Inorg. Chem. **1998,** *37,* 6852−6857

Syntheses, Structures, FAB Mass Spectra, and Magnetic Properties of Chromium Chalcogenide Cluster Complexes $[Cr_6Se_8(PEt_3)_6]$, $[Cr_6Se_8(H)(PEt_3)_6]$, and $[Cr_6S_8(H)(PEt_3)_6]$

Satoshi Kamiguchi, Hideo Imoto,* and Taro Saito

Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku,
Tokyo 113-0033, Japan

Teiji Chihara

Institute of Physical and Chemical Research (RIKEN), Wako-shi, Saitama 351-0198, Japan

Received July 7, 1998

Chromium selenide cluster complexes $[Cr_6Se_8(PEt_3)_6]$ (**1**) and $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**) were prepared by the reaction of anhydrous chromium dichloride, Na_2Se_x, and triethylphosphine in methanol. A similar procedure except for the use of NaS_xH in place of Na_2Se_x gave a sulfide cluster complex $[Cr_6S_8(H)(PEt_3)_6]$ (**3**). The partly deuterated derivative $[Cr_6S_8(D)_{0.8}(H)_{0.2}(PEt_3)_6]$ (**4**) was prepared for comparison. An extra hydrogen atom in **2**−**4** has been confirmed by FAB mass spectra. The reactivity and structural studies have indicated that it is at the center of the Cr_6 octahedral cluster. The molecular structures of **1** and **2** have been determined by X-ray structure analyses. Crystallographic data: $[Cr_6Se_8(PEt_3)_6]$ (**1**) (226 K), triclinic, $P\bar{1}$, $a = 12.887(2)$ Å, $b = 25.332(7)$ Å, $c = 12.061(3)$ Å, $\alpha = 111.23(2)°$, $\beta = 108.25(2)°$, $\gamma = 109.86(2)°$, $Z = 2$; $[Cr_6Se_8(H)(PEt_3)_6]\cdot 2THF$ (**2**) (293 K), rhombohedral, $R\bar{3}$, $a = 17.384(4)$ Å, $c = 19.768(4)$ Å, $Z = 3$. The Cr−Cr bond distances of **2** are 0.13−0.16 Å shorter than those of **1**, indicative of bonding interaction between the insterstitial hydrogen and the six chromium atoms in **2**. The number of cluster valence electrons for **1** is 20 while that for **2** and **3** is 21. Magnetic measurements (2−330 K for **1**, 2.5−330 K for **2**, and 4.5−330 K for **3**) have shown that the number of unpaired spins in the ground state for **1** is zero while that for **2** and **3** is one.

Introduction

The chemistry of metal chalcogenide cluster compounds with the M_6E_8 (E = S, Se, Te) cluster unit consisting of a M_6 octahedron and eight face-capping E atoms has made remarkable progress in the past decade.$^{1-5}$ The $[M_6E_8L_6]$ type molecular complexes of zirconium,^{6} vanadium,^{6} chromium,$^{7-9}$ molybdenum,$^{10-15}$ tungsten,$^{16-22}$ rhenium,$^{23-30}$ iron,$^{31-34}$ and cobalt$^{35-44}$ have been prepared.

We have reported the syntheses of $[Cr_6Se_8(PEt_3)_6]$ and $[Cr_6S_8(PEt_3)_6]$ by the reaction of $CrCl_2$ with Na_2Se or NaSH, respectively, in methanol.^{8} In the course of further studies on

---

(1) Saito, T. In *Early Transition Metal Clusters with Π-Donor Ligands*; VCH: New York, 1995; pp 63−164.
(2) Saito, T. *Adv. Inorg. Chem.* **1996**, *44*, 45.
(3) Perrin, A.; Sergent, M. *New J. Chem.* **1988**, *12*, 337.
(4) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840.
(5) Dance, I.; Fisher, K. *Prog. Inorg. Chem.* **1994**, *41*, 637.
(6) Fenske, D.; Grissinger, A.; Loos, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1991**, *598*/*599*, 121.
(7) Hessen, B.; Siegrist, T.; Palstra, T.; Tanzler, S. M.; Steigerwald, M. L. *Inorg. Chem.* **1993**, *32*, 5165.
(8) Tsuge, K.; Imoto, H.; Saito, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 627.
(9) Kamiguchi, S.; Imoto, H.; Saito, T. *Chem. Lett.* **1996**, 555.
(10) Saito, T.; Yamamoto, N.; Nagase, T.; Tsuboi, T.; Kobayashi, K.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1990**, *29*, 764.
(11) Hilsenbeck, S. J.; Young, V. G.; McCarley, R. E. *Inorg. Chem.* **1994**, *33*, 1822.
(12) Hilsenbeck, S. J.; McCarley, R. E. *Chem. Mater.* **1995**, *7*, 499.
(13) McCarley, R. E.; Hilsenbeck, S. J.; Xie, X. *J. Solid State Chem.* **1995**, *117*, 269.
(14) Amari, S.; Imoto, H.; Saito, T. *Chem. Lett.* **1997**, 967.
(15) Mizutani, J.; Amari, S.; Imoto, H.; Saito, T. *J. Chem. Soc., Dalton Trans.* **1998**, 819.
(16) Saito, T.; Yoshikawa, A.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1989**, *28*, 3588.
(17) Zhang, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 2678.
(18) Ehrlich, G. M.; Warren, C. J.; Vennos, D. A.; Ho, D. M.; Haushalter, R. C.; DiSalvo, F. J. *Inorg. Chem.* **1995**, *34*, 4454.
(19) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1995**, *34*, 6124.
(20) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1996**, *35*, 2713.
(21) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1997**, *36*, 4011.
(22) Xie, X.; McCarley, R. E. *Inorg. Chem.* **1997**, *36*, 4665.
(23) Uriel, S.; Boubekeur, K.; Batail, P.; Orduna, J.; Canadell, E. *Inorg. Chem.* **1995**, *34*, 5307.
(24) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603.
(25) Mironov, Y. V.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 2709.
(26) Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.
(27) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163.
(28) Fedin, V. P.; Fedorov, V. E.; Imoto, H.; Saito, T. *Polyhedron* **1997**, *16*, 1615.
(29) Zheng, Z.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 5173.
(30) Willer, M. W.; Long, J. R.; McLauchlan, C. C.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 328.
(31) Cecconi, F.; Ghilardi, C. A.; Midollini, S. *J. Chem. Soc., Chem. Commun.* **1981**, 640.
(32) Agresti, A.; Bacci, M.; Cecconi, F.; Ghilardi, C. A.; Midollini, S. *Inorg. Chem.* **1985**, *24*, 689.
(33) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1987**, 831.
(34) Goddard, C. A.; Long, J. R.; Holm, R. H. *Inorg. Chem.* **1996**, *35*, 4347.
(35) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1981**, *64*, L47.
(36) Fenske, D.; Hachgenei, J.; Ohmer, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 706.
(37) Fenske, D.; Ohmer, J.; Hachgenei, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 993.
(38) Diana, E.; Gervasio, G.; Rossetti, R.; Valdemarin, F.; Bor, G.; Stanghellini, P. L. *Inorg. Chem.* **1991**, *30*, 294.

