0 Hz in the successful simulation of the ³¹P{¹H} NMR is now understandable, since a very low value of ⁴J(PP') is to be expected between the uncomplexed phosphorus nuclei in such a structure. This observed ³¹P NMR spectrum does not define a unique stereochemistry, but can be assigned to several different isomers. The proposed isomer in Figure 2 with mutually trans chlorine and phosphorus atoms is based on the correspondence of the value of $\nu(\text{Ru-Cl})$ with that of *trans*-RuCl₂(pnps)₂ and other *trans*-dichloro complexes and also on the value of 31 Hz for ²J(P_AP_A) found in RuCl₂((tol)₂(DBT)P)₂.⁸ For a *trans* arrangement, a value of J(P_AP_A) > 100 Hz is expected.⁹ Since the complex RuCl₂((tol)₂(DBP)P)₂ has a *cis* arrangement of chlorines, we cannot make a more detailed spectroscopic comparison between this complex and *trans*-RuCl₂(pnps)₂.

The difference in coordination chemistry between pcps and pnps with ruthenium(II) can be explained on the basis of the difference in the bite angles between the two ligands. The PNP angle found in transition-metal complexes is greater than the corresponding PCP angle, because the delocalization of the nitrogen lone pair of electrons into the P–N bond causes partial multiple bonding between phosphorus and nitrogen.¹⁰ This coordination of a

thiacyclic sulfur atom to ruthenium(II) is a novel example of how ring strain can be reduced by the formation of a 5-membered (P,S) ring rather than a 4-membered (P,P') chelate ring.

Acknowledgment. We thank both the Petroleum Research Fund, administered by the American Chemical Society, and the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for support of this research. We thank the Office of Naval Research for funds to purchase the FTIR spectrometer. We thank Dr. F. Joslin and Dr. J. T. Mague for helpful discussions.

Supplementary Material Available: Tables of crystallographic data, positional parameters, general displacement parameters, bond distances and angles, anisotropic displacements, torsion angles, and least-squares planes (8 pages); a table of values of F_o and F_c (12 pages). Ordering information is given on any current masthead page.

- (10) Haines, R. J.; Pidcock, A.; Safari, M. *J. Chem. Soc. Dalton Trans.* 1977, 830–832. Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W.; Kim, J. H. *Inorg. Chem.* 1982, 21, 3790–3794.

Contribution from the Department of Chemistry,
Indian Institute of Technology, Kanpur 208 016, India

First Report on Manganese(II)–Tetrathiometalate(VI) Complexes: Isolation of [(bpy)₂Mn(μ-S)₂MS₂] (M = Mo, W; bpy = 2,2'-Bipyridine)

B. R. Srinivasan and Sabyasachi Sarkar*

Received January 11, 1990

Recent attempts to complex Mn(II) with [M^{VI}S₄]²⁻ (M = Mo, W) ligands have resulted in the formation of exclusively binary [M–S] species such as [SMo^{IV}(Mo^{VI}S₄)₂]²⁻, [W^{VI}₂(X)₂(μ-S)(S₂)₄]²⁻ (X = O, S), and [SW^{IV}(W^{VI}S₄)(W^{VI}S₃(S₂))]²⁻.¹ The role of Mn(II) to effect these transformations has not been clearly defined, although it has been reported that Mn(II) is very essential for these metal-centered nonredox and redox type condensations to occur. The reaction of 3d metal ions with [MS₄]²⁻ in aqueous solution results in the precipitation of a mixture of X-ray amorphous heterometal sulfide and MS₃,² which can be prevented in the presence of bulky counterion to yield discrete heterometal complexes of the type [M'(M^{VI}S₄)₂]²⁻ (M' = Fe, Co, Ni, Zn).³ However, Cu(II) is reduced by an aqueous solution of (NH₄)₂MS₄ to the polymeric NH₄Cu^IMS₄,⁴ and the use of aromatic diimines as coligands in Cu–thiometalate systems gives rise to the discrete heterometal complexes [LCu(μ-S)₂M(μ-S)₂CuL] (L = 2,2'-bipyridine (bpy), 1,10-phenanthroline).⁵ In most of the thiometalate

(7) Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc. Dalton Trans.* 1984, 1635–1639.

(8) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J. *J. Am. Chem. Soc.* 1984, 106, 5379–5381.

(9) Whinnery, L. L.; Yue, H. J.; Marsella, J. A. *Inorg. Chem.* 1986, 25, 4136–4139.

(1) (a) Manoli, J. M.; Potvin, C.; Sécheresse, F. *Inorg. Chem.* 1987, 26, 340; *Inorg. Chim. Acta* 1987, 133, 27. (b) Müller, A.; Diemann, E.; Wienböcker, U.; Bögge, H. *Inorg. Chem.* 1989, 28, 4046.

(2) Clark, G. M.; Doyle, W. P. *J. Inorg. Nucl. Chem.* 1966, 28, 381.

(3) (a) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 934 and references therein. (b) In the case of Fe(II) and [MoS₄]²⁻ reduction of Fe(II) takes place. See: Müller, A.; Sarkar, S. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 705. Friesen, G. D.; McDonald, J. W.; Newton, W. E.; Euler, W. B.; Hoffman, B. M. *Inorg. Chem.* 1983, 22, 2202. Holm, R. H.; Simhon, E. D. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1985; pp 1–87.

(4) (a) Binnie, W. P.; Redman, M. J.; Mallio, W. J. *Inorg. Chem.* 1970, 9, 1449. (b) Müller, A.; Menge, R. *Z. Anorg. Allg. Chem.* 1972, 393, 259.

(5) (a) Sarkar, S.; Mishra, S. B. S. *Coord. Chem. Rev.* 1984, 59, 239. (b) Sarkar, S.; Mishra, S. B. S. *J. Indian Chem. Soc.* 1985, 62, 821. (c) Sarkar, S.; Mishra, S. B. S. *Indian J. Chem.* 1986, 25A, 871. (d) Potvin, C.; Manoli, J. M.; Sécheresse, F.; Marzak, S. *Inorg. Chim. Acta* 1987, 134, 9.