ESR data allows us to show that the electronic relaxation rate is dominated by spin–rotational interaction, thus making the electronic relaxation time directly proportional to the tumbling correlation time and almost independent of the magnetic field. This shows that higher magnetic field strengths can be used to advantage in the investigation of copper(II) complexes, since the improved chemical shift resolution thus obtained should not be canceled by significant extra line broadenings, an important point in the study of copper(II)–protein complexes.

Acknowledgment. Financial support from the Centre National de la Recherche Scientifique is gratefully acknowledged. All NMR spectra were recorded on spectrometers of the University of Nancy I.

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Preparation and Characterization of Pentanuclear Molybdenum Halide Clusters

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The cyclic voltammogram of $[(n\text{-}C_4H_9)_4N]_2Mo_5Cl_{13}$ shows two quasi-Nernstian redox couples: $E_{1/2}(\text{ox}) = 0.49$ V and $E_{1/2}(\text{red}) = -0.36$ V vs. Ag/AgCl in methylene chloride solution. Both the electrochemically stable $Mo_5Cl_{13}^-$ and $Mo_5Cl_{13}^{3-}$ clusters have been isolated as their tetrabutylammonium salts. The synthesis of $[(n\text{-}C_4H_9)_4N]_2Mo_5Br_{13}$ is described along with its cyclic voltammogram, which also shows two quasi-Nernstian waves at $E_{1/2}(\text{ox}) = 0.41$ V and $E_{1/2}(\text{red}) = -0.33$ V $[(n\text{-}C_4H_9)_4NMo_5Br_{13}$ and $[(n\text{-}C_4H_9)_4N]_3Mo_5Br_{13}$ have been isolated]. The $[(n\text{-}C_4H_9)_4N]_3Mo_5X_{13}$ complexes are paramagnetic, and their temperature-dependent magnetic behavior is interpreted in terms of two thermally populated sublevels of a $^3A_2(e^2)$ ground state. Sublevel splittings of <4 cm^{-1} in $Mo_5Cl_{13}^{3-}$ and 15 (5) cm^{-1} in $Mo_5Br_{13}^{3-}$ are estimated from EPR data.

Our interest in the electronic structures of molybdenum(II) and tungsten(II) halide clusters began with the discovery of intense luminescence from $Mo_6Cl_{14}^{2-}$. The extremely long luminescent lifetime (180 μs in acetonitrile solution at room temperature)[1] and rich excited-state electron-transfer chemistry of this and analogous $Mo_6Br_{14}^{2-}$ and $W_6Cl_{14}^{2-}$ clusters[2] have led us to investigate the chemical and photochemical properties of the pentanuclear clusters of the $Mo_5Cl_{13}^{2-}$ type. Structurally, $Mo_5Cl_{13}^{2-}$ is a square pyramid of molybdenum atoms with four triply bridging chlorides on the faces of the pyramid, four chlorides bridging the basal molybdenum atoms, and five axial chlorides[3] (essentially the $Mo_6Cl_{14}^{2-}$ structure with one metal atom and its axial chloride removed). The open coordination site in these pentanuclear clusters could potentially facilitate ground- and excited-state multielectron-transfer reactions.

Here we report the preparation and the electronic spectroscopic, electrochemical, and magnetic properties of $(n\text{-}Bu_4N)Mo_5X_{13}$, $(n\text{-}Bu_4N)_2Mo_5X_{13}$, and $(n\text{-}Bu_4N)_3Mo_5X_{13}$ (X = Cl, Br) complexes. These experiments have allowed us to evaluate several key features of the Meissner–Korol'kov[4] electronic structural model for these clusters.

Experimental Section

Materials. The methylene chloride (Burdick and Jackson reagent grade) used in reactions and physical characterizations was dried over CaH_2, and vacuum-distilled onto 3-Å molecular sieves. All other materials were of reagent grade and used without further purification.

Cluster Compounds: **$(n\text{-}Bu_4N)_2Mo_5Cl_{13}$** was prepared by the literature method[3] and recrystallized from methylene chloride/petroleum ether.