10.1021/ic9807700 CCC: $15.00 © 1998 American Chemical Society
Published on Web 12/01/1998

the redox properties of the selenide cluster complex, cyclic voltammetry indicated that it actually was a mixture of two compounds. In the present study, we have separated them. The measurements of FAB mass spectra and magnetic susceptibilities have suggested that one of them is $[Cr_6Se_8(PEt_3)_6]$ and the other is $[Cr_6Se_8(H)(PEt_3)_6]$, having an extra hydrogen atom associated with the cluster unit. The measurements have also suggested that the sulfide cluster complex is actually $[Cr_6S_8(H)(PEt_3)_6]$, containing an extra hydrogen atom. The present paper describes the syntheses, structures, FAB mass spectra, and magnetic properties of these complexes. The probable position of the extra hydrogen atom is also discussed.

Experimental Section

All of the manipulations were carried out under dinitrogen or argon using conventional Schlenk techniques. Solvents were dried and distilled under argon from appropriate drying agents (sodium metal wire for benzene and toluene, magnesium for methanol and ethanol, calcium sulfate for acetone, and sodium/benzophenone for THF). Sodium hydrogen sulfide was prepared by a reaction of sodium ethoxide and hydrogen sulfide. Sodium polyselenide (Na_2Se_x; $x = 1.33$) was prepared by a supersonic reaction of sodium metal and selenium powder in THF with a catalytic amount of naphthalene.[45] Triethylphosphine (Kanto Kagaku) and the other reagents (Aldrich) were used as received.

Synthesis of $[Cr_6Se_8(PEt_3)_6]$ (1). A methanol solution (20 cm^3) of Na_2Se_x ($x = 1.33$; 0.52 g, 3.5 mmol) was added dropwise to a suspension of anhydrous chromium dichloride ($CrCl_2$) (0.43 g, 3.5 mmol) in methanol (10 cm^3) at −78 °C. A mixture of a brown solution and a brown precipitate was formed. Subsequently, PEt_3 (20% w/w toluene; 4.9 cm^3, 7.1 mmol) was added to the mixture, which was stirred and allowed to warm slowly (ca. 8 h) to room temperature. The resulting suspension was refluxed for 8 h. The solvent was removed in vacuo, and the black material was extracted with hot benzene (30 cm^3). After benzene was removed in vacuo, the resulting solid was washed with acetone (3 × 30 cm^3) and dried in vacuo to give a black mixture of **1** and **2**. These complexes were separated by a selective oxidation of **2**. To a suspension of this mixture in toluene (90 cm^3) was added an acetone solution (10 cm^3) of ferrocenium hexafluorophosphate (0.030 g, 0.091 mmol). The amount of ferrocenium cation was controlled so that only complex **2** was oxidized. The solution was stirred at room temperature for 5 h, and the solvent was removed in vacuo. The residue was washed with acetone (100 cm^3 and 2 × 10 cm^3) to remove **2**$^+$, dried in vacuo, and extracted with toluene (20 cm^3). Ethanol (85 cm^3) was added to the extract, and the solution was allowed to stand at −20 °C for 4 days to form **1** as black crystals. Yield: 0.044 g (4%). ^{1}H NMR (C_6D_6): $\delta = 1.50$ (54H), −4.18 (36H). Found: C, 26.30; H, 5.25. Calcd for $C_{36}H_{90}Cr_6P_6Se_8$: C, 26.16; H, 5.49.

Synthesis of $[Cr_6Se_8(H)(PEt_3)_6]$ (2). The mixture of **1** and **2** obtained by the reaction of $CrCl_2$, Na_2Se_x, and PEt_3 was suspended in toluene (90 cm^3) as described for the synthesis of **1**. After an acetone solution (10 cm^3) of ferrocenium hexafluorophosphate (0.022 g, 0.066 mmol) was added, the resulting mixture was stirred at room temperature for 5 h, and the solvent was removed in vacuo. The oxidized cluster **2**$^+$ was extracted from the residue with acetone (100 cm^3). An acetone solution (10 cm^3) of cobaltocene (0.017 g, 0.09 mmol) was added to the extract to reduce **2**$^+$. The resulting mixture was stirred at room temperature for 1 h to give a yellow solution and a black precipitate. After the solution was filtered off, the precipitate was washed with acetone (2 × 10 cm^3), dried in vacuo, and extracted with hot THF (75 cm^3). The THF extract was allowed to stand at −20 °C for 5 days to yield **2**·2THF as black crystals. Yield: 0.081 g (8%). ^{1}H NMR (C_6D_6): $\delta = 1.50$ (54H), −0.41 (36H). Found: C, 29.28; H, 5.88. Calcd for $C_{44}H_{107}O_2Cr_6P_6Se_8$: C, 29.40; H, 6.00.

