Syntheses, Structures, and Molecular-Orbital Calculations of Chromium Chevrel-Type Cluster Complexes $[Cr_6E_8(PR_3)_6]$ ($E=S$, $PR_3=PEt_3$, PMe_3; $E=Se$, $PR_3=PEt_3$, PMe_3, PMe_2Ph)

Kiyoshi Tsuge, Hideo Imoto, and Taro Saito*

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Tokyo 113

(Received September 8, 1995)

Hexanuclear chromium cluster complexes $[Cr_6E_8(PR_3)_6]$ ($E=S$, $PR_3=PEt_3$, PMe_3; $E=Se$, $PR_3=PEt_3$, PMe_3, PMe_2Ph) were prepared by the reaction of anhydrous chromium dichloride, a trialkylphosphine, and either NaSH or Na_2Se in methanol. The complexes comprised the Cr_6 octahedra with eight face-bridging chalcogen atoms and six terminal phosphine ligands. Though the overall ligand arrangements were the same, the symmetry of the central Cr_6 octahedra was O_h in PEt_3 complexes, but distorted to D_{3d} and D_{2h} in PMe_3 and PMe_2Ph complexes, respectively. Because of a weakness of the metal–metal interaction, the steric and electronic effect complementarily caused a variation in the chromium octahedra. The electronic effect was analyzed by molecular-orbital calculations using the DV-$X\alpha$ method.

Hexanuclear cluster complexes $[Mo_6E_8L_6]$ ($E=S$, Se)[1—3] have cluster cores that are similar to those of the superconducting Chevrel phases.[4,5] These cluster complexes have been prepared by the reductive dimerization of trinuclear molybdenum cluster complexes[1,2] and by ligand-exchange reactions starting from Mo_6Cl_{12}.[3] Although solid-state compounds comprising M_6E_8 cluster units are known only for molybdenum and rhenium,[6] molecular cluster complexes $[M_6E_8L_6]$ ($M=W$, Co, Fe) have been reported.[7—24] Because of their highly symmetrical structure, they provide an interesting series of compounds for studying the structural, electrochemical, and magnetic properties.[11,13,14,25—30] The possibility of deriving a tungsten analogue of the Chevrel phases from molecular tungsten cluster complexes has also been pursued.[8] Chromium is located at the key position in the periodic table for a comparison of these $[M_6E_8L_6]$ complexes. We report here on the synthesis, as well as molecular and electronic structures of $[Cr_6E_8(PR_3)_6]$ that have been prepared from anhydrous chromium chloride. A tellurium derivative $[Cr_6Te_8(PEt_3)_6]$ has been reported by Steigerwald et al.[31]

Experimental

All of the manipulations were carried out under dinitrogen or argon using conventional Schlenk techniques. The solvents were dried and distilled under argon. 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.[32] All other reagents were used as received from Aldrich.

Synthesis of $[Cr_6S_8(PEt_3)_6]$ (1). A solution of NaS_xH ($x=1.33$) was prepared from NaSH (0.23 g, 4.1 mmol) and S_8 (0.043 g, 0.17 mmol) in MeOH (20 cm^3). This solution was added dropwise to a suspension of $CrCl_2$ (0.50 g, 4.1 mmol) in MeOH (10 cm^3) at −78 °C. A mixture of a brown solution and a brown precipitate was formed. Subsequently, PEt_3 (1.2 cm^3, 8.2 mmol) was added to the mixture, which was stirred and allowed to slowly (ca. 8 h) warm 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 **1**·$2C_6H_6$ as black single crystals. Yield 0.22 g (22%). ^{1}H NMR (C_6D_6) $\delta=1.80$ (54H), 0.04 (36H). Found: C, 39.93; H, 7.17; S, 18.08%. Calcd for $C_{48}H_{102}Cr_6P_6S_8$: C, 40.21; H, 7.17; S, 17.89%.

Synthesis of $[Cr_6S_8(PMe_3)_6]$ (2). The procedure for **1** was followed with PMe_3. The mixture was filtered at room temperature and the filtrate was cooled to −20 °C to yield a very small amount of black crystals of **2** (< 10 mg).

Synthesis of $[Cr_6Se_8(PEt_3)_6]$ (3). A methanol solution of Na_2Se_x ($x=1.33$, 0.62 g, 4.1 mmol in 20 cm^3) was added dropwise to a suspension of $CrCl_2$ (0.5 g, 4.1 mmol) in methanol (10 cm^3) to give a brown mixture. The mixture was stirred and allowed to slowly (ca. 8 h) warm 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). The benzene extract was allowed to stand at room temperature to yield **3** as black single crystals. Though we usually obtained crystals of **3** by this procedure, we occasionally obtained a small amount of crystals of **3**·$2C_6H_6$. The solvent was easily lost, even at ambient pressure. Yield 0.14 g (11%). ^{1}H NMR (C_6D_6) $\delta=1.50$ (54H), −0.39 (25H), −4.18 (11H). Found: C, 26.21; H, 5.36%. Calcd for $C_{36}H_{90}Cr_6P_6Se_8$: C, 26.16; H, 5.49%.

Synthesis of $[Cr_6Se_8(PMe_3)_6]$ (4). The procedure for **3** was followed with a solution of PMe_3 in THF (18.5%, 4.3 cm^3, 8 mmol) to give black crystals. Yield 0.07 g (7%). ^{1}H NMR (C_6D_6) $\delta=$ −0.47 (12H), −2.77 (42H). Found: C, 15.39; H, 3.76%. Calcd for $C_{18}H_{54}Cr_6P_6S_8$: C, 15.44; H, 3.89%.

Synthesis of $[Cr_6Se_8(PMe_2Ph)_6]$ (5). The procedure for **3** was followed with a solution of PMe_2Ph in toluene (23.4%, 6.0 cm^3, 8 mmol) to give black crystals. Yield 0.08 g (6%). ^{1}H NMR (C_6D_6) $\delta=8.37$—8.21 (12H), 7.40 (12H), 6.90 (6H), −0.12 (15H), −2.61 (21H). Found: C, 32.64; H, 3.83%. Calcd for $C_{48}H_{66}Cr_6P_6Se_8$: C, 32.53; H, 3.75%.

X-Ray Structure Determination. Single crystals of **1**, **3**, **4**, and **5** were grown from a benzene solution at room temperature and that of **2** from a methanol solution at −20 °C. They were sealed in glass capillaries for X-ray measurements. The crystallographic data are given in Table 1. Complex **3** was obtained as a mixture of two forms of crystals (**3a** and **3b**) with different space groups. The crystal of **3a** was isomorphous with **1**, and **4** was isomorphous with **2**.

X-Ray measurements of the crystals were performed on a Rigaku AFC-6S diffractometer for **1**, **3**, **4**, and **5** or a Rigaku AFC-5R diffractometer for **2**. The radiation used was Mo $K\alpha$ monochromatized with a graphite monochrometer. The intensities from each crystal did not decay, and the data were corrected for the *Lp* factor and empirically for the absorption. The positions of the chromium and selenium atoms were determined by the direct method (SHELXS86), and other non-hydrogen atoms were located in successive Fourier maps (SHELXS76).[33] the heavy atoms (chromium, chalcogen, and phosphorus) in all of the crystals and the carbon atoms of the phosphine ligands in crystals **1**, **2**, and **4** were refined anisotropically. Other carbon atoms and the hydrogen atoms in the crystal of **2** were refined isotropically. The hydrogen atoms in the other crystals were fixed at the calculated positions. At the final stage of the refinements, an empirical extinction correction proportional to the observed intensities was included for the crystals of **1**, **3a**, **3b**, and **4**. All of the structures were refined by full-matrix least-squares analyses (ANYBLK).[34]

The crystals of **1** and **3a** have two benzene molecules as a crystallization solvent, which are disordered near to the position (0, 0, 1/2) with $\bar{3}$ site-symmetry. An elemental analysis indicated that there are two benzene molecules in the cavity. The benzene molecules are tilted against the *c*-axis, and the site occupancy of the carbon atoms is 1/3. Since the carbon atoms located in the difference Fourier map could not be converged, rigid-body refinements were performed with the C–C distances fixed at 1.40 Å and the C–C–C angles fixed at 120°. The final atomic parameters of **1**, **2**, **3a**, **3b**, **4**, and **5** are listed in Tables 2, 3, 4, 5, 6, and 7. Lists of detailed crystallographic data, the calculated positional parameters, the anisotropic thermal parameters, complete bond lengths and angles are deposited as Document No. 69008 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Cr_6S_8(PEt_3)_6]\cdot 2C_6H_6$ (**1**)

Atom	x/a	y/b	z/c	U_{eq}
Cr	0.06414(5)	−0.03442(5)	0.05355(3)	0.0244(3)
S1	0.0	0.0	0.14472(10)	0.0295(8)
S2	0.11531(7)	−0.06106(8)	−0.04859(6)	0.0281(5)
P	0.14439(8)	−0.08566(9)	0.12137(6)	0.0332(6)
C1	0.1869(3)	−0.1491(4)	0.0767(2)	0.047(3)
C2	0.1157(4)	−0.2374(4)	0.0452(3)	0.062(4)
C3	0.2475(3)	0.0005(3)	0.1612(3)	0.047(3)
C4	0.2358(4)	0.0558(4)	0.2147(3)	0.066(3)
C5	0.0793(3)	−0.1577(3)	0.1918(2)	0.048(3)
C6	0.1254(4)	−0.1936(4)	0.2374(3)	0.076(4)
C01	−0.0266(14)	−0.0324(13)	0.3335(5)	0.132(9)
C02	−0.0995(11)	−0.0639(11)	0.3774(9)	0.069(5)
C03	−0.0960(11)	−0.0131(14)	0.4336(7)	0.114(9)
C04	−0.0196(14)	0.0692(13)	0.4459(5)	0.117(8)
C05	0.0533(11)	0.1007(11)	0.4020(9)	0.146(11)
C06	0.0498(11)	0.0499(14)	0.3458(7)	0.082(7)

Calculations. The molecular orbitals were calculated by the DV-$X\alpha$ method with the SCC approximation[35—40] in a previously reported manner.[25] All of the calculations were performed on a Mips RS3230 computer. The exchange parameter (α) was taken to be 0.70 in all calculations. The geometries of the model compounds were taken from the averaged values of each compound corresponding to their symmetry.