$(n\text{-}Bu_4N)_3Mo_5Cl_{13}$ was prepared by chemical reduction of $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ by stirring it over zinc metal in dry, deoxygenated methylene chloride solution. In a sample reaction $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ (100 mg) was dissolved in 30 mL of deoxygenated methylene chloride and stirred with a slight excess of $n\text{-}Bu_4NCl$ and zinc for 24 h. The solution was filtered and petroleum ether distilled on top of the methylene chloride to crystallize the product. Recovery of the red crystals is about 80%. The solution is air-sensitive, but the crystals only slowly (days) decompose in air. Anal. Calcd for $C_{48}H_{108}N_3$ Mo_5Cl_{13}: C, 34.56; H, 6.53; N, 2.52. Found: C, 34.57; H, 6.63; N, 2.53.

$(n\text{-}Bu_4N)Mo_5Cl_{13}$ was synthesized by chemical oxidation of $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ (100 mg) with chlorine in methylene chloride solution. The chlorine was removed from the reaction mixture by purging with argon and the blue solution was layered with petroleum ether to crystallize the product. Recovery of purple-blue crystals was 95%. Anal. Calcd for $C_{16}H_{36}NMo_5Cl_{13}$: C, 16.24; H, 3.07; N, 1.18. Found: C, 17.49; H, 3.43; N, 1.23.

$(n\text{-}Bu_4N)_2Mo_5Br_{13}$ was synthesized in a manner analogous to the chloride preparation. Aluminum bromide (6.2 g), potassium bromide (1.6 g), bismuth trichloride (1.1 g), bismuth (0.5 g), and potassium hexachloromolybdate(III) (0.5 g) were placed in a quartz tube that was evacuated and sealed off under vacuum. After 3 h of slow heating to 300 °C (*Caution! Explosion danger!*) and 1 h at 300 °C, the tube was allowed to cool to room temperature and broken, and the contents were extracted with 6 N HBr and filtered. The filtrate was treated with $n\text{-}Bu_4NBr$, causing a dull green precipitate to form. This was collected by vacuum filtration and dissolved in methylene chloride; this solution was dried over anhydrous $MgSO_4$ and crystallized with petroleum ether. The yield of crystalline material was 120 mg. Anal. Calcd for $C_{32}H_{72}N_2Mo_5Br_{13}$: C, 19.16; H, 3.59; N, 1.40; Mo, 23.95; Br, 51.90. Found: C, 19.39; H, 3.67; N, 1.49; Mo, 23.75; Br, 51.99.

$(n\text{-}Bu_4N)_3Mo_5Br_{13}$ was synthesized by reduction of $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ in a manner completely analogous to that of the chloride. Both the light green solution and the crystals are air-sensitive. Anal. Calcd for $C_{48}H_{108}N_3Mo_5Br_{13}$: C, 25.67; H, 4.66; N, 1.87. Found: C, 25.19; H, 4.66; N, 1.90.

$(n\text{-}Bu_4N)Mo_5Br_{13}$ was also made in the same manner as the chloride, using bromine as the oxidant of the $(n\text{-}Bu_4N)_2Mo_5Br_{13}$. Crystallization of the methylene chloride solution with petroleum ether resulted in emerald green crystals.

Analytical Procedures. Carbon, hydrogen, nitrogen, molybdenum, and bromide were determined by Galbraith Microanalytical Labs, Inc.

Physical Measurements. Room-temperature magnetic susceptibility measurements were made on a Faraday balance with $HgCo(SCN)_4$ as calibrant. Variable-temperature susceptibility measurements were made at the University of Southern California on a SQUID-based (S.H.E. Corp.) Model 805 variable-temperature susceptometer with a 2 K option. Electronic spectra were recorded on a Cary 17 spectrometer. EPR spectra were measured on a Varian E-Line Century Series spectrometer equipped with an Air-Products Heli-Tran cooling system. Cyclic voltammetry was performed on a PAR model 174A polarographic analyzer with a Houston Instruments 2000 X-Y recorder. Controlled-potential electrolyses were performed with a Model 179 PAR potentiostat.