Synthesis of $[Cr_6S_8(H)(PEt_3)_6]$ (3). Complex **3** was prepared following the procedure previously reported for $[Cr_6S_8(PEt_3)_6]$.[8] A solution of NaS_xH ($x = 1.33$) prepared from NaSH (0.23 g, 4.1 mmol) and S_8 (0.043 g, 0.17 mmol) in methanol (20 cm^3) was added to a suspension of $CrCl_2$ (0.50 g, 4.1 mmol) in methanol (10 cm^3) at −78 °C. A mixture of a brown solution and a brown precipitate formed. PEt_3 (1.2 cm^3, 8.2 mmol) was added to the mixture, which was stirred and allowed to warm slowly (ca. 8 h) to room temperature. The solvent was removed in vacuo, and the resulting solid was extracted with hot benzene (30 cm^3). The benzene extract was allowed to stand at room temperature to yield **3**·$2C_6H_6$ as black crystals. Yield: 0.20 g (21%). ^{1}H NMR (C_6D_6): $\delta = 1.80$ (54H), 0.04 (36H). Found: C, 39.45; H, 7.06; S, 17.62. Calcd for $C_{48}H_{103}Cr_6P_6S_8$: C, 40.18; H, 7.24; S, 17.88.

Synthesis of $[Cr_6S_8(D)_{0.8}(H)_{0.2}(PEt_3)_6]$ (4). The procedure for **3** was followed, except for using MeOD as solvent. Yield: 0.20 g (21%). The IR spectrum and ^{1}H NMR spectrum are identical with those of **3**. Found: C, 39.38; H, 6.87; S, 17.39. Calcd for $C_{48}H_{103}Cr_6P_6S_8$: C, 40.18; H, 7.24; S, 17.88.

Cyclic Voltammetry. Cyclic voltammetry (CV) was performed on a BAS CV-50W cyclic voltammograph. Three electrodes consisting of a platinum working electrode, a platinum wire counter electrode, and a Ag/Ag^+ ($AgNO_3$ (0.01 N) in CH_3CN) reference electrode were used for the measurements. The compounds were dissolved in THF together with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte, and the scanning rate was 100 mV/s.

FAB Mass Spectra. FAB mass spectra of **1**−**4** were obtained with a JEOL JMS-HX 110A double-focusing mass spectrometer equipped with an XMS data system. A fast-atom xenon beam was generated from Xe^+ ions, which were accelerated to 1 kV with a FAB gun emission current of 1 mA. The samples (∼1 μg) were placed on the stainless steel tip of the probe, mixed with *m*-nitrobenzyl alcohol (Aldrich) as a matrix, and exposed to the xenon beam for the desorption.

Magnetic Measurement. Magnetic susceptibilities of **1**, **2**, and **3** were measured in the temperature ranges 2−330, 2.5−330, and 4.5−330 K, respectively, with a Quantum Design MPMS SQUID. The absence of ferromagnetic impurities was checked by the magnetization measurements at 300 K. The magnetic field of the measurements was 100 G over the whole measured temperature range for **1** and 5 kG in the temperature range 4.5−30 K and 10 kG in the range 30−330 K for **2** and **3**, where the magnetization versus magnetic field curves were linear. The crystalline samples (ca. 30 mg for **1**, ca. 90 mg for **2**, and ca. 100 mg for **3**) were put into cellophane sample holders under a dinitrogen atmosphere. The magnetic susceptibilities of the holders were determined separately. Diamagnetic corrections were estimated from Pascal's constants.

X-ray Structure Determination. A single crystal of **1** suitable for X-ray analysis was obtained by allowing a toluene−ethanol solution to stand at room temperature and that of **2** by recrystallization from THF. The crystals were sealed in glass capillaries for the X-ray measurements. Because the crystal of **2** contained THF molecules escaping from the crystal, the solvent was also sealed for **2**. The X-ray measurements of the crystals were performed on a Rigaku AFC-7R diffractometer with graphite-monochromated Mo Kα radiation at 226 K for **1** and at 293 K for **2**. Neither of the crystals showed significant decay over the period of data collection. All calculations were performed using the TEXSAN crystallographic package.[46] The data were corrected for *Lp* factors and empirically for absorption using the ψ-scan method. The positions of the chromium and selenium atoms were determined by the direct method (SHELXS86),[47] and the other non-hydrogen atoms were located using Fourier techniques (DIRDIF94).[48] The THF molecules in the crystal of **2** are orientationally disordered around the

---

(39) Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M. *Inorg. Chem.* **1991**, *30*, 2256.

(40) Hong, M.; Huang, Z.; Lei, X.; Wei, G.; Kang, B.; Liu, H. *Polyhedron* **1991**, *10*, 927.

(41) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1993**, *214*, 13.

(42) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P.; Cinquantini, A.; Bencini, A.; Uytterhoeven, M. G.; Giorgi, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3881.

(43) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Zanello, P. *Polyhedron* **1996**, *5*, 2021.

(44) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A.; Bencini, A. *J. Chem. Soc., Dalton Trans.* **1996**, 3991.

(45) Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109.

(46) *teXsan*: *Crystal Structure Analysis Package*; Molecular Structure Corporation: Houston, TX, 1985 and 1992.

