

Synthesis, structure and properties of $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$; the first discrete transition metal cluster from thiophosphate flux reactions

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The molecular cluster compound $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ forms by the reaction of Cr metal with thiophosphate fluxes.

Understanding the structural and reactivity relationships between molecules and extended solids of comparable compositions is a major challenge of synthetic inorganic chemistry. Many molecular cage and cluster compounds whose structural, and sometimes reactivity, features are comparable to those of metal oxide/chalcogenide/halide solids have been reported.^{1–3} The well known behavior of metal alkoxides to oligomerize both in solution and in the solid state⁴ has triggered studies on systems where a facile conversion of molecules to solids under mild conditions is possible, *e.g.* by using the sol–gel process⁵ or by pyrolysis⁶ of suitable precursors to achieve the desired solid product. The reverse process, an excision⁷ of discrete metal clusters from extended solids, has received less attention so far.⁸ Pioneering work has been done by the groups of Corbett⁹ and Holm¹⁰ who used solid state compounds containing discrete clusters as precursors for the synthesis of soluble species that are not accessible by solution methods. In contrast to tetra-thiometalate complexes¹¹ metal coordination compounds with group 15 tetrathio anions as ligands (so-called Zintl-type ligands) are extremely difficult to stabilize in solution¹² because of their high negative charge and the lack of charge delocalization. The first representatives of this class of compounds are, however, easily accessible through solid state reactions† using polythiophosphate fluxes.¹³

The facile syntheses of the one-dimensional chain compounds $\text{A}_3[\text{Cr}_2(\text{PS}_4)_3]$ ($\text{A} = \text{K}, \text{Tl}$) whose structures contain the polymeric $\text{[Cr}_2(\text{PS}_4)_3]^{3-}$ species¹⁴ indicated that discrete $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ units might form from reaction systems containing a higher tetrathiosphosphate content. In one $\text{Cr–P}_2\text{S}_5\text{–K}_2\text{S}$ system containing the reactants in a 1 : 2 : 3 ratio at 600 °C the title compound formed in 85% yield after one week. The structure‡ of the title compound contains binuclear $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ clusters which are well separated from each other by K^+ cations. The anion portion of the clusters is shown in Fig. 1. The centrosymmetric $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ cluster consists of a $\text{Cr}_2(\text{PS}_4)_2$ core which is terminated on each side by two $[\text{PS}_4]^{3-}$ thiophosphate ligands in a bidentate fashion. In the core two $[\text{PS}_4]^{3-}$ ligands bridge two octahedrally coordinated Cr atoms employing three S atoms each. The remaining S atom is non-bonding. Relative to the idealized T_d anion symmetry, metal coordination decreases the S–P–S angle while the angle unbridged by Cr is considerably expanded. The Cr atoms are coordinated by three $[\text{PS}_4]^{3-}$ ligands where each thiophosphate group furnishes two S atoms to complete the octahedral S coordination of the metal. The Cr···Cr distance within the dimer is 3.523(1) Å. The unique Cr–S distance is comparable to that in $\text{CrP}_3\text{S}_{9+x}$ ¹⁵ the individual Cr–S distances ranging from 2.387(1) to 2.485(1) Å.

Magnetic susceptibility measurements in the temperature range 4–300 K show that the Cr^{3+} centers within the binuclear units are antiferromagnetically coupled. This can be ascribed to a small antiferromagnetic exchange coupling between the Cr atoms in the dimeric units. The magnetic behavior can be modeled with the use of an isotropic Heisenberg–Dirac–Van Vleck dimer model for an $S_1 = S_2 = 3/2$ and an exchange

coupling constant $J = -4 \text{ cm}^{-1}$. The corresponding room temp. moment corrected for diamagnetism, $\mu_{\text{eff}} = 3.78 \mu_B$, is slightly smaller than the spin-only value of $3.87 \mu_B$ for Cr^{III} with $S = 3/2$. The optical spectrum of $\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$ exhibits a sharp optical gap consistent with semiconducting behavior. The experimentally determined value is $E_g = 1.36 \text{ eV}$. Thermal analysis shows that $\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$ melts without decomposition at 433.8 °C.

$\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$ easily dissolves in DMF or acetonitrile upon addition of 2,2,2-cryptand, although so far we were unable to obtain precipitates with large cations in single-crystalline form. This behavior indicates the potential of $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ as a precursor for the synthesis of Zintl anion complexes in solution. The solutions of $\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$ in DMF are stable according to UV–VIS for 1–2 days. In DMF solution the $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ chromophore shows one strong absorption at 615 nm.

$\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$, the first transition metal thiophosphate with PS_4^{3-} ligands has been synthesized from molten polythiophosphate fluxes. Its structure contains the $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ cluster as a molecular analogue of the $[\text{Cr}_2(\text{PS}_4)_3]^{3-}$ units observed in the one-dimensional chain compound $\text{K}_6[\text{Cr}_2(\text{PS}_4)_4]$.¹⁴ The $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ cluster is one of the few known complexes with a complete Zintl anion coordination sphere; it is stable in solution and may be useful as a synthon for ‘wet’ chemistry.