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(1) Maverick, A. W.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 1298.

(2) Maverick, A. W.; Najdzionek J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

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(4) Meissner, H.; Korol'kov, D. V. *Z. Anorg. Allg. Chem.* **1983**, *496*, 175.

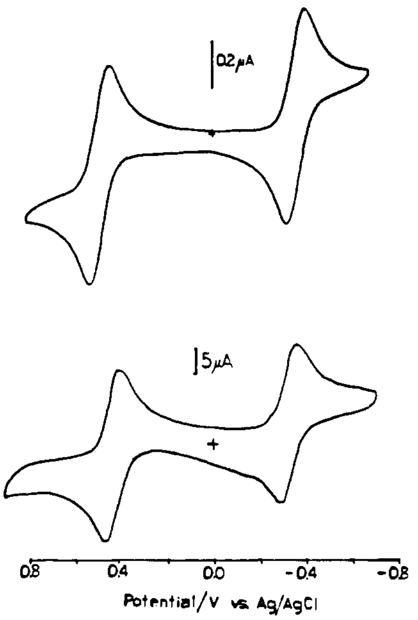

Figure 1. Cyclic voltammogram of (top) $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ and (bottom) $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ in methylene chloride solution with 0.2 M $(n\text{-}Bu_4N)PF_6$ as supporting electrolyte. Potentials are vs. a Ag/AgCl reference electrode.

Table I. Electrochemical Data[a]

cluster ion	$E_{1/2}$(ox), V	$E_{1/2}$(red), V
$Mo_5Cl_{13}^{2-}$	0.49	−0.36
$Mo_5Br_{13}^{2-}$	0.41	−0.33

[a] All cyclic voltammograms performed in a 0.2 M solution of $(n\text{-}Bu_4N)PF_6$ in methylene chloride. All potentials are vs. a Ag/AgCl reference electrode.

Results and Discussion

Electrochemistry. Cyclic voltammetry done on methylene chloride solutions of $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ and $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ revealed one wave corresponding to an oxidation and one wave corresponding to a reduction for each complex (Figure 1). The oxidation couple in the $Mo_5Cl_{13}^{2-}$ system has an $E_{1/2} = 0.49$ V.[5] The reduction couple occurs at $E_{1/2} = -0.36$ V. The analogous couples in the $Mo_5Br_{13}^{2-}$ system occur at $E_{1/2} = 0.41$ V and $E_{1/2} = -0.33$ V (oxidation and reduction, respectively). All waves displayed quasi-Nernstian behavior with a plot of i_p vs. $v^{1/2}$ linear over the scan rate range 20–500 mV s^{-1}, which indicates that the electron transfer at the electrode is not rate-limiting at these scan rates. The peak separation for the same range of scan rates was 70 ± 5 mV for both systems, increasing slightly with higher scan rate; the discrepancy from the 59 mV predicted for one-electron transfer is probably due to uncompensated solution resistance. The cathodic to anodic peak current ratios (reduction) and anodic to cathodic peak current ratios (oxidation) were 1.10 ± 0.10, again indicating quasi-Nernstian behavior.

Comparison of the cyclic voltammograms of the two clusters shows that the bromide is more easily oxidized than the chloride, which is in accordance with our results for the Mo_6 system.[2] Somewhat surprisingly, the bromide is also more easily reduced than the chloride in the pentanuclear clusters, although by only 30 mV. In the Mo_6 clusters we have observed reversible reductive electrochemistry in only the $Mo_6Cl_{14}^{2-}$ system.[6]

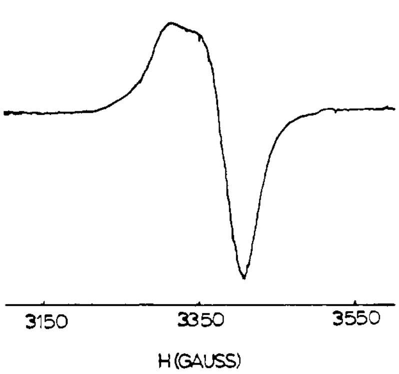

Figure 2. X-Band (9.265 GHz) EPR spectrum of $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ in frozen (77 K) methylene chloride.