Table 1. Crystal Parameters and X-ray Diffraction Data for **1** and **2**·2THF

	1	**2**·2THF
formula	$C_{36}H_{90}Cr_6P_6Se_8$	$C_{44}H_{107}O_2Cr_6P_6Se_8$
fw	1652.61	1797.83
space group	$P\bar{1}$ (No. 2)	$R\bar{3}$ (No. 148)
a, Å	12.887(2)	17.384(4)
b, Å	25.332(7)	
c, Å	12.061(3)	19.768(4)
α, deg	111.23(2)	
β, deg	108.25(2)	
γ, deg	109.86(2)	
V, Å^3	2994(2)	5173(2)
λ, Å	0.7107	0.7107
T, K	226	293
Z	2	3
μ, cm^{-1}	60.99	53.04
ρ_{calcd}, g/cm^3	1.833	1.731
R,[a] R_w[b]	0.045, 0.037	0.038, 0.032

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum[w|F_o|^2]\}^{1/2}$; $w = 1/\{\sigma^2(F_o) + p^2|F_o|^2/4\}$; $p = 0.0115$ for **1** and 0.0033 for **2**.

3-fold axis. The four carbon atoms and one oxygen atom of the THF molecule were positionally disordered. Thus each of the mixed carbon−oxygen sites of the THF molecule was refined as a carbon atom with a site-occupancy factor of $^4/_{15}$ and an oxygen atom with that of $^1/_{15}$, and their positional and thermal parameters were constrained to move together. The atoms of the THF molecules in the crystal of **2** were refined isotropically, and all the other non-hydrogen atoms in the crystals of **1** and **2** were refined anisotropically. The hydrogen atoms of the triethylphosphine ligands were located on calculated positions. At the final stage of the refinements, an empirical extinction correction proportional to the observed intensities was included. The final cycle of full-matrix least-squares refinement was based on 9491 observed reflections ($|F_o| > 3\sigma(F_o)$) for **1** and on 2087 observed reflections ($|F_o| > 4\sigma(F_o)$) for **2**. The crystallographic data are given in Table 1. The final atomic parameters of **1** and **2** are listed in Tables 2 and 3.

Other Physical Measurements. The FT-IR spectra were measured with a JASCO FT/IR-300E spectrometer. The ^{1}H NMR (500 MHz) spectra were measured in C_6D_6 with a JEOL α-500 spectrometer using C_6H_6 as the internal standard.

Results and Discussion

Syntheses. The reaction of $CrCl_2$ with Na_2Se_x and PEt_3 in MeOH gave a mixture of $[Cr_6Se_8(PEt_3)_6]$ (**1**) and $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**) (in a ratio of ca. 4:5). The CV of these complexes are shown in Figure 1. Complex **1** exhibits an oxidation step at −0.50 V and a reduction step at −1.75 V, while the oxidation and the reduction step of **2** are observed at −0.81 and −1.48 V, respectively. Since the potential of the oxidation step for **2** is less positive than that for **1**, complex **2** is easier to oxidize. We could separate **1** and **2** by exploiting this difference of their redox properties. By adding ferrocenium hexafluorophosphate, complex **2** was oxidized selectively and turned to $[Cr_6Se_8(H)(PEt_3)_6]^+$ ($\mathbf{2}^+$). Since this oxidized cluster was acetone-soluble and complex **1** was acetone-insoluble, the extraction with acetone could separate the oxidized cluster $\mathbf{2}^+$ from cluster **1**. Reduction of the oxidized cluster $\mathbf{2}^+$ by cobaltocene returned it to the neutral cluster **2**. When we used $NaSe_xH$[49] instead of Na_2Se_x, the ratio of **1** to **2** decreased (ca. 1:3).

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Parameters for $[Cr_6Se_8(PEt_3)_6]$ (**1**)