Results

Synthesis. The hexanuclear sulfide chromium cluster complexes $[Cr_6S_8(PR_3)_6]$ ($PR_3 = PEt_3$, PMe_3) were prepared by the reaction of anhydrous chromium dichloride with NaS_xH and PR_3 (Eq. 1). The selenide analogues $[Cr_6Se_8(PR_3)_6]$ ($PR_3 = PEt_3$, PMe_3, PMe_2Ph) were prepared by a similar procedure using Na_2Se_x in place of NaS_xH (Eq. 2).

Table 1. Crystal Parameters and X-Ray Diffraction Data for **1**—**5**

	1	**2**	**3a**	**3b**	**4**	**5**
Formula	$C_{48}H_{102}Cr_6P_6S_8$	$C_{18}H_{54}Cr_6P_6S_8$	$C_{48}H_{102}Cr_6P_6Se_8$	$C_{36}H_{90}Cr_6P_6Se_8$	$C_{18}H_{54}Cr_6P_6Se_8$	$C_{48}H_{66}Cr_6P_6Se_8$
Fw	1433.7	1025.0	1808.8	1652.6	1400.1	1772.6
Space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$P\bar{1}$	$R\bar{3}$	$P2_1/c$
a/Å	17.301(3)	11.806(2)	17.511(8)	12.888(2)	11.824(2)	12.283(7)
b/Å				25.363(3)		20.063(5)
c/Å	19.740(2)	25.442(4)	19.960(7)	12.041(2)	26.175(3)	12.864(5)
α/deg				110.78(1)		
β/deg				108.57(2)		104.76(3)
γ/deg				109.92(1)		
V/Å^3	5116.7(13)	3071.1(10)	5301(4)	2996.7(13)	3169.0(10)	3065(2)
Z	3	3	3	2	3	2
μ/cm^{-1}	13.05	21.54	51.1	60.2	85.1	58.8
Abs cor[a)]	0.925—0.981	0.913—0.994	0.759—0.984	0.437—0.976	0.550—0.988	0.719—0.970
Obsd reflcns[b)]	1612, (> 3σ)	1482, (> 3σ)	1469, (> 4σ)	5169, (> 3σ)	1238, (> 3σ)	2437, (> 3σ)
R, $R_w^{c)}$	0.047, 0.029	0.036, 0.019	0.069, 0.033	0.069, 0.032	0.038, 0.023	0.063, 0.038

a) Relative absorption correction coefficient (empirical ψ-scan method). b) Number of observed reflections with the criterion for the observations in parentheses. c) $w = 1/\sigma^2(F_o)$.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Cr_6S_8(PMe_3)_6]$ (**2**)

Atom	x/a	y/b	z/c	U_{eq}
Cr	0.13196(5)	−0.00169(5)	−0.04210(2)	0.0277(2)
S1	0.0	0.0	−0.11070(5)	0.0322(6)
S2	0.22921(7)	0.22622(7)	−0.03910(3)	0.0305(4)
P	0.31169(8)	−0.00120(9)	−0.08491(3)	0.0344(4)
C1	0.3149(8)	0.0108(8)	−0.1562(2)	0.070(3)
C2	0.4708(4)	0.1336(6)	−0.0669(3)	0.072(3)
C3	0.3285(6)	−0.1420(6)	−0.0722(2)	0.062(3)
H1	0.349(5)	−0.025(5)	−0.168(2)	0.06(2)
H2	0.250(4)	−0.036(4)	−0.170(2)	0.04(2)
H3	0.319(4)	0.090(3)	−0.169(2)	0.032(13)
H4	0.524(5)	0.114(4)	−0.077(2)	0.07(2)
H5	0.491(5)	0.203(5)	−0.088(2)	0.11(3)
H6	0.484(4)	0.124(4)	−0.031(2)	0.06(2)
H7	0.390(4)	−0.137(4)	−0.084(2)	0.04(2)
H8	0.340(4)	−0.153(3)	−0.0367(14)	0.04(2)
H9	0.272(4)	−0.217(4)	−0.086(2)	0.05(2)

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Cr_6Se_8(PEt_3)_6]\cdot 2C_6H_6$ (**3a**)

Atom	x/a	y/b	z/c	U_{eq}
Cr	0.10067(11)	0.06521(11)	0.44547(7)	0.0277(8)
Se1	0.0	0.0	0.34918(8)	0.0348(9)
Se2	0.06402(7)	0.18307(7)	0.44995(5)	0.0357(6)
P	0.2312(2)	0.1445(2)	0.37603(13)	0.041(2)
C1	0.3365(8)	0.1859(7)	0.4187(5)	0.062(4)
C2	0.3568(7)	0.1204(8)	0.4485(5)	0.070(4)
C3	0.2361(7)	0.0772(7)	0.3068(5)	0.058(3)
C4	0.3181(8)	0.1256(8)	0.2615(5)	0.076(4)
C5	0.2458(7)	0.2431(7)	0.3356(5)	0.056(3)
C6	0.1797(7)	0.2306(7)	0.2836(5)	0.070(4)
C01	−0.019(2)	−0.028(2)	−0.1589(9)	0.18(2)
C02	−0.091(2)	−0.063(2)	−0.116(2)	0.051(10)
C03	−0.093(2)	−0.012(2)	−0.0622(11)	0.12(2)
C04	−0.022(2)		−0.0520(9)	0.14(2)
C05	0.050(2)	0.108(2)	−0.095(2)	0.17(2)
C06	0.052(2)	0.057(2)	−0.1488(11)	0.031(8)

$$6CrCl_2 + 6NaS_xH + 6PR_3 \longrightarrow [Cr_6S_8(PR_3)_6] + 6NaCl + 6HCl \quad (x \approx 1.33) \qquad (1)$$

$$6CrCl_2 + 6Na_2Se_x + 6PR_3 \longrightarrow [Cr_6Se_8(PR_3)_6] + 12NaCl \quad (x \approx 1.33) \qquad (2)$$

In preparing the selenide derivatives, the reaction mixture was refluxed before extraction with hot benzene. Without refluxing, the crystallization of the complexes was slow, the amount of crystals was small, and black materials precipitated upon crystallization. In contrast to the preparation of the selenide derivatives using sodium polyselenide, sulfide cluster complexes could not be prepared with sodium polysulfide, Na_2S_x. We obtained only a methanol-insoluble material in the reaction of $CrCl_2$ and Na_2S_x.

Table 5. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[Cr_6Se_8(PEt_3)_6]$ (**3b**)

