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Supplementary Material Available: Listings of positional and thermal parameters and mean square displacement tensors of atoms (2 pages). Ordering information is given on any current masthead page.

Hexakis(μ_3-thio)pentakis[(η^5-cyclopentadienyl)titanium], [((η^5-C_5H_5)Ti)$_5$(μ_3-S)$_6$]: Preparation and Molecular and Electronic Structure[†]

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In earlier work we have described [(CpCr)$_4$(μ_3-O)$_4$] and [(CpV)$_5$(μ_3-O)$_6$] (Cp = η^5-C_5H_5),[1] which together with [(CpTi)$_6$(μ_3-O)$_8$] described by Caulton and co-workers[2] provide a series of novel oxygen-containing clusters which obey Euler's theorem. A theoretical study of these clusters showed that there were 12 cluster orbitals occupied by 2 ((CpTi)$_6$O$_8$), 8 ((CpV)$_5$O$_6$), or 12 ((CpCr)$_4$O$_4$) electrons.[3] According to this analysis a wide variety of more or less distorted octahedral (CpM)$_6$A$_8$, trigonal-bipyramidal (CpM)$_5$A$_6$, and tetrahedral (CpM)$_4$A$_4$ clusters (M = first-row transition metal and A = μ_3-atom from groups 15 or 16) should be obtainable. In the tetrahedral case several thio derivatives [(CpM)$_4$S$_4$]$^{n+}$ (M = Cr, Fe, Co) are known.[4] We have been seeking other members of these series, particularly nontetrahedral derivatives, and report here the preparation and structure of the first trigonal-bipyramidal thio cluster, [(CpTi)$_5$(μ_3-S)$_6$].[5]

In their report on (CpTi)$_6$O$_8$ Caulton and co-workers suggested that the cluster was actually obtained from Cp$_2$Ti(CO)$_2$ and H$_2$O.[2] We have confirmed this suggestion and find that the reaction between Cp$_2$Ti(CO)$_2$ and H$_2$O (3:4 mol ratio) in toluene at 80 °C is quantitative and gives (CpTi)$_6$O$_8$ as the *only* titanium-containing product according to the equation:

$$6Cp_2Ti(CO)_2 + 8H_2O \rightarrow (CpTi)_6O_8 + 6C_5H_6 + 12CO + 5H_2 \quad (1)$$

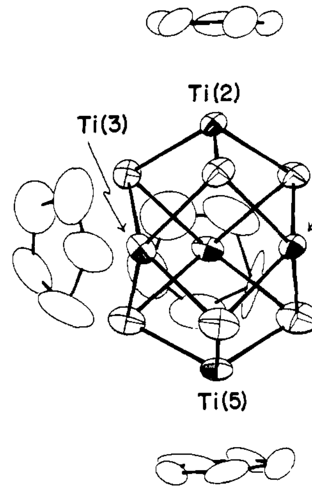

Figure 1. ORTEP drawing of (CpTi)$_5$S$_6$. Hydrogen atoms are omitted for clarity. Ti–Ti distances: Ti(1)–Ti(2) 3.152 (5); Ti(1)–Ti(3) 3.148 (5); Ti(1)–Ti(4) 3.214 (5); Ti(1)–Ti(5) 3.145 (5); Ti(2)–Ti(3) 3.173 (5); Ti(2)–Ti(4) 3.169 (5); Ti(3)–Ti(4) 3.172 (5); Ti(3)–Ti(5) 3.161 (5); Ti(4–)–Ti(5) 3.076 (5) Å. Ti–S distances: Ti(1)–S(3) 2.468 (6); Ti(1)–S(4) 2.485 (7); Ti(1)–S(5) 2.480 (7); Ti(1)–S(6) 2.463 (7); Ti(2)–S(2) 2.274 (6); Ti(2)–S(3) 2.308 (6); Ti(2)–S(4) 2.277 (7); Ti(3)–S(1) 2.443 (7); Ti(3)–S(2) 2.506 (7); Ti(3)–S(3) 2.461 (6); Ti(3)–S(5) 2.444 (7); Ti(4)–S(1) 2.458 (6); Ti(4)–S(2) 2.487 (7); Ti(4)–S(4) 2.488 (6); Ti(4)–S(6) 2.504 (8); Ti(5)–S(1) 2.286 (7); Ti(5)–S(5) 2.268 (7); Ti(5)–S(6) 2.263 (8) Å.