atom	x/a	y/b	z/c	U_{iso}
Se1	0.08480(6)	0.01817(3)	0.27983(7)	0.0223(2)
Se2	0.04498(6)	0.13014(3)	0.19643(7)	0.0229(2)
Se3	−0.20219(6)	−0.11023(3)	−0.01374(7)	0.0232(2)
Se4	0.24415(6)	−0.00176(3)	0.09592(7)	0.0225(2)
Se5	0.25737(6)	0.51395(3)	0.62445(7)	0.0260(2)
Se6	0.05168(6)	0.49493(3)	0.75509(7)	0.0258(2)
Se7	0.00505(6)	0.38978(3)	0.29813(7)	0.0269(2)
Se8	0.20181(6)	−0.36982(3)	−0.42823(7)	0.0252(2)
Cr1	−0.09073(9)	0.01146(5)	0.1046(1)	0.0204(3)
Cr2	0.16394(9)	0.07281(5)	0.1673(1)	0.0202(3)
Cr3	0.02403(9)	−0.06409(5)	0.0477(1)	0.0205(3)
Cr4	0.03148(10)	0.43435(5)	0.5301(1)	0.0232(3)
Cr5	0.14519(10)	0.57159(5)	0.6871(1)	0.0239(3)
Cr6	0.11827(10)	0.51122(5)	0.4251(1)	0.0233(3)
P1	−0.2065(2)	0.02450(9)	0.2255(2)	0.0274(5)
P2	0.3612(2)	0.15708(8)	0.3770(2)	0.0279(5)
P3	0.0520(2)	−0.14038(8)	0.1109(2)	0.0281(5)
P4	0.0707(2)	0.35685(9)	0.5790(2)	0.0303(5)
P5	0.3227(2)	0.66039(9)	0.9103(2)	0.0346(5)
P6	0.2574(2)	0.52231(9)	0.3299(2)	0.0316(5)
C1	−0.1921(7)	0.1056(3)	0.3001(8)	0.043(2)
C2	−0.2467(8)	0.1232(4)	0.1970(8)	0.049(3)
C3	−0.1591(6)	0.0166(4)	0.3741(7)	0.038(2)
C4	−0.1854(8)	−0.0521(4)	0.3438(8)	0.050(3)
C5	−0.3788(7)	−0.0334(4)	0.1215(8)	0.040(2)
C6	−0.4566(7)	−0.0286(4)	0.1938(9)	0.060(3)
C7	0.3537(7)	0.2208(3)	0.5051(7)	0.040(2)
C8	0.2720(8)	0.1960(4)	0.5610(8)	0.050(3)
C9	0.4331(7)	0.1252(3)	0.4719(7)	0.036(2)
C10	0.5583(8)	0.1759(4)	0.6075(9)	0.065(3)
C11	0.4885(7)	0.2081(3)	0.3613(8)	0.041(2)
C12	0.5410(7)	0.1729(4)	0.2848(9)	0.055(3)
C13	−0.0046(7)	−0.1467(3)	0.2283(7)	0.036(2)
C14	0.0147(9)	−0.1914(4)	0.2797(9)	0.066(3)
C15	0.2164(7)	−0.1218(4)	0.1963(8)	0.043(2)
C16	0.3018(7)	−0.0605(4)	0.3378(8)	0.051(3)
C17	−0.0270(7)	−0.2264(3)	−0.0296(8)	0.043(2)
C18	−0.1676(9)	−0.2633(4)	−0.1015(10)	0.069(3)
C19	0.2028(7)	0.3960(3)	0.7511(8)	0.041(2)
C20	0.2374(9)	0.3526(4)	0.7938(10)	0.073(3)
C21	−0.0628(7)	0.2917(3)	0.5636(7)	0.036(2)
C22	−0.1039(8)	0.3156(4)	0.6693(9)	0.051(3)
C23	0.1091(8)	0.3057(4)	0.4652(9)	0.048(3)
C24	0.2303(9)	0.3418(4)	0.4709(10)	0.063(4)
C25	0.3049(8)	0.7303(4)	0.9946(8)	0.057(3)
C26	0.2995(9)	0.7696(4)	0.9236(9)	0.061(3)
C27	0.3609(7)	0.6407(4)	1.0422(8)	0.051(3)
C28	0.4046(8)	0.5903(4)	1.0172(9)	0.065(3)
C29	0.4719(7)	0.6978(4)	0.9111(8)	0.047(2)
C30	0.5895(8)	0.7543(4)	1.0510(9)	0.071(3)
C31	0.4017(7)	0.6043(3)	0.4248(8)	0.042(2)
C32	0.4916(7)	0.6257(4)	0.5687(9)	0.051(3)
C33	0.1893(8)	0.5095(4)	0.1591(8)	0.049(3)
C34	0.0821(9)	0.4396(5)	0.0455(9)	0.070(3)
C35	0.3194(7)	0.4662(3)	0.3152(8)	0.044(2)
C36	0.4042(8)	0.4690(4)	0.2505(10)	0.063(3)

The reaction of $CrCl_2$ with NaS_xH and PEt_3 in MeOH gave $[Cr_6S_8(H)(PEt_3)_6]$ (**3**). In this reaction, only a very small amount of the non-hydride formed as indicated by the CV and ^{1}H NMR spectra. The FAB mass spectra and the magnetic measurements have shown that complex **3** has an extra hydrogen atom associated with the Cr_6S_8 cluster unit (vide infra). Thus, the cluster complex $[Cr_6S_8(PEt_3)_6]$ reported previously[8] has been reformulated as a hydride complex **3**. A similar procedure using MeOD in place of MeOH gave the deuterated derivative $[Cr_6S_8(D)(PEt_3)_6]$ together with a small amount of undeuterated derivative (in a ratio of ca. 4:1). The formation of both deuterated and undeuterated derivatives by the reaction in MeOD

---

(47) Sheldrick, G. M. *SHELXS86, a program for crystal structure determination*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(48) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(49) Klayman, D. L.; Griffin, T. S. *J. Am. Chem. Soc.* **1973**, *95*, 197.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Cr_6Se_8(H)(PEt_3)_6]\cdot 2THF$ (**2**)

atom	x/a	y/b	z/c	U_{iso}
Se1	0.0000	0.0000	0.15221(5)	0.0311(1)
Se2	−0.11894(3)	0.06583(3)	0.05077(3)	0.0305(2)
Cr	0.03613(5)	0.10054(5)	0.05482(4)	0.0261(2)
P	0.08799(10)	0.23125(10)	0.12360(8)	0.0369(4)
C1	0.1610(4)	0.2401(4)	0.1936(3)	0.048(2)
C2	0.1962(5)	0.3210(5)	0.2390(4)	0.078(3)
C3	0.0036(4)	0.2488(4)	0.1639(3)	0.056(2)
C4	−0.0511(5)	0.1807(5)	0.2184(4)	0.074(3)
C5	0.1515(4)	0.3389(4)	0.0804(3)	0.053(2)
C6	0.2393(4)	0.3574(4)	0.0490(4)	0.069(2)
OC11	−0.076(2)	−0.023(3)	0.368(2)	0.11(1)
OC12	−0.046(3)	0.030(3)	0.423(2)	0.13(1)
OC13	0.046(3)	0.088(2)	0.410(2)	0.13(1)
OC14	0.081(2)	0.014(3)	0.386(2)	0.102(9)
OC15	−0.023(4)	−0.053(2)	0.348(1)	0.13(1)

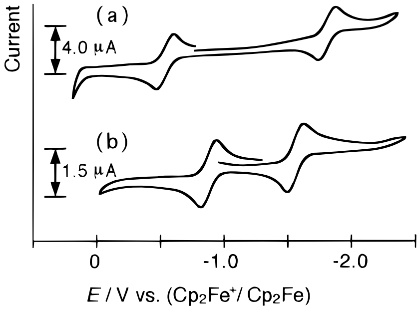

Figure 1. Cyclic voltammograms of (a) $[Cr_6Se_8(PEt_3)_6]$ (**1**) and (b) $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**).

indicates that the extra hydrogen atom for **3** and **4** has come from the hydroxyl group of methanol and NaSH.