Atom	x/a	y/b	z/c	U_{eq}
Cr1	−0.0879(2)	0.01066(8)	0.1002(2)	0.0246(8)
Cr2	0.1579(2)	0.06994(8)	0.1614(2)	0.0238(8)
Cr3	0.0234(2)	−0.06133(9)	0.0474(2)	0.0253(8)
Cr4	0.0309(2)	0.43696(9)	0.5309(2)	0.0280(8)
Cr5	0.1405(2)	0.56862(9)	0.6805(2)	0.0292(9)
Cr6	0.1134(2)	0.51052(8)	0.4276(2)	0.0280(9)
Se1	0.08402(13)	0.01784(6)	0.27989(13)	0.0308(6)
Se2	0.04400(13)	0.12911(6)	0.19442(14)	0.0382(6)
Se3	−0.20207(13)	−0.10968(6)	−0.01354(14)	0.0318(6)
Se4	0.24392(13)	−0.00159(6)	0.09771(14)	0.0311(6)
Se5	0.25712(13)	0.51380(6)	0.62506(14)	0.0336(6)
Se6	0.05220(13)	0.49493(6)	0.75547(14)	0.0367(6)
Se7	0.00476(14)	0.39037(6)	0.29984(14)	0.0404(6)
Se8	0.20110(13)	−0.37093(6)	−0.42963(14)	0.0371(6)
P1	−0.2040(3)	0.0237(2)	0.2209(3)	0.0335(15)
P2	0.3567(3)	0.15508(15)	0.3724(3)	0.0335(15)
P3	0.0510(3)	−0.13866(15)	0.1104(4)	0.036(2)
P4	0.0706(3)	0.3592(2)	0.5801(4)	0.038(2)
P5	0.3185(4)	0.6572(2)	0.9050(4)	0.043(2)
P6	0.2520(3)	0.5209(2)	0.3306(4)	0.038(2)
C1	−0.1911(12)	0.1048(6)	0.2980(13)	0.048(4)
C2	−0.2441(12)	0.1235(6)	0.1962(13)	0.052(4)
C3	−0.1581(12)	0.0160(5)	0.3714(13)	0.043(4)
	−0.1875(13)	−0.0536(6)	0.3394(13)	0.058(4)
C5	−0.3773(12)	−0.0335(5)	0.1181(13)	0.047(4)
C6	−0.4546(15)	−0.0276(6)	0.193(2)	0.086(5)
C7	0.3511(11)	0.2193(5)	0.4986(12)	0.041(4)
C8	0.2708(12)	0.1959(6)	0.5587(13)	0.054(4)
C9	0.4302(12)	0.1247(5)	0.4713(12)	0.041(4)
C10	0.5558(14)	0.1763(6)	0.6083(15)	0.077(5)
C11	0.4838(12)	0.2068(5)	0.3577(12)	0.039(4)
C12	0.5387(13)	0.1719(6)	0.2860(14)	0.063(5)
C13	−0.0057(12)	−0.1461(5)	0.2271(13)	0.049(4)
C14	0.0108(15)	−0.1918(7)	0.280(2)	0.089(6)
C15	0.2146(13)	−0.1214(6)	0.1960(14)	0.057(4)
C16	0.3022(13)	−0.0602(6)	0.3411(14)	0.061(4)
C17	−0.0209(13)	−0.2233(6)	−0.0288(13)	0.058(4)
C18	−0.1674(14)	−0.2611(6)	−0.1030(15)	0.074(5)
C19	0.2026(13)	0.3971(6)	0.7532(14)	0.056(4)
C20	0.235(2)	0.3527(7)	0.795(2)	0.099(6)
C21	−0.0630(12)	0.2926(6)	0.5632(13)	0.052(4)
C22	−0.1049(13)	0.3145(6)	0.6643(14)	0.065(5)
C23	0.1099(13)	0.3076(6)	0.4665(13)	0.055(4)
C24	0.2331(14)	0.3439(6)	0.4726(14)	0.072(5)
C25	0.3017(13)	0.7273(6)	0.9927(14)	0.066(5)
C26	0.3010(14)	0.7680(6)	0.9249(15)	0.076(5)
C27	0.3577(14)	0.6398(6)	1.0428(14)	0.067(5)
C28	0.404(2)	0.5914(7)	1.017(2)	0.100(6)
C29	0.4687(14)	0.6935(6)	0.9099(14)	0.063(5)
C30	0.586(2)	0.7516(7)	1.050(2)	0.086(5)
C31	0.3935(13)	0.6021(6)	0.4205(13)	0.050(4)
C32	0.4873(13)	0.6257(6)	0.5625(14)	0.057(4)
C33	0.1854(13)	0.5077(6)	0.1575(14)	0.061(5)
C34	0.0777(15)	0.4375(7)	0.048(2)	0.084(5)
C35	0.3155(12)	0.4663(5)	0.3181(13)	0.049(4)
C36	0.3987(14)	0.4692(6)	0.2519(14)	0.074(5)

Structure. Selected interatomic distances and angles for complexes **1**, **2**, **3a**, **3b**, **4**, and **5** are listed in Tables 8, 9, 10, 11, 12, and 13. As shown in Fig. 1, the chromium complex **1** has a Cr_6S_8 cluster unit comprising a Cr_6 octahedron and eight face-capping sulfur atoms. One tri-

Table 6. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [$Cr_6Se_8(PMe_3)_6$] (**4**)

Atom	x/a	y/b	z/c	U_{eq}
Cr	0.13540(9)	−0.00134(9)	−0.04194(4)	0.0269(4)
Se1	0.0	0.0	−0.11351(4)	0.0307(5)
Se2	0.24116(5)	0.23817(5)	−0.04037(3)	0.0297(3)
P	0.3142(2)	−0.0002(2)	−0.08462(6)	0.0347(8)
C1	0.3321(6)	−0.1442(6)	−0.0741(3)	0.057(4)
C2	0.3107(7)	0.0077(8)	−0.1534(2)	0.072(5)
C3	0.4737(6)	0.1324(7)	−0.0676(3)	0.071(5)

Table 7. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [$Cr_6Se_8(PMe_2Ph)_6$] (**5**)

Atom	x/a	y/b	z/c	U_{eq}
Cr1	0.4468(2)	0.08763(11)	0.0047(2)	0.0278(12)
Cr2	0.3631(2)	−0.02200(11)	−0.1089(2)	0.0303(13)
Cr3	0.5741(2)	0.02656(12)	−0.1080(2)	0.0298(13)
Se1	0.39605(13)	0.08336(7)	−0.19327(11)	0.0313(9)
Se2	0.26431(12)	0.03879(7)	0.00646(11)	0.0301(8)
Se3	0.49263(13)	−0.07479(8)	−0.20158(11)	0.0324(9)
Se4	0.63691(12)	0.12556(7)	0.00568(11)	0.0295(9)
P1	0.3783(4)	0.1987(2)	−0.0008(3)	0.037(2)
P2	0.1827(3)	−0.0484(2)	−0.2276(3)	0.037(2)
P3	0.6768(3)	0.0632(2)	−0.2333(3)	0.038(2)
C1	0.4493(12)	0.2604(7)	−0.0628(10)	0.043(4)
C2	0.3884(12)	0.2353(7)	0.1297(10)	0.041(4)
C3	0.2321(12)	0.2119(7)	−0.0715(11)	0.036(4)
C4	0.150(2)	0.2117(8)	−0.0184(13)	0.066(6)
C5	0.035(2)	0.2218(8)	−0.0720(13)	0.068(6)
C6	0.0088(14)	0.2294(8)	−0.1807(13)	0.062(5)
C7	0.089(2)	0.2269(8)	−0.2372(13)	0.064(5)
C8	0.2019(13)	0.2187(8)	−0.1799(12)	0.051(5)
C9	0.1002(13)	0.0218(7)	−0.2880(11)	0.054(5)
C10	0.0844(13)	−0.0890(8)	−0.1625(11)	0.057(5)
C11	0.1813(11)	−0.1048(7)	−0.3398(10)	0.036(4)
C12	0.1195(12)	−0.0915(8)	−0.4471(11)	0.050(5)
C13	0.1230(14)	−0.1383(8)	−0.5276(12)	0.060(5)
C14	0.1900(14)	−0.1922(8)	−0.5057(13)	0.058(5)
C15	0.2509(12)	−0.2051(7)	−0.4033(11)	0.045(4)
C16	0.2457(12)	−0.1621(7)	−0.3214(11)	0.042(4)
C17	0.6208(13)	0.1388(8)	−0.3073(11)	0.056(5)
C18	0.8237(12)	0.0884(7)	−0.1730(11)	0.047(4)
C19	0.6961(11)	0.0055(7)	−0.3380(10)	0.028(4)
C20	0.7585(13)	−0.0519(8)	−0.3062(11)	0.050(5)
C21	0.7794(13)	−0.0956(8)	−0.3844(12)	0.059(5)
C22	0.7331(13)	−0.0822(8)	−0.4900(12)	0.056(5)
C23	0.6705(14)	−0.0276(9)	−0.5205(12)	0.067(5)
C24	0.6498(13)	0.0167(8)	−0.4450(12)	0.054(5)

a) Equivalent positions. ′: $-x$, $-y$, $-z$.

Table 8. Selected Interatomic Distances (Å) and Angles (Degree) for [$Cr_6S_8(PEt_3)_6$]·$2C_6H_6$ (**1**)[a]

Cr–Cr^{ii}	2.596(1)	Cr–Cr^{v}	2.592(1)
Cr–S1	2.342(2)	Cr–S2	2.339(1)
Cr–S2^{iv}	2.327(1)	Cr–S2^{v}	2.337(1)
Cr–P	2.395(1)		
mean Cr–Cr	2.59	mean Cr–S	2.34
mean Cr–P	2.40		
Cr^{ii}–Cr–Cr^{iii}	60.0	Cr^{ii}–Cr–Cr^{iv}	90.0
Cr^{ii}–Cr–Cr^{v}	59.94(1)	Cr^{iv}–Cr–Cr^{v}	60.12(3)
S1–Cr–S2	170.65(5)	S1–Cr–S2^{iv}	89.50(4)
S1–Cr–S2^{v}	89.26(4)	S2–Cr–S2^{iv}	90.00(4)
S2–Cr–S2^{v}	89.76(4)	S2^{iv}–Cr–S2^{v}	170.89(5)
S1–Cr–P	95.77(5)	S2–Cr–P	93.58(5)
S2^{iv}–Cr–P	92.23(4)	S2^{v}–Cr–P	96.87(4)
Cr–S1–Cr^{ii}	67.32(5)	Cr–S2–Cr^{iv}	67.33(4)
Cr–S2–Cr^{v}	67.49(4)	Cr^{iv}–S2–Cr^{v}	67.66(4)

a) Equivalent positions. ii: $-y$, $x-y$, z; iii: $-x+y$, $-x$, z; iv: y, $-x+y$, $-z$; v: $x-y$, x, $-z$.