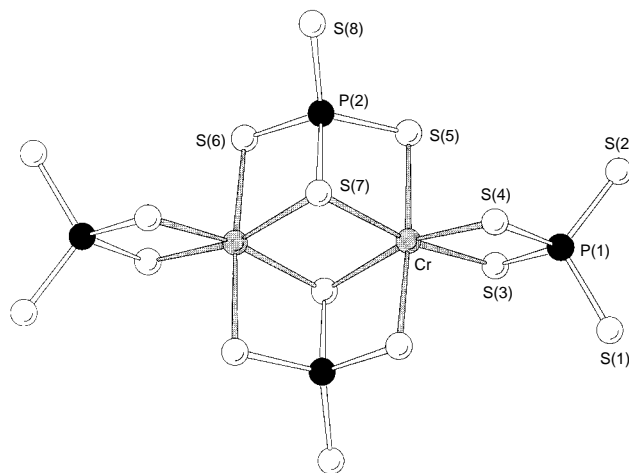


Fig. 1 Structure of the $[\text{Cr}_2(\text{PS}_4)_4]^{6-}$ anion with atomic labeling scheme. Selected bond lengths (Å) and angles (°): Cr–S(3) 2.387(1), Cr–S(4) 2.391(1), Cr–S(5) 2.416(1), Cr–S(6) 2.399(1), Cr–S(7) 2.451(1), Cr–S(7a) 2.485(1), P(1)–S(1) 2.003(2), P(1)–S(2) 2.004(2), P(1)–S(3) 2.090(2), P(1)–S(4) 2.073(2), P(2)–S(5) 2.048(2), P(2)–S(6) 2.045(2), P(2)–S(7) 2.114(2), P(2)–S(8) 1.967(2), S(3)–Cr–S(4) 84.05(4), S(6)–Cr–S(5) 85.94(5), S(3)–Cr–S(6) 99.37(5), S(3)–Cr–S(7) 167.52(5), S(3)–Cr–S(7a) 92.36(4), S(4)–Cr–S(5) 96.59(4), S(4)–Cr–S(6) 84.59(4), S(4)–Cr–S(7) 97.68(4), S(4)–Cr–S(7a) 165.09(4), S(5)–Cr–S(6) 174.66(5), S(5)–Cr–S(7) 81.58(4), S(5)–Cr–S(7a) 97.59(4), S(6)–Cr–S(7) 93.10(4), S(6)–Cr–S(7a) 81.72(4), S(1)–P(1)–S(2) 113.68(7), S(1)–P(1)–S(3) 198.73(7), S(1)–P(1)–S(4) 112.29(7), S(2)–P(1)–S(3) 111.13(7), S(2)–P(1)–S(4) 109.84(7), S(3)–P(1)–S(4) 100.39(6), S(5)–P(2)–S(6) 109.89(7), S(5)–P(2)–S(7) 99.61(6), S(5)–P(2)–S(8) 115.94(8), S(6)–P(2)–S(7) 100.39(6), S(6)–P(2)–S(8) 113.28(7), S(7)–P(2)–S(8) 115.93(7).

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Footnotes and References

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† A mixture of Cr powder (0.104 g, 2 mmol), P₂S₅ (0.221 g, 2 mmol), K₂S (0.331 g, 3 mmol) and S (0.096 g, 3 mmol) was loaded into a silica tube in a glovebox. The tube was sealed under vacuum, heated to 600 °C for 4 d and then cooled slowly to room temp. at 4 °C h⁻¹. K₆[Cr₂(PS₄)₄] can be isolated in high yields (> 85%) in the form of dark green platelets. The air-sensitive crystals are soluble in aprotic polar solvents upon addition of 2,2,2-cryp-

‡ *Crystal data* for K₆[Cr₂(PS₄)₄] at 25 °C: orthorhombic, space group *Pbca* (no. 61), *a* = 13.110(3), *b* = 12.050(2), *c* = 18.720(4) Å, *U* = 2957.3(8) Å³, *Z* = 4, λ = 0.71073 Å, *D_c* = 2.191 g cm⁻³, μ (Mo-K α) = 2.92 mm⁻¹, crystal platelike, dimensions 0.1 × 0.2 × 0.2 mm, θ_{\max} = 54°, data collected at 25 °C on a Nicolet P2₁ four circle diffractometer, 6456; unique data, 3.226; data with *F_o*² > 4 σ (*F_o*²), 2449; number of variables, 129. Structure solved and refined using SHELXS86 and SHELXL93. An empirical absorption correction based on ψ scans was applied to the data. Final *R*, *R_w* = 0.038, 0.094 (0.062, 0.094 for all data). CCDC 182/673.

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