In contrast to the preparation of the two selenide cluster complexes using sodium polyselenide, only intractable materials formed in the reaction using Na_2S_x instead of NaS_xH.

FAB Mass Spectra. With *m*-nitrobenzyl alcohol (NBA) as a matrix, we measured the positive-ion FAB mass spectra of **1**−**4**. The comparisons of the isotope patterns of the molecular ion peaks of these complexes with the calculated patterns are summarized in Figures 2 and 3.

It is known that some neutral compounds show the molecular ion peaks corresponding to $[M]^{+\bullet}$ rather than protonated $[M-H]^+$ in the positive-ion FAB mass spectra measured with NBA.[50] We have found that the molybdenum cluster complex $[Mo_6S_8(PEt_3)_6]$[10] shows the peak corresponding to $[Mo_6S_8(PEt_3)_6]^+$. The molecular ion peak for **1** is also assignable to $[Cr_6Se_8(PEt_3)_6]^+$ (Figure 2a), indicating that complex **1** is $[Cr_6Se_8(PEt_3)_6]$. The peak corresponding to the $[M-H]^+$ was not observed.

The pattern of the molecular ion peak for **2** is very similar to that for **1**, but it is shifted in the positive direction by 1 mass unit (Figure 2b). This shows that the molecular ion peak for **2** is assignable to $[Cr_6Se_8(H)(PEt_3)_6]^+$, having an extra hydrogen atom. This peak cannot be ascribable to $[M-H]^+$ because $[Cr_6Se_8(PEt_3)_6]$ (**1**) exhibited only the molecular ion corresponding to $[M]^{+\bullet}$ as described above.

The molecular ion peak for **3** is due to $[Cr_6S_8(H)(PEt_3)_6]^+$ (Figure 3c), suggesting that complex **3** has an extra hydrogen. This is also supported by the molecular ion peak for **4** obtained by the reaction in MeOD. The peak for **4** corresponds to $[Cr_6S_8(D)_{0.8}(H)_{0.2}(PEt_3)_6]^+$ (Figure 3d), in which the deuterated and the undeuterated derivative are mixed in a ratio of ca. 4:1.

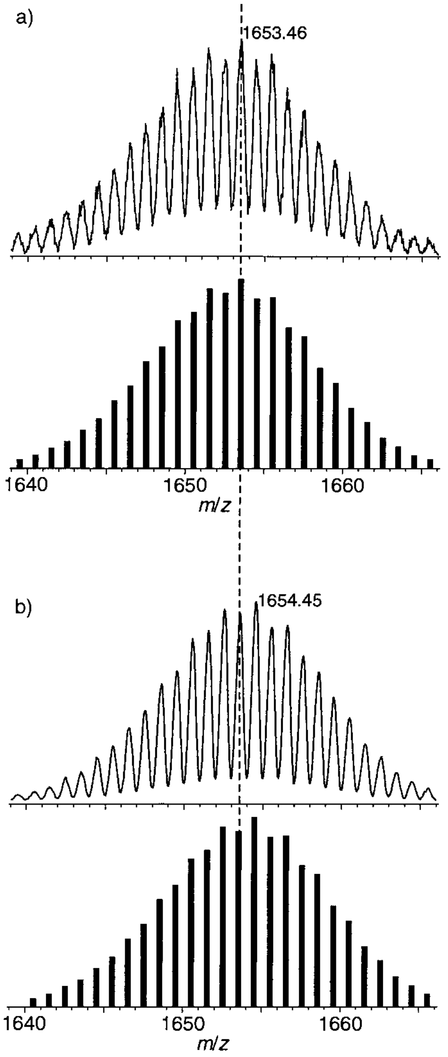

Figure 2. Measured and calculated isotope patterns for the molecular ions of (a) $[Cr_6Se_8(PEt_3)_6]$ (**1**) and (b) $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**).

Magnetic Properties. The measured temperature dependence of the effective magnetic moments ($\mu_{eff} = (8\chi_M T)^{1/2}\mu_B$) of **1**−**3** versus temperature is shown in Figure 4. All these complexes are paramagnetic over the whole temperature range measured. The μ_{eff} values decrease as the temperature is lowered, and the magnetic properties could not be explained by using the Curie−Weiss model even if the temperature-independent paramagnetism (TIP) was included. This indicates that there are intracluster antiferromagnetic interactions between the spins on six chromium atoms. The excited spin states become less populated in lower temperatures, and the magnetic susceptibility at very low temperatures represents the ground state of each chromium complex.

The μ_{eff} value for **1** at 2 K is 0.2 μ_B. The number of unpaired spins approaches zero at very low temperatures due to antiferromagnetic interactions, and $S = 0$ should be the ground state. This magnetic property is compatible with the even number of cluster valence electrons (CVE) (20 e). On the other hand, the μ_{eff} value for **2** at 2 K is 2.0 μ_B, and that for **3** at 4.5 K is 1.7 μ_B; these values are close to the value (1.73 μ_B) of the spin-only magnetic moment for the $S = {}^1/_2$ state. Therefore, complexes **2** and **3** have one unpaired spin in the ground state and have an odd number of CVE (21 e), consistent with the presence of an extra hydrogen atom. These results accord with the FAB mass spectra demonstrating that complexes **2** and **3** are hydrides.

---

(50) Barber, M.; Bell, D.; Eckersley, M.; Morris, M.; Tetler, L. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 18.