Table 9. Selected Interatomic Distances (Å) and Angles (Degree) for [$Cr_6S_8(PMe_3)_6$] (**2**)[a]

Cr–Cr^{ii}	2.7158(8)	Cr–Cr^{iv}	2.6547(8)
Cr–S1	2.346(1)	Cr–S2	2.3398(9)
Cr–S2^{iii}	2.3409(9)	Cr–S2^{iv}	2.3503(8)
Cr–P	2.3826(9)		
mean Cr–Cr	2.69	mean Cr–S	2.34
mean Cr–P	2.38		
Cr^{ii}–Cr–Cr^{iii}	60.00	Cr^{ii}–Cr–Cr^{iv}	90.00
Cr^{ii}–Cr–Cr^{v}	59.24(1)	Cr^{iv}–Cr–Cr^{v}	61.53(2)
S1–Cr–S2	87.74(2)	S1–Cr–S2^{iii}	87.71(2)
S1–Cr–S2^{iv}	166.54(3)	S2–Cr–S2^{iii}	168.41(3)
S2–Cr–S2^{iv}	90.98(2)	S2^{iii}–Cr–S2^{iv}	90.96(2)
S1–Cr–P	104.73(3)	S2–Cr–P	95.03(3)
S2^{iii}–Cr–P	96.43(3)	S2^{iv}–Cr–P	88.73(3)
Cr–S1–Cr^{ii}	70.72(3)	Cr–S2–Cr^{ii}	70.93(3)
Cr–S2–Cr^{v}	68.95(3)	Cr^{ii}–S2–Cr^{v}	68.93(3)

a) Equivalent positions. ii: $-y$, $x-y$, z; iii: $-x+y$, $-x$, z; iv: y, $-x+y$, $-z$; v: $x-y$, x, $-z$.

alkylphosphine ligand coordinates to each chromium atom. Since these cluster molecules have highly symmetrical structures, their packings are simple. The packing of complex **1** can be approximated as simple cubic. The value of c/a for **1** is 1.14, which is close to the value 1.22 expected for idealized simple cubic. Two benzene molecules are clathrated in the center of the cube as a crystal solvent. The packing of **2** can be regarded as ccp, since the c/a ratio (2.15) is close to the value for the idealized ccp (2.45). Complex **3** crystallizes in two forms, **3a** and **3b**. The space group of the crystal of **3b** is R$\bar{3}$ and is isomorphous with **1**. The space group of the crystal of **3a** is P$\bar{1}$, and the molecules are arranged nearly two-dimensionally close packed in the bc plane, and the lay-

Table 10. Selected Interatomic Distances (Å) and Angles (Degree) for $[Cr_6Se_8(PEt_3)_6]\cdot 2C_6H_6$ (**3a**)[a]

Cr–Cr^{ii}	2.683(3)	Cr–Cr^{iv}	2.672(2)
Cr–Se1	2.468(2)	Cr–Se2	2.450(2)
Cr^{ii}–Se2	2.441(2)	Cr^{v}–Se2	2.443(2)
Cr–P	2.428(3)		
mean Cr–Cr	2.68	mean Cr–Se	2.46
mean Cr–P	2.43		
Cr^{ii}–Cr–Cr^{iii}	60.00	Cr^{ii}–Cr–Cr^{iv}	90.00
Cr^{ii}–Cr–Cr^{v}	59.86(3)	Cr^{iv}–Cr–Cr^{v}	60.27(7)
Se1–Cr–Se2	89.47(6)	Se1–Cr–Se2^{iii}	89.68(6)
Se1–Cr–Se2^{iv}	172.43(8)	Se2–Cr–Se2^{iii}	172.22(8)
Se2–Cr–Se2^{iv}	89.81(6)	Se2^{iii}–Cr–Se2^{iv}	90.02(6)
Se1–Cr–P	94.02(8)	Se2–Cr–P	96.16(9)
Se2^{iii}–Cr–P	91.62(9)	Se2^{iv}–Cr–P	93.54(9)
Cr–Se1–Cr^{ii}	65.83(7)	Cr–Se2–Cr^{ii}	66.51(8)
Cr–Se2–Cr^{v}	66.18(7)	Cr^{ii}–Se2–Cr^{v}	66.32(7)

a) Equivalent positions. ii: $-y, x-y, z$; iii: $-x+y, -x, z$; iv: $y, -x+y, -z$; v: $x-y, x, -z$.

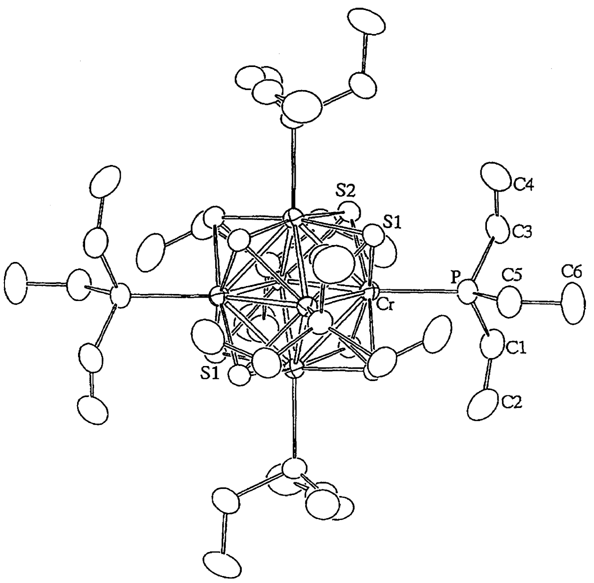

Fig. 1. ORTEP drawing of $[Cr_6S_8(PEt_3)_6]$ (**1**). The molecule of **1** has the crystallographically imposed 3 symmetry. The 3-fold axis runs through the S1 atoms.

ers are piled in the *a* direction. The packing of complex **4** is isomorphous with the sulfide analog **2**. In the crystal of **5**, the molecules are arranged nearly two-dimensionally close packed in the *bc* plane.

Though the molecules of **1**, **2**, **3**, **4**, and **5** have similar structures consisting of the Cr_6E_8 cluster core and six phosphine ligands, the Cr–Cr bond lengths are considerably different among the five complexes and the virtual symmetries of the Cr_6 octahedra are O_h in the PEt_3, D_{3d} in the PMe_3 and D_{2h} in the PMe_2Ph complexes. In the PEt_3 complexes, the differences in intramolecular Cr–Cr distances are below 0.02 Å and the Cr_6 octahedra have a pseudo octahedral symmetry. In contrast, the differences in the intramolecular Cr–Cr distances are more than 0.06 Å in the PMe_3 and PMe_2Ph complexes. The Cr_6 cores are trigonal antiprisms (D_{3d}) in the PMe_3 complexes, since the space group $R\bar{3}$ imposes $\bar{3}$ symmetry on each molecule. The differences in the intra-triangle and inter-triangle Cr–Cr distances are more than 0.06 Å in both the sulfide and selenide PMe_3 complexes. The molecules of the PMe_2Ph complex have a crystallographically imposed inversion center, and there are six crystallographically independent Cr–Cr distances (Table 13). The longest one is 2.76 Å, and the other five distances are in the range of 2.70±0.02 Å. Therefore, one pair of the Cr–Cr distances are especially longer than the other five pairs, and the Cr_6 octahedron has D_{2h} symmetry in the PMe_2Ph complex.

Electronic Spectra. The electronic spectra (300—1500 nm) of **1**, **3**, **4**, and **5** in benzene (measured by a Hitachi U-3500 spectrometer) were very similar. The spectra were dominated by the tail of strong absorption in the ultra-violet region, as shown in Fig. 2. However, three distinct shoulder peaks were observed at 370—420 nm, 630—680 nm, and 850—890 nm.

Discussion

Synthesis. Molybdenum and tungsten cluster complexes of the $[M_6E_8L_6]$ type were prepared by cluster condensation[1,2,7] of trinuclear cluster complexes or a substitution reaction on the Mo_6 or W_6 core starting from Mo_6Cl_{12}[3] or W_6Cl_{12}.[8] Chromium Chevrel-type cluster complexes could not be prepared by similar cluster syntheses using either condensation or substitution, since there are no suitable trinuclear or hexanuclear chromium cluster compounds. The telluride analogue $[Cr_6Te_8(PEt_3)_6]$ has been prepared from either $[CrCl_2(PEt_3)_2]$ or $Cr(DMPD)_2$ (DMPD=2,4-dimethylpentadienyl) with $TePEt_3$ and PEt_3.[31] We have prepared $[Cr_6E_8(PR_3)_6]$ (E=S, PR_3=PEt_3, PMe_3; E=Se, PR_3=PEt_3, PMe_3, PMe_2Ph) starting from $CrCl_2$. This is a kind of self-assembly of mononuclear species, just like the syntheses of iron and cobalt derivatives.[9—24] As described in Results, the sulfide derivatives could not be prepared by the reaction of sodium sulfide. Therefore, the choice of the chalcogen source is very important in the self-assembly method.[30] The

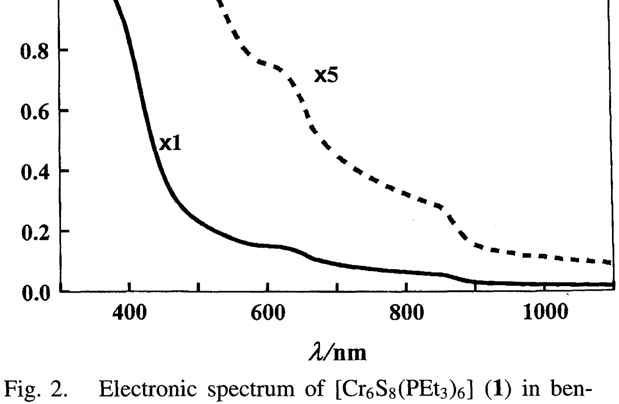

Fig. 2. Electronic spectrum of $[Cr_6S_8(PEt_3)_6]$ (**1**) in benzene (0.136 mol m^{-3}). No absorption peak was observed between 1100 and 1500 nm.