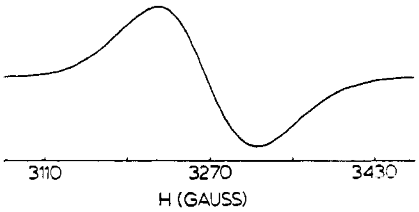

Figure 3. X-Band (9.196 GHz) EPR spectrum of $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ in frozen (70 K) methylene chloride.

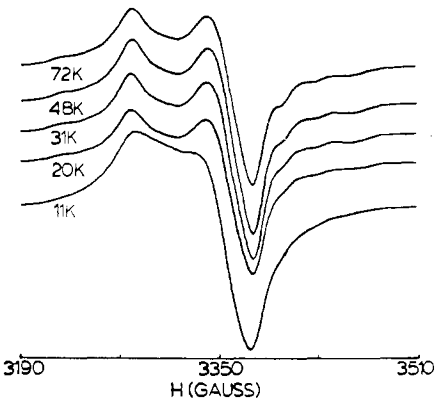

Figure 4. Variable-temperature X-band (9.198 GHz) EPR spectra of $(n\text{-}Bu_4N)_3Mo_5Cl_{13}$ in frozen methylene chloride.

Bulk electrolysis of $Mo_5Cl_{13}^{2-}$ in methylene chloride solution at a potential anodic to the oxidation couple resulted in a purple-blue solution with a CV identical with that of the starting material. The product was not isolated since chemical oxidation resulted in the same material (identified by its optical absorption spectrum). Electrolysis at a potential cathodic to the reduction wave resulted in clean conversion to $Mo_5Cl_{13}^{3-}$ (identical CV). Again, chemical means proved more convenient to work up the product. The electrochemical behavior of the $Mo_5Br_{13}^{2-}$ cluster is similar to that of the chloride (Table I).

Electronic Spectra. Electronic spectral data for the cluster compounds are set out in Table II. The low-energy features in these spectra are remarkably insensitive to the ligand composition and the oxidation level of the cluster, thereby implying that the donor and acceptor orbitals are confined to (but delocalized over) the Mo_5 framework. It is highly likely that the orbital that is singly occupied in $Mo_5X_{13}^{2-}$ is the acceptor in one or more of these transitions. According to the Meissner–Korol'kov EHMO calculation, this orbital is of e symmetry and is 96% Mo_5.[4]

EPR Spectra. The X-band (9.265 GHz) EPR spectrum of $Mo_5Cl_{13}^{2-}$ in a frozen methylene chloride solution (77 K) is displayed in Figure 2. The spectrum can be accounted for by an axially symmetric doublet ground state ($g_\perp = 1.96$ and $g_\parallel = 2.00$). No hyperfine splitting was observed. The EPR spectrum of $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ in frozen methylene chloride solution (70 K) is isotropic with $g = 2.01$ (Figure 3). Again, no hyperfine splitting was observed.

The EPR spectrum of $Mo_5Cl_{13}^{3-}$ in frozen methylene chloride solution shows a well-defined anisotropic signal with an absorption

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(5) All potentials are vs. a Ag/AgCl reference electrode with 0.2 M tetrabutylammonium hexafluorophosphate in methylene chloride as electrolyte.

(6) Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1984**, *106*, 824. We do see cathodic current for the reduction of $Mo_6Br_{14}^{2-}$ in acetonitrile, but the process appears to be irreversible at scan rates up to 500 mV/s.