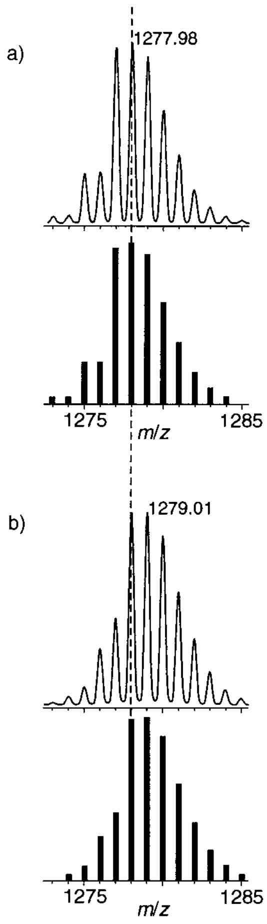

Figure 3. Measured and calculated isotope patterns for the molecular ions of (a) $[Cr_6S_8(H)(PEt_3)_6]$ (**3**) and (b) $[Cr_6S_8(D)_{0.8}(H)_{0.2}(PEt_3)_6]$ (**4**).

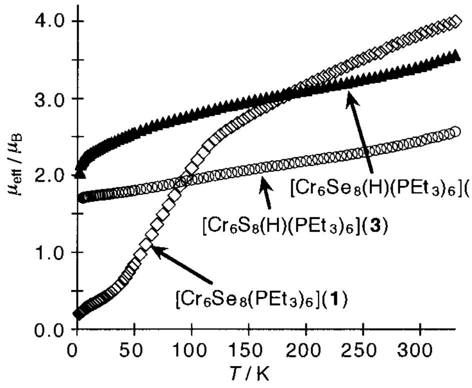

Figure 4. Temperature dependence of the magnetic susceptibilities of $[Cr_6Se_8(PEt_3)_6]$ (**1**), $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**), and $[Cr_6S_8(H)(PEt_3)_6]$ (**3**) in the form of μ_{eff} vs T. The μ_{eff}/μ_B values were calculated as $(8\chi_M T)^{1/2}$.

Steigerwald et al. have reported a telluride analogue $[Cr_6Te_8(PEt_3)_6]$.[7] This complex is paramagnetic and obeys the Curie–Weiss law from 100 to 300 K. The μ_{eff} value is close to 2.8 μ_B, corresponding to two unpaired spins. It is conceivable that the magnetic behavior of the telluride and the selenide cluster **1** depends on the extent of the antiferromagnetic coupling between the chromium atoms.

Structures. Ranges and mean values of selected interatomic distances and angles for selenide complexes **1** and **2** are listed in Table 4. Both complexes comprise a Cr_6 regular octahedron and eight face-capping selenium atoms (Figure 5). One triethylphosphine ligand coordinates to each chromium atom.

Table 4. Ranges and Mean Values of Selected Interatomic Distances (Å) and Angles (deg) for **1** and **2**

	1	2
Cr–Cr	2.796(2)–2.816(1)	2.655(1)–2.656(1)
mean	2.81	2.66
Cr–Se	2.458(1)–2.477(1)	2.441(1)–2.461(1)
mean	2.47	2.45
Cr–P	2.405(2)–2.411(2)	2.403(2)
mean	2.41	
Cr–Cr–Cr[a]	59.58(3)–60.67(4)	59.98(2)–60.03(4)
mean	60.0	60.0
Cr–Cr–Cr[b]	89.23(4)–90.77(4)	90.0
mean	90.0	
Cr–Se–Cr	68.97(4)–69.90(4)	65.31(4)–65.76(4)
mean	69.3	65.5
Se–Cr–Se[c]	88.76(4)–89.95(4)	89.78(3)–90.05(3)
mean	89.4	89.9
Se–Cr–P	92.28(6)–99.05(6)	91.29(5)–95.61(5)
mean	95.7	93.5

[a] Within triangular faces. [b] Within equatorial squares. [c] Between neighboring selenides.

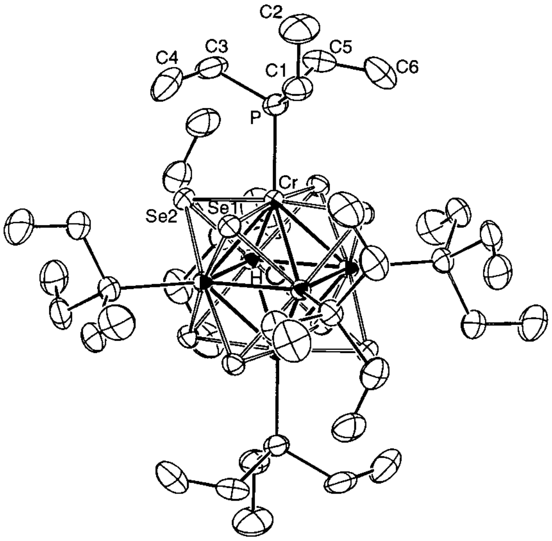

Figure 5. ORTEP drawing of $[Cr_6Se_8(H)(PEt_3)_6]$ (**2**) with 50% probability ellipsoids. The proposed location of the interstitial hydride is shown in this drawing. Hydrogen atoms of ethyl groups are omitted for clarity.

Complexes **2** and **3** have an extra hydrogen atom as indicated by the FAB mass spectra and magnetic measurements. There are three possible positions of the hydrogen atom in **2** and **3**: (1) interstitial, (2) bridging, or (3) chalcogen-bonded. In the first case, the hydrogen atom is inside the octahedron, while in the second and third cases, the hydrogen atom is outside the octahedron. An absorption due to a chromium–hydrogen or a chalcogen–hydrogen stretch for **2** and **3** was not observed in the FT-IR spectra.[51] The ^1H NMR spectra did not show any hydride protons probably because of the paramagnetism of the cluster complexes. The final difference Fourier map of **2** shows a peak at the center of the Cr_6 octahedron (1.2 e/Å^3), while that of **1** exhibited no peak. If the hydrogen atom is at the interstitial position, the Cr–H bond distance is 1.88 Å for **2** and 1.84 Å for **3**. These lengths are slightly longer than those of $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ (1.73 Å (average))[52] and $[Cp''_4Cr_4(\mu\text{-}H)_5(\mu_3\text{-}H)_2]$ (where $Cp'' = \eta^5$-tetramethyl-ethyl-cyclopentadienyl) (1.79 Å (aver-

---

(51) Oxton, I. A.; Kettle, S. F. A.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1979**, 687.