Table 11. Selected Interatomic Distances (Å) and Angles (Degree) for $[Cr_6Se_8(PEt_3)_6]$ (**3b**)[a)]

Cr1–Cr2	2.706(3)	Cr1–Cr2′	2.698(3)	Se1–Cr1–Se2	89.58(7)	Se1–Cr1–Se3	89.73(7)
Cr1–Cr3	2.710(3)	Cr1–Cr3′	2.709(3)	Se1–Cr1–Se4′	171.87(11)	Se2–Cr1–Se3	171.15(10)
Cr2–Cr3	2.699(2)	Cr2–Cr3′	2.711(3)	Se2–Cr1–Se4′	89.74(8)	Se3–Cr1–Se4′	89.69(7)
Cr4–Cr5	2.700(2)	Cr4–Cr5′	2.707(3)	Se1–Cr2–Se2	89.79(8)	Se1–Cr2–Se3′	171.80(10)
Cr4–Cr6	2.701(3)	Cr4–Cr6′	2.700(3)	Se1–Cr2–Se4	90.18(7)	Se2–Cr2–Se3′	89.21(8)
Cr5–Cr6	2.711(3)	Cr5–Cr6′	2.718(3)	Se2–Cr2–Se4	171.89(10)	Se3′–Cr2–Se4	89.67(8)
Cr1–Se1	2.453(3)	Cr1–Se2	2.465(2)	Se1–Cr3–Se2′	171.31(11)	Se1–Cr3–Se3	89.60(8)
Cr1–Se3	2.459(2)	Cr1–Se4′	2.453(3)	Se1–Cr3–Se4	90.10(7)	Se2′–Cr3–Se3	89.11(8)
Cr2–Se1	2.457(2)	Cr2–Se2	2.453(2)	Se2′–Cr3–Se4	89.88(8)	Se3–Cr3–Se4	171.35(11)
Cr2–Se3′	2.457(2)	Cr2–Se4	2.456(2)	Se5–Cr4–Se6	89.84(7)	Se5–Cr4–Se7	89.40(8)
Cr3–Se1	2.455(2)	Cr3–Se2′	2.451(2)	Se5–Cr4–Se8′	172.09(11)	Se6–Cr4–Se7	171.94(11)
Cr3–Se3	2.463(2)	Cr3–Se4	2.461(2)	Se6–Cr4–Se8′	90.02(8)	Se7–Cr4–Se8′	89.62(8)
Cr4–Se5	2.457(2)	Cr4–Se6	2.445(2)	Se5–Cr5–Se6	89.69(8)	Se5–Cr5–Se7′	171.04(10)
Cr4–Se7	2.460(3)	Cr4–Se8′	2.460(2)	Se5–Cr5–Se8	89.81(8)	Se6–Cr5–Se7′	89.42(8)
Cr5–Se5	2.458(2)	Cr5–Se6	2.451(2)	Se6–Cr5–Se8	171.23(10)	Se7′–Cr5–Se8	89.71(8)
Cr5–Se7′	2.465(3)	Cr5–Se8	2.450(2)	Se5–Cr6–Se6′	171.28(11)	Se5–Cr6–Se7	89.60(8)
Cr6–Se5	2.458(3)	Cr6–Se6′		Se5–Cr6–Se8	89.58(7)	Se6′–Cr6–Se7	89.70(7)
Cr6–Se7	2.451(2)	Cr6–Se8	2.460(2)	Se6′–Cr6–Se8	89.82(8)	Se7–Cr6–Se8	171.40(10)
Cr1–P1	2.417(4)	Cr2–P2	2.424(4)	Se1–Cr1–P1	95.91(12)	Se2–Cr1–P1	94.74(10)
Cr3–P3	2.431(4)	Cr4–P4	2.413(4)	Se3–Cr1–P1	94.10(10)	Se4′–Cr1–P1	92.22(11)
Cr5–P5	2.418(4)	Cr6–P6	2.419(4)	Se1–Cr2–P2	91.06(11)	Se2–Cr2–P2	95.16(11)
mean Cr–Cr	2.71	mean Cr–Se	2.46	Se3′–Cr2–P2	97.13(11)	Se4–Cr2–P2	92.95(11)
mean Cr–P	2.42			Se1–Cr3–P3	93.43(11)	Se2′–Cr3–P3	95.23(11)
				Se3–Cr3–P3	93.57(11)	Se4–Cr3–P3	95.08(12)
Cr2–Cr1–Cr2′	89.83(8)	Cr2–Cr1–Cr3	59.78(6)	Se5–Cr4–P4	93.99(12)	Se6–Cr4–P4	91.36(12)
Cr2–Cr1–Cr3′	60.09(7)	Cr2′–Cr1–Cr3	60.18(7)	Se7–Cr4–P4	96.69(11)	Se8′–Cr4–P4	93.92(11)
Cr2′–Cr1–Cr3′	59.89(6)	Cr3–Cr1–Cr3′	90.12(8)	Se5–Cr5–P5	94.69(12)	Se6–Cr5–P5	96.26(12)
Cr1–Cr2–Cr1′	90.17(8)	Cr1–Cr2–Cr3	60.17(6)	Se7′–Cr5–P5	94.27(12)	Se8–Cr5–P5	92.50(11)
Cr1–Cr2–Cr3′	60.00(7)	Cr1′–Cr2–Cr3	60.24(6)		94.98(12)	Se6′–Cr6–P6	93.74(12)
Cr1′–Cr2–Cr3′	60.11(7)	Cr3–Cr2–Cr3′	90.29(8)	Se7–Cr6–P6	92.83(10)	Se8–Cr6–P6	95.77(10)
Cr1–Cr3–Cr1′	89.88(8)	Cr1–Cr3–Cr2	60.05(6)	Cr1–Se1–Cr2	66.91(7)	Cr1–Se1–Cr3	67.02(7)
Cr1–Cr3–Cr2′	59.71(7)	Cr1′–Cr3–Cr2	59.87(6)	Cr2–Se1–Cr3	66.66(6)	Cr1–Se2–Cr2	66.78(7)
Cr1′–Cr3–Cr2′	59.91(7)	Cr2–Cr3–Cr2′	89.71(8)	Cr1–Se2–Cr3′	66.86(7)	Cr2–Se2–Cr3′	67.13(7)
Cr5–Cr4–Cr5′	90.60(8)	Cr5–Cr4–Cr6	60.26(6)	Cr1–Se3–Cr2′	66.58(7)	Cr1–Se3–Cr3	66.81(7)
Cr5–Cr4–Cr6′	60.46(7)	Cr5′–Cr4–Cr6	60.34(7)	Cr2′–Se3–Cr3	66.89(7)	Cr1′–Se4–Cr2	66.68(7)
Cr5′–Cr4–Cr6′	60.19(7)	Cr6–Cr4–Cr6′	90.48(8)	Cr1′–Se4–Cr3	66.90(7)	Cr2–Se4–Cr3	66.58(7)
Cr4–Cr5–Cr4′	89.40(8)	Cr4–Cr5–Cr6	59.90(6)	Cr4–Se5–Cr5	66.63(7)	Cr4–Se5–Cr6	
Cr4–Cr5–Cr6′	59.78(7)	Cr4′–Cr5–Cr6	59.77(7)	Cr5–Se5–Cr6	66.95(7)	Cr4–Se6–Cr5	66.92(7)
Cr4′–Cr5–Cr6′	59.72(7)	Cr6–Cr5–Cr6′	89.88(8)	Cr4–Se6–Cr6′	66.89(7)	Cr5–Se6–Cr6′	67.32(7)
Cr4–Cr6–Cr4′	89.52(8)	Cr4–Cr6–Cr5	59.84(6)	Cr4–Se7–Cr5′	66.69(7)	Cr4–Se7–Cr6	66.74(7)
Cr4–Cr6–Cr5′	59.94(7)	Cr4′–Cr6–Cr5	60.04(7)	Cr5′–Se7–Cr6	67.13(7)	Cr4′–Se8–Cr5	66.93(7)
Cr4′–Cr6–Cr5′	59.77(7)	Cr5–Cr6–Cr5′	90.12(8)	Cr4′–Se8–Cr6	66.57(7)	Cr5–Se8–Cr6	67.03(7)

a) Equivalent positions. ′: $-x$, $-y$, $-z$.

terminal phosphine ligands also influence the successful synthesis of the cluster complexes. We could prepare the sulfide derivatives with PEt_3 and PMe_3 by the described procedure, but not the PMe_2Ph or PPh_3 analogues. Though the selenide derivatives with PEt_3, PMe_3, and PMe_2Ph could be prepared, we have not been able to prepare a PPh_3 derivative. In the case of a diphosphine, a trinuclear chromium sulfide cluster $[Cr_3S_5(dmpe)_3]$ has been prepared[41)] by almost the same procedure as that for the synthesis of $[Cr_6S_8(PR_3)_6]$.

A similar influence of ligands has been reported for the iron clusters. Though $[Fe_6S_8(PEt_3)_6]^{2+}$ was successfully prepared, only intractable materials were obtained with PMe_3.[12)] Steigerwald and others have found that similar procedures with different phosphine ligands lead to a different nuclearity of the cluster core of iron telluride,[42)] a tetranuclear or a hexanuclear iron telluride cluster complexes using P^iPr_3 or PMe_3, respectively. No hexanuclear nickel cluster complex has been obtained by a similar procedure using PEt_3.[18,43)]

Structure. The structures of the Cr_6 core are affected by the terminal phosphine ligands. While the Cr_6 cores in the PEt_3 complexes are close to perfect octahedra, the Cr_6 octahedra in the PMe_3 and PMe_2Ph complexes are distorted to D_{3d} or D_{2h}, respectively, and the averaged Cr–Cr distances in the PMe_3 complexes are longer than in the PEt_3 and PMe_2Ph complexes. These variations of the chromium octahedra are in contrast with the molybdenum clusters, which always have a virtually regular octahedral geometry.[1,2,44)] In order to account for the difference of the distortion in the chromium and molybdenum cluster complexes with the same cluster components, the steric and electronic effects have been analyzed.