Table II. Electronic Spectral Data[a]

cluster ion	band 1	2	3	4	5
$Mo_5Cl_{13}^{3-}$	796 [150]	580 s [300]	482 [1000]	350 [3700]	312 [5600]
$Mo_5Cl_{13}^{2-}$	723 [960]	543 [1300]	458 [2400]	272 s [13000]	
$Mo_5Cl_{13}^{-}$	742 [2040]	557 [1830]	489 [2360]		
$Mo_5Br_{13}^{3-}$	753 s	588 s	473		
$Mo_5Br_{13}^{2-}$	730 [370]	570 [890]	473 [1800]		
$Mo_5Br_{13}^{-}$	768 [1660]	612 [1390]	520 [1510]		

[a] All complexes are the *n*-Bu_4N salt in methylene chloride solution at 300 K. Spectra recorded from 1200 to 250 nm. Reported in nm [ϵ (M^{-1} cm^{-1})].

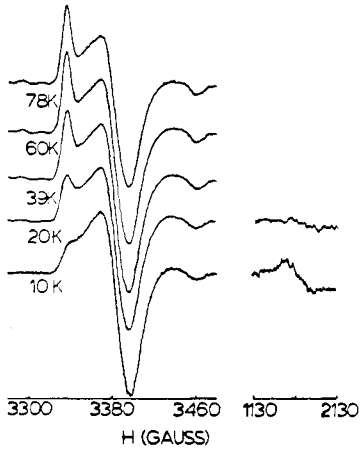

Figure 5. Variable-temperature X-band (9.195 GHz) EPR spectra of $(n\text{-}Bu_4N)_3Mo_5Br_{13}$ in frozen methylene chloride.

at $g = 1.95$ and one at $g = 2.00$ at 70 K (Figure 4). Hyperfine splitting of about 30 G was observed in the spectrum. When the sample is cooled to liquid-helium temperature, the signal loses the clear anisotropy of the 70 K spectrum, but does not quite become isotropic by 9 K. The hyperfine signals are lost, and no signal is observed at half-field at any of the temperatures studied. Comparing the spectra at high (70 K) and low (9 K) temperatures, the absorption at $g = 1.95$ diminishes as the temperature is lowered, but the signal does not quite disappear by 9 K.

The EPR spectrum of $Mo_5Br_{13}^{3-}$ displays much the same general features. The signal at 70 K shows two distinct absorptions ($g = 1.97$ and $g = 2.01$) (Figure 5). The hyperfine splitting that is resolved in the chloride is not observed in the bromide spectrum. Upon cooling, the signal at $g = 2.01$ gradually diminishes, and the spectrum becomes almost isotropic at 9 K. A signal at $g = 4.3$ can be detected at 9 K, but diminishes as the temperature is raised to 25 K. The appearance of the spectrum at 9 K is almost that of a simple triplet state[7] with the allowed ($\Delta M_s = 1$) transition occurring at $g = 2$, and the forbidden ($\Delta M_s = 2$) transition at about half-field ($g = 4.3$).

The EPR spectra of the $Mo_5X_{13}^{3-}$ clusters may be interpreted in terms of two thermally equilibrated paramagnetic electronic states. From a simple intensity vs. temperature calculation, we estimate the splitting of the two states to be <4 cm^{-1} and 15 (5) cm^{-1} for X = Cl and X = Br, respectively.

Magnetic Susceptibility. In agreement with Beers and McCarley,[8] we found that the room-temperature effective magnetic moment of $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$ is 1.7 μ_B. The $(n\text{-}Bu_4N)_2Mo_5Br_{13}$ cluster has $\mu_{eff} = 1.6$ μ_B. Both of these values are consistent with a simple spin-doublet ground state. The oxidized clusters, $(n\text{-}Bu_4N)Mo_5Cl_{13}$ and $(n\text{-}Bu_4N)Mo_5Br_{13}$, are diamagnetic, whereas $(n\text{-}Bu_4N)_3Mo_5Cl_{13}$ was found to be paramagnetic at room temperature ($\mu_{eff} = 0.56$ μ_B).

