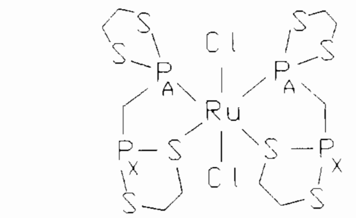

Figure 2. Structure of *trans*-$RuCl_2(pcps)_2$.

products. For the case of pnps the product is the P,P′-bonded chelate complex *trans*-$RuCl_2(pnps)_2$ (IR: ν(RuCl) 330 cm^{-1}. ^{31}P{^{1}H} NMR: δ 122.5 s) (eq 2).[7] For the case of pcps, the

$$\mathrm{RuCl_2(PPh_3)_3 + 2pnps \rightarrow \textit{trans}\text{-}RuCl_2(pnps)_2 + 3PPh_3} \tag{2}$$

product $RuCl_2(pcps)_2$ shows a distinctly different ^{31}P{^{1}H} NMR spectrum from that found for *trans*-$RuCl_2(pnps)_2$. The ^{31}P{^{1}H} NMR spectrum of $RuCl_2(pcps)_2$ 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 ^{31}C{^{1}H} 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 $RuCl_2(pcps)_2$ is also formed upon the reaction of 2 equiv of pcps with $RuCl_2(AsPh_3)_3$. The complex $RuCl_2(pcps)_2$ in dichloromethane solution is a nonconductor of electricity.

These spectral data correspond to a chelate complex $RuCl_2(pcps)_2$ 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 $RuCl_2((tol)_2(DBT)P)_2$ 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, $RuCl_2(pcps)_2$ three fused 5-membered rings are formed with the coordinated phosphorus and sulfur atoms being common to each ring. The solution structure of $RuCl_2(pcps)_2$ is shown in Figure 2. All attempts to obtain single crystals of the complex have given powders. The ^{31}P{^{1}H} 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 ^{31}P{^{1}H} 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 ^{31}P 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 ν(Ru–Cl) with that of *trans*-$RuCl_2(pnps)_2$ and other *trans*-dichloro complexes and also on the value of 31 Hz for $^2J(P_AP_A)$ found in $RuCl_2((tol)_2(DBT)P)_2$.[8] For a trans arrangement, a value of $J(P_AP_A) > 100$ Hz is expected.[9] Since the complex $RuCl_2((tol)_2(DBP)P)_2$ has a cis arrangement of chlorines, we cannot make a more detailed spectroscopic comparison between this complex and *trans*-$RuCl_2(pnps)_2$.

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.

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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.

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

First Report on Manganese(II)–Tetrathiometalate(VI) Complexes: Isolation of $[(bpy)_2Mn(\mu\text{-}S)_2MS_2]$ (M = Mo, W; bpy = 2,2′-Bipyridine)

B. R. Srinivasan and Sabyasachi Sarkar*

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Recent attempts to complex Mn(II) with $[M^{VI}S_4]^{2-}$ (M = Mo, W) ligands have resulted in the formation of exclusively binary {M–S} species such as $[SMo^{IV}(Mo^{VI}S_4)_2]^{2-}$, $[W^{VI}_2(X)_2(\mu\text{-}S)(S_2)_4]^{2-}$ (X = O, S), and $[SW^{IV}(W^{VI}S_4)(W^{VI}S_3(S_2))]^{2-}$.[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 $[MS_4]^{2-}$ in aqueous solution results in the precipitation of a mixture of X-ray amorphous heterometal sulfide and MS_3,[2] which can be prevented in the presence of bulky countercation to yield discrete heterometal complexes of the type $[M'(M^{VI}S_4)_2]^{2-}$ (M′ = Fe, Co, Ni, Zn).[3] However, Cu(II) is reduced by an aqueous solution of $(NH_4)_2MS_4$ to the polymeric $NH_4Cu^IMS_4$,[4] and the use of aromatic diimines as coligrands in Cu–thiometalate systems gives rise to the discrete heterometal complexes $[LCu(\mu\text{-}S)_2M(\mu\text{-}S)_2CuL]$ (L = 2,2′-bipyridine (bpy), 1,10-phenanthroline).[5] In most of the thiometalate

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complexes of 3d metals tetracoordination[3] around the heterometal is a common feature and in some cases penta[6a] and hexacoordination[6b] have also been achieved. Hexacoordinate Ru complexes $[(bpy)_2Ru(\mu\text{-}S)_2MS_2]$ prepared by reacting $[(bpy)_2RuCl_2]$ with $[MS_4]^{2-}$ in an aqueous alcoholic medium have also been reported.[7]

Unlike other 3d metal ions, Mn(II) in an aqueous solution of $[MS_4]^{2-}$ neither immediately precipitate a mixture of amorphous metal sulfides nor forms any Mn–thiometalate complexes in the presence of bulky countercations. However, in the presence of 2,2′-bipyridine, Mn(II) forms discrete Mn–thiometalate complexes, which we describe here.