Steric Effect. In a crystal, the structure of a molecule is influenced by the steric demand between neighboring

Table 12. Selected Interatomic Distances (Å) and Angles (Degree) for $[Cr_6Se_8(PMe_3)_6]$ (**4**)[a]

Cr–Cr^{ii}	2.787(2)	Cr–Cr^{iv}	2.722(2)
Cr–Se1	2.469(1)	Cr–Se2	2.458(1)
Cr–P	2.385(2)		
mean Cr–Cr	2.75	mean Cr–Se	2.47
mean Cr–P	2.39		
Cr^{ii}–Cr–Cr^{iii}	60.00	Cr^{ii}–Cr–Cr^{iv}	90.00
Cr^{ii}–Cr–Cr^{v}	59.21(2)	Cr^{iv}–Cr–Cr^{v}	61.58(4)
Se1–Cr–Se2	87.90(3)	Se1–Cr–Se2^{iii}	87.74(3)
Se1–Cr–Se2^{iv}	168.96(4)	Se2–Cr–Se2^{iii}	170.85(4)
Se2–Cr–Se2^{iv}	91.46(3)	Se2^{iii}–Cr–Se2^{iv}	91.29(3)
Se1–Cr–P	102.73(5)	Se2–Cr–P	93.57(5)
Se2^{iii}–Cr–P	95.23(5)	Se2^{iv}–Cr–P	88.31(5)
Cr–Se1–Cr^{ii}	68.71(4)	Cr–Se2–Cr^{ii}	68.93(4)
Cr–Se2–Cr^{v}	66.92(4)	Cr^{ii}–Se2–Cr^{v}	66.81(4)

a) Equivalent positions. ii: $-y, x-y, z$; iii: $-x+y, -x, z$; iv: $y, -x+y, -z$; v: $x-y, x, -z$.

molecules. The peripheral ligands play an important role in determining the whole structure of a molecule.[45—47] These chromium cluster complexes come into contact with each other through the alkyl groups of the phosphine ligands. The direct effects of crystal packing, therefore, should be reflected in the positions of the phosphorus atoms. Since the six phosphine ligands are at the terminal positions of the Cr_6 octahedron, they form a P_6 octahedron around the Cr_6 octahedron. The P–P distances and the virtual symmetry of P_6 octahedra are listed in Table 14 with virtual symmetry of Cr_6 octahedra. In all of these compounds, the P_6 octahedron has the same symmetry as the Cr_6 octahedron. Because of their crystallographically imposed symmetries, the octahedra have two crystallographically independent distances in the PMe_3 cluster and six distances in the PMe_2Ph cluster complexes. Both of the PMe_3 complexes (**2** and **4**) have D_{3d} symmetry and the six phosphorus atoms make a trigonal antiprism. The intra-triangle P–P distances are longer than the inter-triangle P–P distances, just as the intra-triangle Cr–Cr distances are longer than the inter-triangle Cr–Cr distances (Fig. 3). This distortion of the P_6 octahedra is due to the crystal packing.

Table 13. Selected Interatomic Distances (Å) and Angles (Degree) for $[Cr_6Se_8(PMe_2Ph)_6]$ (**5**)[a]

Cr1–Cr2	2.695(3)	Cr1–Cr2′	2.718(3)
Cr1–Cr3	2.684(3)	Cr1–Cr3′	2.694(3)
Cr1–P1	2.376(4)	Cr2–Cr3	2.767(3)
Cr2–Cr3′	2.700(3)	Cr2–P2	2.408(4)
Cr3–P3	2.401(4)	Cr1–Se1	
Cr1–Se2	2.452(3)	Cr1–Se3′	2.464(3)
Cr1–Se4	2.453(3)	Cr2–Se1	2.456(3)
Cr2–Se2	2.466(3)	Cr2–Se3	2.458(3)
Cr2–Se4′	2.466(3)	Cr3–Se1	2.463(3)
Cr3–Se2′	2.458(3)	Cr3–Se3	2.444(3)
Cr3–Se4	2.470(3)		
mean Cr–Cr	2.71	mean Cr–Se	2.46
mean Cr–P	2.40		
Cr2–Cr1–Cr2′	91.90(9)	Cr2–Cr1–Cr3	61.90(8)
Cr2–Cr1–Cr3′	60.13(7)	Cr2′–Cr1–Cr3	59.97(8)
Cr2′–Cr1–Cr3′	61.49(8)	Cr3–Cr1–Cr3′	91.16(9)
Cr1–Cr2–Cr1′	88.10(9)	Cr1–Cr2–Cr3	58.84(7)
Cr1–Cr2–Cr3′	59.90(8)	Cr1′–Cr2–Cr3	58.82(8)
Cr1′–Cr2–Cr3′	59.39(8)	Cr3–Cr2–Cr3′	89.26(9)
Cr1–Cr3–Cr1′	88.84(9)	Cr1–Cr3–Cr2	59.25(8)
Cr1–Cr3–Cr2′	60.64(8)	Cr1′–Cr3–Cr2	59.69(8)
Cr1′–Cr3–Cr2′	59.97(8)	Cr2–Cr3–Cr2′	90.74(9)
Se1–Cr1–Se2	90.25(9)	Se1–Cr1–Se3′	171.50(12)
Se1–Cr1–Se4	90.35(9)	Se2–Cr1–Se3′	89.19(9)
Se2–Cr1–Se4	174.46(11)	Se3′–Cr1–Se4	89.40(9)
Se1–Cr2–Se2	90.12(9)	Se1–Cr2–Se3	87.51(8)
Se1–Cr2–Se4′	170.29(11)	Se2–Cr2–Se3	169.65(11)
Se2–Cr2–Se4′	91.45(8)	Se3–Cr2–Se4′	89.25(9)
Se1–Cr3–Se2′	171.40(12)	Se1–Cr3–Se3	87.69(8)
Se1–Cr3–Se4	89.97(9)	Se2′–Cr3–Se3	89.53(9)
Se2′–Cr3–Se4	91.52(8)	Se3–Cr3–Se4	170.91(11)
Se1–Cr1–P1	90.43(13)	Se2–Cr1–P1	93.27(14)
Se3′–Cr1–P1	98.06(13)	Se4–Cr1–P1	92.23(13)
Se1–Cr2–P2	97.93(13)	Se2–Cr2–P2	88.64(13)
Se3–Cr2–P2	101.66(13)	Se4′–Cr2–P2	91.70(13)
Se1–Cr3–P3	96.79(13)	Se2′–Cr3–P3	91.66(13)
Se3–Cr3–P3	98.24(13)	Se4–Cr3–P3	90.75(13)
Cr1–Se1–Cr2	66.43(8)	Cr1–Se1–Cr3	66.02(8)
Cr2–Se1–Cr3	68.45(8)	Cr1–Se2–Cr2	66.47(8)
Cr1–Se2–Cr3′	66.54(8)	Cr2–Se2–Cr3′	66.51(7)
Cr1′–Se3–Cr2	67.03(8)	Cr1′–Se3–Cr3	66.56(7)
Cr2–Se3–Cr3	68.72(8)	Cr1–Se4–Cr2′	67.09(8)
Cr1–Se4–Cr3	66.07(8)	Cr2′–Se4–Cr3	66.32(7)

a) Equivalent positions. ′: $-x, -y, -z$.

Table 14. P–P and M–M Distances (Å) and Virtual Symmetry of P_6 and M_6 Octahedra in Complexes **1**—**5** and Molybdenum Analogs

Complex	P–P; range (av)	Virtual symmetry of P_6 octahedron	M–M; range (av)	Virtual symmetry of Cr_6 octahedron
$[Cr_6S_8(PEt_3)_6]$	5.92—6.03 (5.98)	O_h	2.59—2.60 (2.59)	O_h
$[Cr_6S_8(PMe_3)_6]$	5.68—6.39 (6.03)	D_{3d}	2.66—2.72 (2.69)	D_{3d}
$[Cr_6Se_8(PEt_3)_6]$	6.09—6.13,[a] 6.03—6.24[b] (6.12)	O_h	2.68,[a] 2.70—2.72[b] (2.69)	O_h
$[Cr_6Se_8(PMe_3)_6]$	5.78—6.44 (6.11)	D_{3d}	2.72—2.79 (2.75)	D_{3d}
$[Cr_6Se_8(PMe_3Ph)_6]$	5.75—6.49 (6.09)	D_{2h}	2.68—2.77 (2.71)	D_{2h}
$[Mo_6S_8(PEt_3)_6]$[c]	6.18—6.29 (6.24)	O_h	2.66 (2.66)	O_h
$[Mo_6S_8(PMe_3)_6]$[d]	5.92—6.53 (6.22)	D_{3d}	2.66 (2.66)	O_h
$[Mo_6S_8(PMe_2Ph)_6]$[d]	5.95—6.52 (6.24)	D_{2h}	2.66 (2.66)	O_h

a) in 3a. b) in 3b. c) Ref. 1. d) Ref. 44.