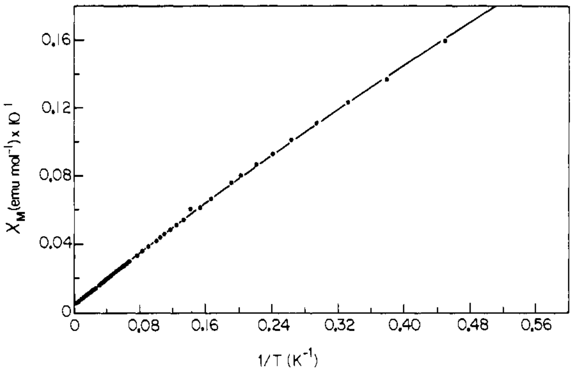

Figure 6. Magnetic susceptibility of powdered $(n\text{-}Bu_4N)_3Mo_5Cl_{13}$ as a function of reciprocal temperature. Fit is to Curie–Weiss behavior with a Curie constant of 3.9×10^{-2} emu K mol^{-1}.

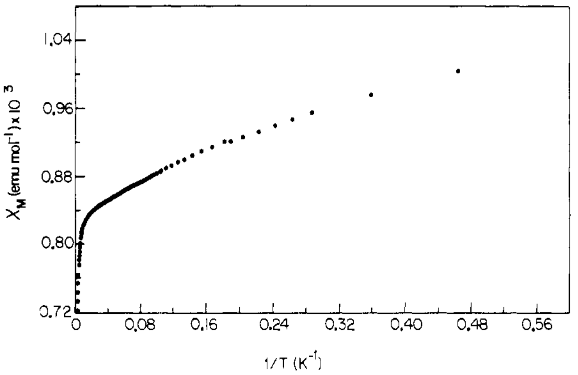

Figure 7. Magnetic susceptibility of powdered $(n\text{-}Bu_4N)_3Mo_5Br_{13}$ as a function of reciprocal temperature.

The plots of molar susceptibility vs. $1/T$ for the two $Mo_5X_{13}^{3-}$ clusters are shown in Figures 6 and 7. The $Mo_5Cl_{13}^{3-}$ cluster appears to follow Curie–Weiss behavior over the temperature range 5–300 K, with a very slight deviation at temperatures below 5 K. These results accord very well with the EPR analysis, which indicated a very small (<4 cm^{-1}) splitting of two thermally equilibrated states. The magnetic susceptibility data for the $(n\text{-}Bu_4N)_3Mo_5Br_{13}$ powder sample deviate from simple Curie–Weiss behavior and can be fit reasonably well by using the energy spacing derived from the EPR experiment.

When materials with low magnetic moments are discussed, consideration should be given to the possibility that paramagnetic impurities (in this case the 2– cluster) may dominate the magnetic properties of interest (the 3– anion's magnetic data). The data above provide evidence that the behavior observed is not due to 2– anion impurities: (a) the EPR spectra of $Mo_5Cl_{13}^{3-}$ and $Mo_5Cl_{13}^{2-}$ have similar *g* values, but the shapes are not the same at 70 K, and the hyperfine structure observed in $Mo_5Cl_{13}^{3-}$ is not found in the 2– spectrum; (b) the $\Delta M_s = 2$ transition that is observed in the $Mo_5Br_{13}^{3-}$ EPR at 10 K cannot arise from a spin = $^1/_2$ system; (c) the clear deviation from Curie–Weiss behavior in the $Mo_5Br_{13}^{3-}$ magnetic data indicates that the paramagnetism is not due to 2– contamination.

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[7] Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance, Elementary Theory and Practical Applications"; McGraw-Hill: New York, 1972, p 238.

[8] Beers, W. W.; McCarley, R. E. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, 1982, American Chemical Society: Washington, DC; INOR 199.