Materials and Methods

$(NH_4)_2MS_4$ (M = Mo, W) were prepared by literature methods.[8] DMF was dried over alumina, vacuum-distilled, and stored over 4-Å molecular sieves for use in electrochemistry. C, H, and N were analyzed at the Microanalytical Laboratories, IIT, Kanpur, India. Sulfur in the compounds was oxidized to sulfate by alkaline bromine and estimated as barium sulfate. IR spectra as CsI pellets and electronic spectra in DMF were recorded on Perkin-Elmer 580 and Shimadzu UV-160 spectrophotometers, respectively. Magnetic susceptibility measurements were carried out on a Gouy balance. X-Band EPR spectra were recorded on a Varian E-109 EPR system from 0 to 6000 G, with DPPH as standard. X-ray powder patterns were recorded on a Siefert Isodebyeflex-2002 diffractometer using Cu Kα radiation with a Ni filter. Cyclic voltammetry was performed in DMF (0.1 M $(n\text{-}Bu_4N)BF_4$) with an auxiliary platinum electrode, a glassy-carbon working electrode, and a Ag/AgCl reference electrode at a scan rate of 100 mV s^{-1} on a Bioanalytical Systems CV-27 voltammograph, in connection with a C1B cell stand and a Omnigraphic 100 X-Y recorder.

Experimental Details

Synthesis of $[(bpy)_2Mn(\mu\text{-}S)_2MoS_2]$ (1). An aqueous alcoholic solution containing $MnCl_2{\cdot}4H_2O$ (200 mg, ~1 mmol) in water (5 mL) and bpy (320 mg, ~2 mmol) in ethanol (20 mL) was added in drops, with stirring, to an aqueous solution of $(NH_4)_2MoS_4$ (260 mg, 1 mmol) in water (20 mL). The color of the solution changed immediately, and after a few minutes a dark brown solid separated out. The stirring was continued for 2 h, and the product was isolated by filtration. The product was washed well with water, ethanol, and ether and dried under vacuum; yield 560 mg. Anal. Found (calcd): C, 40.95 (40.61); H, 3.02 (2.71); N, 9.68 (9.48); S, 21.68 (21.66). X-ray powder data (Cu Kα): 7.49, 5.86, 4.97, 4.75, 4.62, 3.90, 3.80, 3.65, 2.82, 2.43 Å. IR data: 505, 490 ($\nu(MS_{term})$), 455, 435 ($\nu(MS_{br})$), 410 (ring deformation of bpy), 350 (ν(MnS)), 235, 215 (ν(MnN)) cm^{-1}. Electronic spectrum (in DMF): 530 (sh), 478 (ε 11 820), 401 (2850), 322 (19 400), 281 nm (38 975).

Synthesis of $[(bpy)_2Mn(\mu\text{-}S)_2WS_2]$ (2). The use of $(NH_4)_2WS_4$ (350 mg, ~1 mmol) instead of $(NH_4)_2MoS_4$ in a reaction similar to that described above resulted in the formation of orange-red **2** in near-quantitative yield. Anal. Found (calcd): C, 35.72 (35.35); H, 2.48 (2.36); N, 8.45 (8.25); S, 19.02 (18.85). X-ray powder data (Cu Kα): 7.49, 5.53, 4.98, 4.77, 4.48, 3.91, 3.81, 3.66, 2.84, 2.43 Å. IR data: 490, 480 ($\nu(MS_{term})$), 455, 435 ($\nu(MS_{br})$), 410 (ring deformation of bpy), 350 (ν(MnS)), 230, 210 (ν(MnN)) cm^{-1}. Electronic spectrum (in DMF): 440 (sh), 400 (ε 19 300), 330 (sh), 284 nm (62 400).

Results and Discussion

The reaction of $MnCl_2$, bpy, and $(NH_4)_2MS_4$ in a 1:2:1 ratio in an aqueous alcoholic medium results in the formation of the complexes **1** and **2** in high yield. The high formation tendency of **1** or **2** is evident from the fact that the use of excess or less amounts of 2,2′-bipyridine results exclusively in the formation of **1** or **2**. The use of coligand in the reaction system $Mn^{2+}/[MS_4]^{2-}/H_2O$ provides the key to the facile formation of Mn–thiometalate complexes, as 2,2′-bipyridine can stabilize the $\{Mn(\mu\text{-}S)_2MS_2\}$ core, to form the neutral hexacoordinate **1** or **2**.