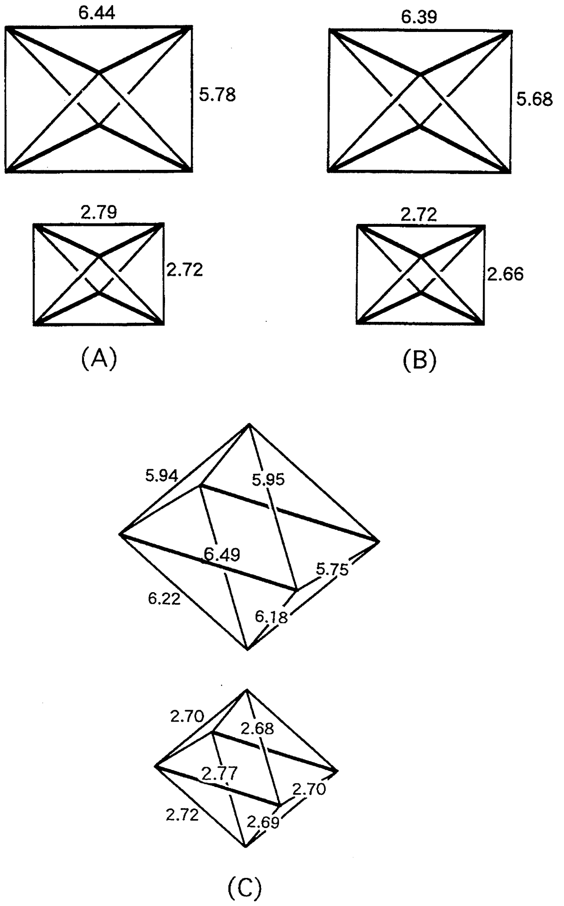

Fig. 3. The schematic representation of the P_6 and Cr_6 octahedra in the PMe_3 and PMe_2Ph complexes (Å); upper: P_6 octahedron, lower: Cr_6 octahedron. (A); $[Cr_6S_8(PMe_3)_6]$ (**2**), (B); $[Cr_6Se_8(PMe_3)_6]$ (**4**), (C); $[Cr_6Se_8(PMe_2Ph)_6]$ (**5**).

In both sulfide **2** and selenide **4** the methyl groups make the nearly close-packed layer, which is vertical to the 3-fold axis (Fig. 4). If the P_6 octahedron has octahedral symmetry, the layers of the methyl groups would be puckered and could not be neatly stacked. By an elongation of the intra-triangular P–P distances the layer of the methyl groups becomes flatter, allowing them to be stacked neatly. In the PMe_2Ph complex (as shown schematically in Fig. 3) the longest P–P distance is 6.49 Å, and the other five are 5.75—6.23 Å, close to the average P–P distance in the PEt_3 complex (6.11 Å). Therefore, the P_6 octahedron also has one pair of especially long distances, just as the Cr_6 octahedron. As shown in Fig. 5, $[Cr_6Se_8(PMe_2Ph)_6]$ is packed so that the phenyl groups of one cluster complex are inserted between the phenyl groups of neighboring cluster complexes. The arrangement of the phenyl groups seems to exert an interaction that pushes the phosphorus atoms slightly apart. Thus, two edges of the P_6 pseudo-octahedron become longer than the other ten edges.

By a comparison of the Cr_6 and P_6 octahedra, it is apparent that the distortion of the Cr_6 octahedra parallels the distortion of the surrounding P_6 octahedra, which is caused by the crystal-packing effect. While the Cr_6 octahedra are affected by the P_6 octahedra, the Mo_6 octahedra in $[Mo_6E_8(PR_3)_6]$ are little influenced by the crystal packing. As listed in Table 14, the distortions of the P_6 octahedra in the PMe_3 or PMe_2Ph derivatives are comparable to those of the chromium clusters. Nevertheless, the Mo_6 octahedra in those complexes are as regular as that of the PEt_3 derivative. This seems to be an indication that the Mo–Mo bonding is stronger than the

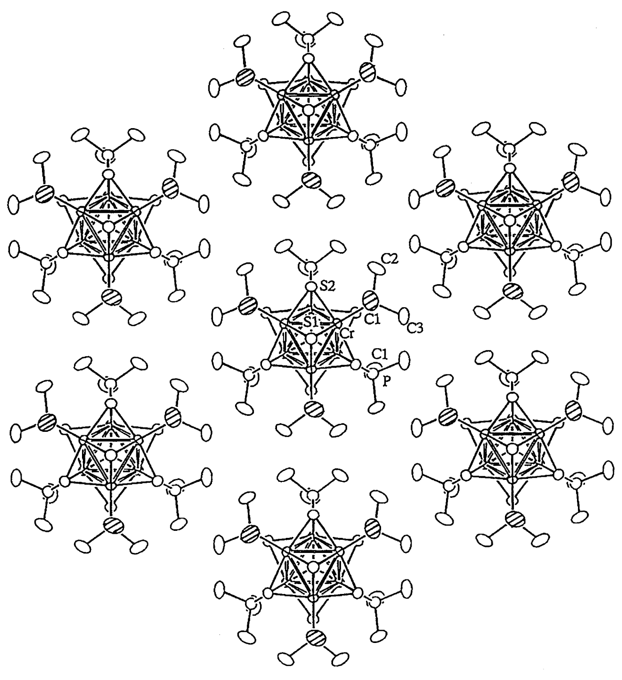

Fig. 4. The packing arrangement in the crystal of $[Cr_6S_8(PMe_3)_6]$ (**2**); viewed from 3-hold *c* axis. Hatched carbon atoms (C1) are arranged in a nearly closed packing manner. These layers are stacked along *c* axis.

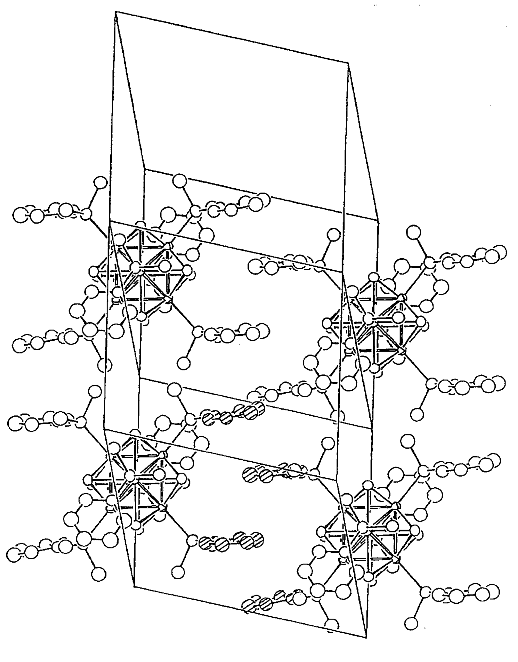

Fig. 5. The packing arrangement in the crystal of $[Cr_6S_8(PMe_2Ph)_6]$ (**5**). The hatched phenyl groups of neighboring cluster complexes insert into each other.

Cr–Cr bonding, and that the Mo_6 octahedra are free from any crystal-packing distortion of the ligands.

Electronic Effect. The average Cr–Cr distance in the PMe_3 complex **2** and **4** is longer than that of the corresponding PEt_3 complex **1** and **3**, respectively. Since the average P–P distances are almost the same in these complexes, the longer Cr–Cr distance in the PMe_3 complex is not simply due to a steric origin. The DV-$X\alpha$ calculations on $[Cr_6S_8(PH_3)_6]$, which is a model compound of $[Cr_6S_8(PR_3)_6]$, have revealed that the molecular-orbital levels are very sensitive to the Cr–Cr distance (Fig. 6). We calculated the energy levels by changing the Cr–Cr distance and the Cr_6 symmetry for four cases: (A) d(Cr–Cr)=2.59 Å in O_h, (B) d(Cr–Cr)=2.59 Å in D_{3d}, (C) d(Cr–Cr)=2.69 Å in O_h, and (D) d(Cr–Cr)=2.69 Å in D_{3d}. The average Cr–Cr distance in **1** is 2.59 Å and is 2.69 Å in **2**. Spin-polarized calculations were performed, and 20 valence electrons were filled in the lower valence orbitals. The results given in Fig. 6 are shown according to the usual representations with two electrons in an orbital by combining the up-spin and down-spin orbital schemes.

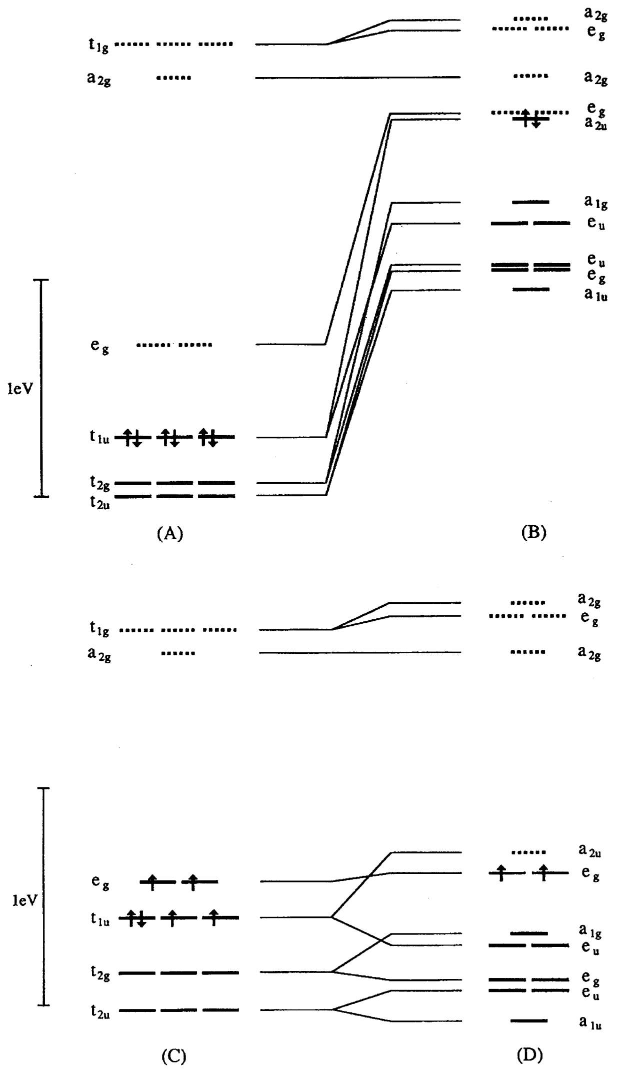

Fig. 6. Electronic level scheme near Fermi level for model complex $[Cr_6S_8(PH_3)_6]$. (A) d(Cr–Cr)=2.59 Å in O_h symmetry; (B) d(Cr–Cr)=2.59 Å in D_{3d} symmetry; (C) d(Cr–Cr)=2.69 Å in O_h symmetry; (D) d(Cr–Cr)=2.69 Å in D_{3d} symmetry. Solid and broken lines show occupied and unoccupied levels, respectively.