Inorg. Chem. **1986**, *25*, 634-643

The EHMO calculation of Meissner and Korol'kov predicts a $^3A_2(e^2)$ ground state for $Mo_5X_{13}^{3-}$ clusters.[4] Our results indicate that the $Mo_5X_{13}^{3-}$ ground state is paramagnetic, and at least for $Mo_5Br_{13}^{3-}$, the EPR spectrum is characteristic of a triplet state at low (10 K) temperatures.[9] At higher temperatures, the lowest electronic states are in thermal equilibrium in each cluster trianion. The low magnetic moments of these even electron clusters are not unprecedented for high nuclearity metal systems. Recent work has shown that $H_2Os_{10}C(CO)_{24}$ exhibits Curie paramagnetic behavior with $\mu_{eff} = 0.62\ \mu_B$ per cluster molecule.[10] Although more sophisticated electronic structural models undoubtedly will be required to understand in quantitative detail the magnetic properties of the $Mo_5X_{13}^{3-}$ clusters, it is worth pointing out in closing that the broad $g \sim 2$ EPR spectra and the low effective magnetic moments are reminiscent of conduction band electrons in bulk metals.

Acknowledgment. We thank L. G. Butler for assistance with the analysis of the magnetic susceptibility data, and R. E. McCarley for helpful discussions. This research was supported by National Science Foundation Grant CHE84-19828.

Registry No. $(n\text{-}Bu_4N)_3Mo_5Cl_{13}$, 99727-62-5; $(n\text{-}Bu_4N)_2Mo_5Cl_{13}$, 55913-48-9; $(n\text{-}Bu_4N)Mo_5Cl_{13}$, 99727-64-7; $(n\text{-}Bu_4N)_2Mo_5Br_{13}$, 99748-38-6; $(n\text{-}Bu_4N)_3Mo_5Br_{13}$, 99727-66-9; $(n\text{-}Bu_4N)Mo_5Br_{13}$, 99766-94-6; $K_3[MoCl_6]$, 13600-82-3.

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(9) McCarley and co-workers have determined the crystal structure of $(PhEt_3N)_2Mo_5Cl_{13}$ (McCarley, R. E., private communication). They find that the cluster is distorted rhombically from C_{4v} symmetry, which would split the e level. Clearly, it would be of great interest to see if this distortion is retained in the structure of the reduced (3−) species, because our data indicate that the 3− ground state is a spin-triplet. The implication from our work is that the distortion in the 3− cluster is not large.

(10) Benfield, R. E.; Edwards, P. P.; Stacy, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 525.

Contribution from the School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, Department of Chemistry, University of Delaware, Newark, Delaware 19711, and Crystalytics Company, Lincoln, Nebraska 68501

$(CH_3C_5H_4)_2V_2S_4$ as an Organometallic Ligand: Preparation of Iron, Cobalt, Nickel, and Iridium Derivatives and Structures of a V_4Ni Cluster and Three V_2Fe Clusters