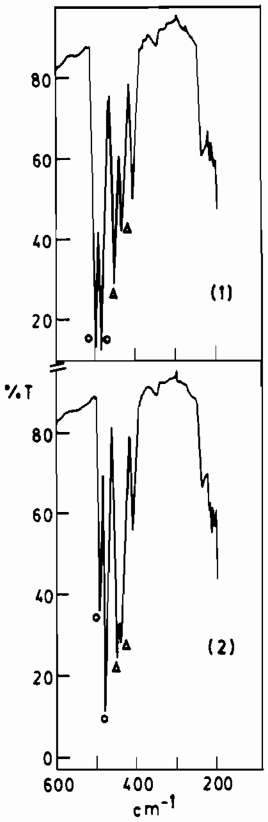

Figure 1. IR spectra (CsI pellet) in the ν(MS) region illustrating the bands characteristic of bidentate coordination of $[MS_4]^{2-}$ in $[(bpy)_2Mn(\mu\text{-}S)_2MoS_2]$ (**1**) and $[(bpy)_2Mn(\mu\text{-}S)_2WS_2]$ (**2**): (○) $\nu(MS_{term})$; (△) $\nu(MS_{br})$.

The bidentate coordination of $[MS_4]^{2-}$ to Mn(II) in **1** and **2** has been unambiguously arrived at from the infrared spectral data. The IR spectra of **1** and **2** (Figure 1) exhibit four distinct bands in the 400–500-cm^{-1} region, as expected for the T_d $[MS_4]^{2-}$ anions, which assume a C_{2v} microsymmetry on bidentate coordination in the $\{Mn(\mu\text{-}S)_2MS_2\}$ moiety.[9] The electronic spectra of **1** and **2** in DMF are characteristic of perturbed $[MS_4]^{2-}$ groups, as expected on bidentate coordination.[3,7,10] Cyclic voltammograms of **1** and **2** in DMF display irreversible reductions at −1.09 and −1.36 V for **1** and −1.36 and −1.64 V for **2** and irreversible oxidations at +0.46 and +0.75 V for **1** and +0.60 and +0.80 V for **2**. While the two irreversible reductions in each case may be associated with bipyridine ring reductions,[7,11] the irreversible oxidations cannot be unambiguously assigned for either the oxidation of Mn(II) or the oxidation of terminal sulfido groups.

The ground state for Mn(II) in these complexes is found to be $^6S_{5/2}$ (μ_{eff} for **1** is 6.12 μ_B and for **2** is 6.14 μ_B). The EPR spectra of the polycrystalline samples of **1** and **2** and the solution spectrum of **2** in DMF as well as the polycrystalline spectra of **2** doped in $[(bpy)_2M'(\mu\text{-}S)_2WS_2]$ (M′ = Co, Zn)[12] are shown in Figure 2. A broad signal for polycrystalline samples of **1** ($g \approx 2.03$) and **2** ($g \approx 2.03$) and six-line hyperfine spectra for **2** in DMF ($g = 2.001$, $A = 92.6$ G) and **2** in host lattices were observed. The spectra of **1** in solution and in doped systems are similar to those of **2**. No new lines appear even at 77 K for **2** doped in the cobalt lattice. Almost similar powder EPR spectra of **2** in the para-

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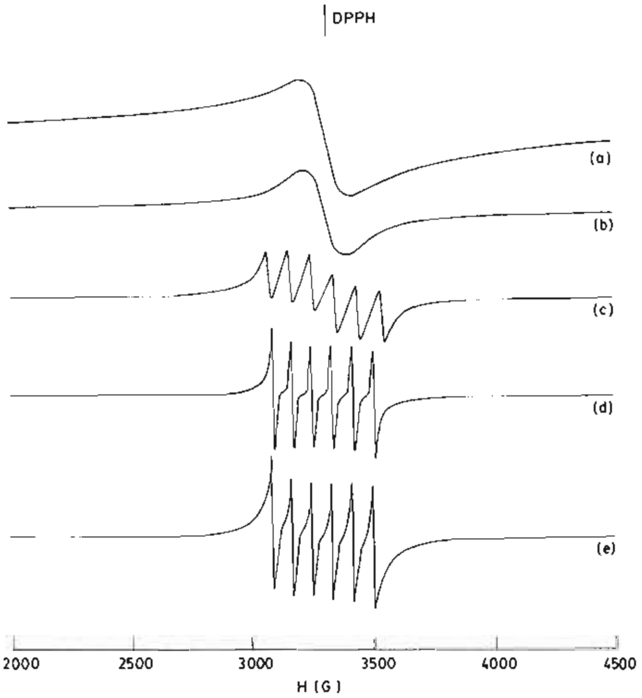

Figure 2. First-derivative EPR spectra (X-band, 9.4 GHz) at 298 K: (a) **1** in polycrystalline form; (b) **2** in polycrystalline form; (c) **2** in DMF; (d) **2** doped (1%) into $[(bpy)_2Co(\mu\text{-}S)_2WS_2]$ in polycrystalline form; (e) **2** doped (1%) into $[(bpy)_2Zn(\mu\text{-}S)_2WS_2]$ in polycrystalline form.