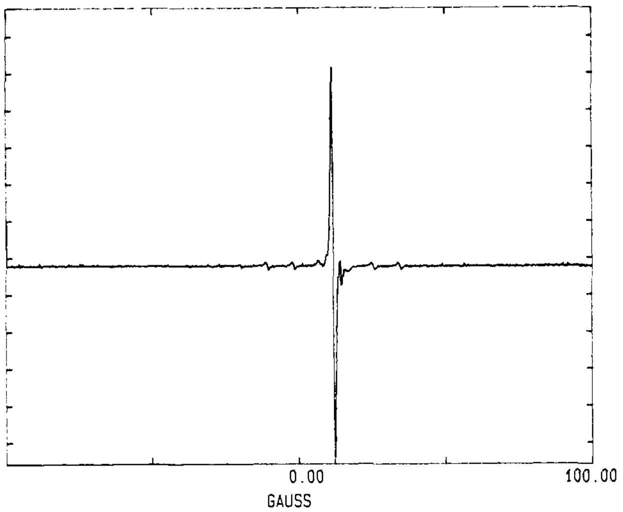

Figure 2. ESR spectrum of (CpTi)$_5$S$_6$ at 20 °C.

This remarkable specificity suggested that a similar reaction with H$_2$S would take place. It does, but the product is (CpTi)$_5$(μ_3-S)$_6$ (73% yield based on the Cp$_2$Ti(CO)$_2$ used) not (CpTi)$_6$S$_8$, thus illustrating our contention that the clusters obeying Euler's theorem are closely related. Analysis of the gaseous and solid products of the reaction between Cp$_2$Ti(CO)$_2$ (6.4 mmol) and gaseous H$_2$S (7.7 mmol) in toluene at 80 °C for 72 h suggests that the stoichiometry of the reaction producing (CpTi)$_5$S$_6$ is

$$10Cp_2Ti(CO)_2 + 12H_2S \rightarrow 2(CpTi)_5S_6 + 7H_2 + 20CO + 10C_5H_6 \quad (2)$$

though other sulfur-containing products are obtained. The new cluster is dark green-brown, moderately air sensitive, very soluble in toluene and forms large crystals when the toluene solutions are layered with hexane.[6]

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(6) Analyses of the bulk material (powder) shows it contains one molecule of toluene of crystallization per (CpTi)$_5$S$_6$ unit; this toluene is not present in the crystal examined by X-ray diffraction. Analytical results (by Beller Laboratorium, Göttingen, W. Germany) of samples from two distinct preparations: Calcd for (CpTi)$_5$S$_6$·C$_6$H$_5$CH$_3$ (C$_{32}$H$_{33}$S$_6$Ti$_5$): C, 45.2; H, 3.9; S, 22.6; Ti, 28.2%. Found: C, 45.7, 45.6; H, 4.2, 4.3; S, 15.2, 10.8; Ti 27.7, 28.7%. The problem of incorrect sulfur analyses in cyclopentadienyl metal complexes has been discussed by other workers.[7]

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The crystal structure determination[8] shows that $(CpTi)_5S_6$ contains sulfur bridging the triangular faces of a distorted trigonal bipyramid of titanium atoms (Figure 1). The distortion takes the form of a displacement of one of the equatorial titanium atoms (Ti(4) in Figure 1) away from one other equatorial titanium (Ti(1)) and toward an axial titanium (Ti(5)). The distance Ti(4)–Ti(1) is 3.214 (5) Å, Ti(4)–Ti(5) is 3.076 (5) Å, and the average for all other Ti–Ti distances is 3.160 (5) Å with a range from 3.145 (5) to 3.173 (5) Å. All the Ti–Ti distances are longer than those of $(CpTi)_6O_8$ (average Ti–Ti 2.891 (1) Å[2]) because of the larger covalent radius of sulfur (1.02 Å) vs. oxygen (0.73 Å); $(CpV)_5O_6$ is an essentially perfect trigonal bipyramid with V–V distances ranging from 2.738 (3) to 2.762 (2) Å.[1]