(52) Petersen, J. L.; Brown, R. K.; Williams, J. M. *Inorg. Chem.* **1981**, *20*, 158.

age)).[53] There have been several precedent examples of the interstitial hydride in the octahedral metal clusters.[54−66] The existence of an interstitial hydrogen atom in the Cr_6 octahedron is supported also by its reactivity (vide infra).

Though the Cr−Se and Cr−P bond distances of **2** are almost the same as those of **1**, the 12 Cr−Cr bond distances (2.66 Å (average)) of **2** are shorter by 0.13−0.16 Å than those of **1** (2.81 Å (average)). The interstitial hydrogen atom is considered to have bonding interactions with the six chromium atoms in **2**. Therefore, the Cr−H bond probably attracts the chromium atoms toward the center of the Cr_6 octahedron, and the Cr−Cr bond distances of **2** become shorter than those of **1**. We previously reported that the 12 Cr−Cr bond distances in the structure of $[Cr_6Se_8(PEt_3)_6]$ were 2.71 ± 0.01 Å.[8] These values are between those of **1** and **2**, indicating that the crystals in the previous paper are mixed crystals of **1** and **2**.

The chromium−chalcogen bond lengths of **2** are longer by 0.10−0.14 Å than those of the sulfide complex **3** (2.34 Å (average)),[8] as expected from the difference in the covalent radii of S (1.04 Å) and Se (1.17 Å).[67] The 12 Cr−Cr bond distances of **2** are longer by 0.07 Å than those of **3** (2.59 Å (average)).[8]

The Reactivity of the Hydride. The reactivities of the hydrides in cluster compounds are sometimes related to their positions. It has been reported that the reaction of $[Re_7H_2C(CO)_{21}]^-$ with methanol, acetone, or THF removes the edge-bridging hydrides as protons and the cluster framework decomposes.[68] The chalcogen-bonded hydrogen atom in $[Re_6S_7(SH)Br_6]^{3-}$ and $[Re_6Se_7(SeH)I_6]^{3-}$ is also eliminated by primary amines at room temperature.[24] On the other hand, the interstitial hydride in $[HRu_6(CO)_{18}]^-$ is stable in a methanol solution of KOH and in a THF solution of KH.[57]

We have studied the reactivity of **2** with ethanol, acetone, THF, and ^{n}BuNH$_2$ in toluene solutions at room temperature. If the deprotonated cluster $[Cr_6Se_8(PEt_3)_6]^-$ (**1**$^-$) forms, it should exhibit the same CV as that of **1** except the rest potential. However, the CV of the products of the reactions did not change, which indicated that the hydride in **2** was not removed by these reagents. Also the hydride in **3** was not eliminated. These results suggest that the hydrogen atoms in **2** and **3** are inert because of the steric protection by the Cr_6 octahedral skeleton and also because of the Cr−H bondings.

Acknowledgment. We thank Dr. R. Kato and Dr. Y. Hosokoshi for use of the SQUID magnetometer, Mr. H. Tsuchiya, Cryogenic Center in Tokyo University, for operating the SQUID magnetometer, and Mr. Y. Esumi for helpful discussion on the FAB mass spectra.

Supporting Information Available: Magnetic susceptibility plots (3 pages). Two X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

IC9807700

---

(53) Heintz, R. A.; Koetzle, T. F.; Ostrander, R. L.; Rheingold, A. L.; Theopold, K. H.; Wu, P. *Nature* **1995**, *378*, 359.

(54) Simon, V. A. *Z. Anorg. Allg. Chem.* **1967**, *355*, 311.

(55) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Chem. Commun.* **1976**, 945.

(56) Hart, D. W.; Teller, R. G.; Wei, C.-Y.; Bau, R.; Longoni, G.; Campanella, S.; Chini, P.; Koetzle, T. F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 80.

(57) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

(58) Imoto, H.; Corbett, J. D. *Inorg. Chem.* **1980**, *19*, 1241.

(59) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; McPartlin, M.; Nelson, W. J. H.; Rouse, K. D.; Allibon, J.; Mason, S. A. *J. Chem. Soc., Chem. Commun.* **1980**, 295.

(60) Hart, D. W.; Teller, R. G.; Wei, C.-Y.; Bau, R.; Campanella, S.; Chini, P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1981**, *103*, 1458.

(61) Imoto, H.; Simon, A. *Inorg. Chem.* **1982**, *21*, 308.

(62) Fitch, A. N.; Barrett, S. A.; Fender, B. E. F. *J. Chem. Soc., Dalton Trans.* **1984**, 501.

(63) Simon, A.; Stollmaier, F.; Gregson, D.; Fuess, H. *J. Chem. Soc., Dalton Trans.* **1987**, 431.

(64) Chu, P. J.; Ziebarth, R. P.; Corbett, J. D.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 5324.

(65) Meyer, H.-J.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 963.

(66) Gade, L. H.; Johnson, F. G.; Lewis, J. *Croat. Chem. Acta* **1995**, *68*, 693.

(67) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, New York, 1960; p 224.

(68) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Sironi, A.; Molinari, H. *J. Chem. Soc., Dalton Trans.* **1990**, 1901.