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The reactions of iron, cobalt, nickel, and iridium complexes with $(CH_3C_5H_4)_2V_2S_4$ (**1**) have been studied, resulting in the preparation of a series of new mixed-metal clusters. Reaction of **1** with $Fe(CO)_5/Me_3NO$ yields $(CH_3C_5H_4)_2V_2S_4Fe(CO)_3$ (**2**) while $(CH_3C_5H_4)_2V_2S_4Fe(NO)_2$ (**3**) is obtained from **1** and $Fe(CO)_2(NO)_2$. The $\mu\text{-}\eta^2\text{-}S_2$ ligands in **2** and **3** are electrophilic and react with PBu_3 or $Pt(C_2H_4)(PPh_3)_2$ to give V_2FeS_3 or V_2FePtS_4 clusters, respectively. The compound $(CH_3C_5H_4)_2V_2S_4CoC_5H_5$ can be prepared from **1** and $C_5H_5Co(CO)_2$ or $CpCo(CO)I_2$ and Zn. The cluster $(CH_3C_5H_4)_2V_2S_4Ir(PPh_3)Cl$ can be prepared from **1** and $IrCl(N_2)(PPh_3)_2$; ^1H NMR studies on this compound show that the vanadium centers are equivalent. $[(C_5H_5)Ni(CO)]_2$ reacts with **1** to give $[(CH_3C_5H_4)_2V_2S_4]_2Ni$ (**4**), which can be desulfurized to give $[(CH_3C_5H_4)_2V_2S_3]_2Ni$. The V_4NiS_8 cluster also reacts with $Pt(C_2H_4)(PPh_3)_2$ to give V_4NiS_8Pt and $V_4NiS_8Pt_2$ derivatives. The compound $(CH_3C_5H_4)_2V_2S_3Fe(NO)_2$ reacts with $CoI(NO)_2$ and zinc to give $(CH_3C_5H_4)VS_3FeCo_2(NO)_6$, an analogue of Roussin's "black salt", $Fe_4S_3(NO)_7^-$. The structures of **2**, **2**-S, **3**, and **4** were determined by X-ray crystallographic techniques. The crystals of **2** were monoclinic, with $a = 9.853$ (2) Å, $b = 15.652$ (3) Å, $c = 12.821$ (3) Å, $\beta = 105.89$ (2)°, and $Z = 4$; the space group was $P2_1/c$. Conventional full-matrix least-squares refinement with non-hydrogen atoms anisotropic and hydrogen atoms isotropic gave $R = 0.028$ and $R_w = 0.036$ for 2889 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure consists of an isosceles triangle of metal atoms capped by two μ_3-S moieties, with the V–V edge spanned by a $\mu\text{-}\eta^2\text{-}S_2$ ligand. The V–Fe distances are unusually long, and the V–V distances are unusually short. The crystals of **2**-S were monoclinic with $a = 10.397$ (2) Å, $b = 25.504$ (7) Å, $c = 14.135$ (4) Å, $\beta = 106.63$ (2)°, and $Z = 8$; the space group was $P2_1/c$. Modified full-matrix least-squares refinement with non-hydrogen atoms anisotropic and fixed hydrogen atoms isotropic gave $R = 0.038$ and $R_w = 0.051$ for 8422 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure is similar to that of **2** but with the V–V edge spanned by a μ-S ligand. The crystals of **3** were monoclinic with $a = 10.190$ (3) Å, $b = 12.680$ (5) Å, $c = 14.016$ (5) Å, $\beta = 103.01$ (3)°, and $Z = 4$; the space group was $P2_1/c$. Conventional full-matrix least-squares refinement with the non-hydrogen atoms anisotropic and the hydrogen atoms isotropic gave $R = 0.031$ and $R_w = 0.030$ for 5227 reflections having $2\theta < 55°$ and $I > 3\sigma(I)$. The structure of **3** is very similar to that for **2**, except that the iron is coordinated to two nearly linear nitrosyl ligands. The unusual V–Fe bond lengths of **2**, **2**-S, and **3** are rationalized by V–S(μ-S) and V–S(μ_3-S) π interactions, which are competitive with V–Fe bonding. Crystals of the V_4Ni cluster **4** were orthorhombic with $a = 16.014$ (4) Å, $b = 14.477$ (3) Å, $c = 12.990$ (3) Å, and $Z = 4$; the space group was *Pbcn*. Refinement with the least-squares matrix blocked into random units and with anisotropic non-hydrogen atoms gave $R = 0.081$ and $R_w = 0.081$ for 1693 reflections having $2\theta < 50°$ and $F_o > 3\sigma(F_o)$. The molecule consists of tetrahedral Ni situated on a crystallographic 2-fold axis bound via two μ_3-S atoms to each of two $[(CH_3C_5H_4)_2V_2(\mu\text{-}S_2)]$ fragments. The V–V distance is 2.484 (2) Å, and the V–Ni distances are 2.813 ± 0.03 Å.

Introduction

Sulfido complexes are known to function as ligands for other metals and this is the basis upon which a number of cluster compounds are prepared.[1] Along these lines, the coordination chemistry of bis(methylcyclopentadienyl)divanadium tetrasulfide $(CH_3C_5H_4)_2V_2S_4$ (**1**) has been the subject of our studies (Scheme I).[2-4] Two distinguishing characteristics of **1** are (i) it is formally highly electron-deficient and its complexes should exhibit novel structural and chemical properties, and (ii) the derivatives of **1**, i.e. V_2MS_4 complexes, are themselves ligands, thereby permitting

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