magnetic cobalt ($g = 2.002$, $A = 84$ G) and the diamagnetic zinc ($g = 2.002$, $A = 84$ G) host lattices suggest that Co–Co spin interaction is very fast with no interaction between Mn and Co.[13] The line width of the derivative curve is approximately 8 G for Mn-doped complexes, and the isotropic nitrogen superhyperfine splitting could not be seen. From the intensity ratio between the forbidden lines ($\Delta M_I = \pm 1$) and the allowed lines ($\Delta M_I = 0$)[14] an approximate value of D, the axial field splitting parameter, has been estimated to be on the order of 15.6×10^{-4} cm^{-1}. Thus in **2** (and also in **1**), though the central Mn(II) contains a N_4S_2 donor site, it still retains a nearly octahedral symmetry.

Our attempts to incorporate another $[MS_4]^{2-}$ ligand in **1** or **2** at the expense of a 2,2′-bipyridine ligand and to utilize the terminal sulfide groups in **1** or **2** for further coordination with a third metal have not been successful.

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Contribution from the School of Chemical Sciences,
Department of Physics, and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

Pressure-Induced Skeletal Isomerization of $[Au_9(PPh_3)_8][PF_6]_3$ in the Solid State

Jeffery L. Coffer, John R. Shapley,* and Harry G. Drickamer*

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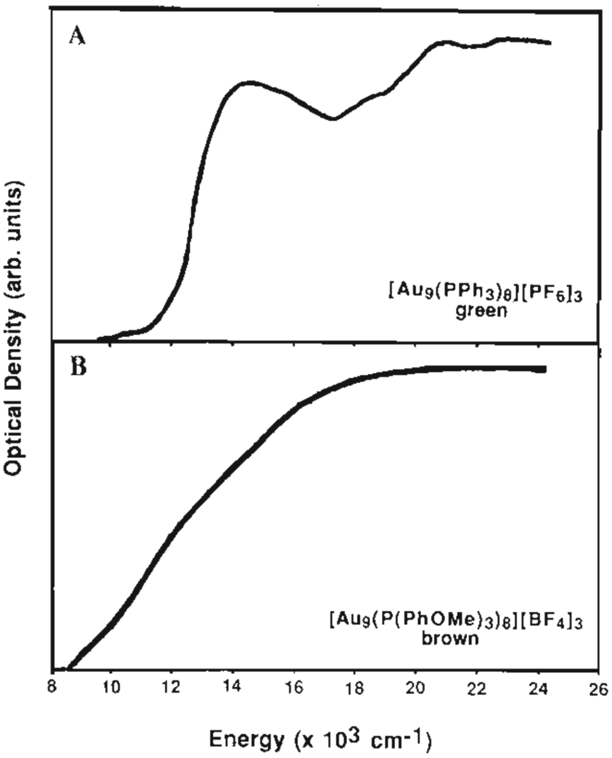
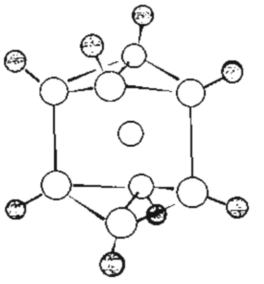


Figure 1. Optical absorption spectra for (A) "green" $[Au_9(PPh_3)_8][PF_6]_3$ and (B) "brown" $[Au_9(P(p\text{-}C_6H_4OMe)_3)_8][BF_4]_3$.

Molecular gold clusters are of widespread interest from a standpoint of structure, bonding, and reactivity.[1] Clusters of high nuclearity have been isolated,[2] most of which possess terminal triarylphosphines as ligands. One particularly interesting class gold compounds are clusters of the core formula $[Au_9(PPh_3)_8]^{3+}$, for which two different structural forms have been isolated and crystallographically identified.[1,3,4] The first is the "green" form (**1**), viewed as a D_{2h} fragment of an icosahedron, while the second is the "brown" form (**2**), described in terms of a D_{4d} centered-crown structure. The observed geometry under ambient conditions is highly dependent upon the choice of triarylphosphine ligand and counterion. We report in this work the ability of pressure to transform the cluster $[Au_9(PPh_3)_8][PF_6]_3$ from an initial "green" form to the "brown" form, as detected by changes in its optical spectrum. Pressure-induced structural rearrangements have been observed previously for monometallic copper complexes[5] and also



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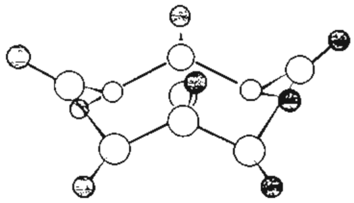

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