The results of a calculation for (A) shown that t_{1u} is a fully occupied HOMO, that e_g is LUMO, and that the gap between the orbitals is c.a. 0.4 eV. Although lowering the symmetry to D_{3d} in (B) splits t_{1u} to e_u and a_{2u}, both orbitals are lower than e_g (LUMO), and a_{2u} becomes HOMO. Therefore, there is no energy gain for the lower symmetry, and a regular octahedron is favorable for the Cr_6 cluster with a Cr–Cr distance of 2.59 Å, which is observed in $[Cr_6S_8(PEt_3)_6]$. On the other hand, the results for (C) show that in the O_h symmetry, the cluster is in a high-spin state with a partial occupation of the t_{1u} and e_u orbitals. Lowering the symmetry to D_{3d} (D) splits the t_{1u} orbital to e_u and a_{2u}. Although the e_g orbital remains LUMO, e_u is fully occupied with considerable energy gain. Therefore, if the Cr–Cr distance is long (2.69 Å), a structure deformed in the D_{3d} symmetry is favorable. We have already explained that the distortion of the P_6 to the D_{3d} symmetry required from the crystal-packing effect is transmitted to Cr_6, resulting in a distortion of the Cr_6 core in the D_{3d} symmetry. Now, the D_{3d} symmetry requires an elongation of the average Cr–Cr distance to gain some electronic energy. Similar calculations concerning the molybdenum congener have shown that a change in the Mo–Mo distances does not cause any favorable effect on the change in the symmetry from O_h to D_{3d}, even with a 0.1 Å longer Mo–Mo distance, because the cluster is always in the low-spin state as (A).

The present work was supported by a Grant-in-Aid for Scientific Research (A) No. 06403009 and a Grant-in-Aid for Scientific Research on Priority Areas No. 04241102 from the Ministry of Education, Science and Culture.

References

1) T. Saito, N. Yamamoto, T. Yamagata, and H. Imoto, *J. Am. Chem. Soc.*, **110**, 1646 (1988).

2) T. Saito, N. Yamamoto, T. Nagase, T. Tsuboi, K. Kobayashi, T. Yamagata, H. Imoto, and K. Unoura, *Inorg. Chem.*, **29**, 764 (1990).

3) S. J. Hilsenbeck, V. G. Young, Jr., and R. E. McCarley, *Inorg. Chem.*, **33**, 1822 (1994).

4) R. Chevrel and M. Sergent, *J. Solid State Chem.*, **3**, 515 (1971).

5) R. Chevrel and M. Sergent, in "Topics in Current Physics," ed by Ø. Fisher and M. B. Maple, Springer, Heidelberg (1982), Vol. 32, Chaps. 2 and 3.

6) A. Perrin and M. Sergent, *New J. Chem.*, **12**, 337 (1988).

7) T. Saito, A. Yoshikawa, T. Yamagata, H. Imoto, and K. Unoura, *Inorg. Chem.*, **28**, 3588 (1989).

8) X. Zhang and R. E. McCarley, *Inorg. Chem.*, **34**, 2678 (1995).

9) F. Cecconi, C. A. Ghilardi, and S. Midollini, *J. Chem. Soc., Chem. Commun.*, **1981**, 640.

10) F. Cecconi, C. A. Ghilardi, and A. Midollini, *Inorg. Chim. Acta*, **64**, L47 (1981).

11) F. Cecconi, C. A. Ghilardi, and A. Midollini, *Inorg. Chim. Acta*, **76**, L183 (1983).

12) A. M. Bacci, F. Cecconi, C. A. Ghilardi, and S. Midollini, *Inorg. Chem.*, **24**, 689 (1985).

13) F. Cecconi, C. A. Ghilardi, S. Midollini, and A. Orlandini, *Polyhedron*, **5**, 2021 (1986).

14) F. Cecconi, C. A. Ghilardi, S. Midollini, and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, **1987**, 831.

15) D. Fenske, J. Hachgenei, and J. Ohmer, *Angew. Chem., Int. Ed. Engl.*, **24**, 706 (1985).

16) D. Fenske, J. Ohmer, and J. Hachgenei, *Angew. Chem., Int. Ed. Engl.*, **24**, 993 (1985).

17) D. Fenske, J. Ohmer, and K. Merzweiler, *Z. Naturforsch., Teil B*, **42**, 803 (1987).

18) D. Fenske, J. Ohmer, J. Hachgenei, and K. Merzweiler, *Angew. Chem., Int. Ed. Engl.*, **27**, 1277 (1988).

19) M. C. Hong, A. Y. Huang, X. J. Lei, G. W. Wei, B. S. Kang, and H. Q. Liu, *Jiegou Huaxue* (*J. Struct. Chem.*), **9**, 77 (1990).

20) M. C. Hong, A. Y. Huang, X. J. Lei, G. W. Wei, B. S. Kang, and H. Q. Liu, *Polyhedron*, **10**, 927 (1991).

21) M. C. Hong, F. L. Jiang, Z. Y. Huang, X. J. Lei, and H. Q. Liu, *Huaxue Xuebao* (*Acta Chim. Sinica*), **50**, 654 (1992).

22) M. C. Hong, X. J. Lei, Z. Y. Huang, F. L. Jiang, and H. Q. Liu, *Kexue Tongbao* (*Chin. Sci. Bull.*), **37**, 1798 (1992).

23) F. L. Jiang, A. Y. Huang, J. Q. Shi, X. J. Lei, M. C. Hong, and H. Q. Lui, *Jiegou Huaxue* (*J. Struct. Chem.*), **12**, 312 (1993).

24) E. Diana, G. Gervasio, R. Rosseti, F. Valderamnn, G. Bor, and P. L. Stanghellini, *Inorg. Chem.*, **30**, 294 (1991).

25) H. Imoto, T. Saito, and H. Adachi, *Inorg. Chem.*, **34**, 2415 (1995).

26) P. Zanello, *Coord. Chem. Rev.*, **83**, 199 (1988).

27) A. Bencini, C. A. Ghilardi, A. Orlandini, S. Midollini, and C. Zanchini, *J. Am. Chem. Soc.*, **114**, 9898 (1992); A. Bencini, S. Midollini, and C. Zanchini, *Inorg. Chem.*, **31**, 2132 (1992).

28) A. Bencini, M. G. Uytterhoeven, and C. Zanchini, *Int. J. Quant. Chem.*, **52**, 903 (1994).

29) A. Bencini, C. A. Ghilardi, S. Midollini, A. Orlandini, U. Russo, M. G. Uytterhoeven, and C. Zanchini, *J. Chem. Soc., Dalton Trans.*, **1995**, 963.

30) A. Bencini and S. Midollini, *Coord. Chem. Rev.*, **120**, 87 (1992).

31) B. Hessen, T. Siegrist, T. Palstra, S. M. Tanzler, and M. L. Steigerwald, *Inorg. Chem.*, **32**, 5165 (1993).

32) D. P. Thompson and P. Boudjouk, *J. Org. Chem.*, **53**, 2109 (1988).

33) a) G. M. Sheldrick, "SHELXS86, a program for crystal structure determination," University of Göttingen, Federal Republic of Germany (1986); b) G. M. Sheldrick, "SHELXS76, a program for crystal structure determination," University of Cambridge, U.K. (1976).

34) H. Imoto, S. Hayakawa, N. Morita, and T. Saito, *Inorg. Chem.*, **29**, 2007 (1990).

35) C. J. Slater, in "The Calculation of Molecular Orbitals," John Wiley & Sons, New York (1979), p. 52.

36) F. W. Averill and D. E. Ellis, *J. Chem. Phys.*, **59**, 6412 (1973), and reference therein.

37) A. Rosén, D. E. Ellis, H. Adachi, and F. W. Averill, *J. Chem. Phys.*, **65**, 3629 (1976).

38) H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, **45**, 875 (1978).

39) C. Satoko, M. Tsukada, and H. Adachi, *J. Phys. Soc. Jpn.*, **45**, 1333 (1978).

40) H. Adachi, S. Shiokawa, M. Tsukada, C. Satoko, and S. Sugano, *J. Phys. Soc. Jpn.*, **47**, 1528 (1979).

41) A. M. Arif, J. G. Hefner, R. A. Jones, T. A. Albright, and S.-K. Kang, *J. Am. Chem. Soc.*, **108**, 1701 (1986).

42) M. L. Steigerwald, T. Siegrist, E. M. Gyorgy, B. Hessen, Y.-U. Kwon, and S. M. Tanzler, *Inorg. Chem.*, **33**, 3389 (1994).

43) F. Cecconi, C. A. Ghilardi, and S. Midollini, *Inorg. Chem.*, **22**, 3802 (1983).

44) J. Sasahara, Master's Thesis, The University of Tokyo, (1993).

45) D. Braga, F. Grepioni, and E. Parsini, *J. Chem. Soc., Dalton Trans.*, **1985**, 287.

46) D. Braga and F. Grepioni, *Acc. Chem. Res.*, **27**, 51 (1994).

47) D. Braga, *Chem. Rev.*, **92**, 633 (1992).