The new cluster is paramagnetic, as would be expected for a species with an odd number of electrons. The ESR spectrum (toluene solution) shows a single line at $g = 1.993$ with weak satellites attributable to hyperfine interaction with the Ti isotopes (Figure 2). The spectrum at −80 °C is essentially identical with that at 20 °C, though the satellites are not observed at the lower temperature. The bulk magnetic susceptibility per mole at 20 °C is 6.525×10^{-4}. This corresponds to a magnetic moment of 1.25 μ_B, which is low compared to the spin-only value for one electron of 1.73 μ_B due mainly to the lack of a diamagnetic correction for any of the ligands or titanium atoms.[9] However, both the narrow line ESR spectrum and the bulk magnetic moment indicate the presence of one unpaired electron in $(CpTi)_5S_6$.

Both the distortion of $(CpTi)_5S_6$ and its one unpaired electron can be understood in terms of the theoretical model presented previously.[3] The new cluster has three electrons to be accommodated in the 12 cluster orbitals. In a perfect trigonal-bipyramidal structure (D_{3h} symmetry) the electron configuration would be $(1a'_1)^2(1e')^1$. Therefore Jahn–Teller distortion of the D_{3h} structure is expected. Since both the $1a'_1$ and $1e'$ orbitals are almost completely localized on the equatorial titanium atoms, the distortion must involve these atoms, as is observed. The distortion is such that $(CpTi)_5S_6$ has no symmetry within experimental error.

Since the three cluster electrons are localized on the equatorial titanium atoms, one may naively consider each of these atoms to be Ti(III) (d^1) and the axial titanium atoms to be Ti(IV) (d^0). This assignment of oxidation states is in agreement with the observed Ti–S distances. The equatorial Ti–S distances average 2.474 (7) Å with a range from 2.443 (7) to 2.506 (7) Å; the axial Ti–S distances are much shorter, averaging 2.279 (7) Å with a range from 2.263 (8) to 2.308 (6) Å. The Ti–S distances may be compared to those in $Cp^*_2TiS_3$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$) and Cp_2TiS_5, 2.413 (4) Å[10a] and 2.420 and 2.446 Å.[10b] The Ti(4)–S distances are identical with those of the other equatorial titanium atoms (Ti(1)–S and Ti(3)–S); the trigonal pyramid of sulfur atoms is distorted with the trigonal bipyramid of titanium atoms in order to retain the Ti–S bonding. This is in accord with the theoretical model in which the 12 cluster orbitals of $(CpM)_5A_6$ are essentially pure metal orbitals and are nonbonding with respect to the M–A interaction.

Analogous reactions to those between $Cp_2Ti(CO)_2$ and H_2O or H_2S do not occur with $Cp_2Zr(CO)_2$ presumably because of the instability of the Zr(III) oxidation state. On reaction with H_2O, $Cp_2Zr(CO)_2$ gives only ZrO_2 and with H_2S the product is the known[7] complex $(Cp_2ZrS)_2$.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths (7 pages). Ordering information is given on any current masthead page.

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(8) Data for $((C_5H_5)Ti)_5S_6$ ($M = 757.4$) were obtained from a wedge-shaped chip cut from a large irregular crystal and were measured on a Picker FACS-1 diffractometer. Space group $P2_1/n$, $a = 16.978$ (5) Å, $b = 17.008$ (9) Å, $c = 10.122$ (3) Å, $\beta = 92.44$ (2)°, $Z = 4$, $D_c = 1.72$, 1383 observed ($(I) > 3\sigma(I)$) reflections out of 3828 with $2\theta \leq 45°$. The data were corrected for absorption and all atoms except H were refined anisotropically to a conventional R of 0.074, $R_w = 0.077$. The structure was solved by MULTAN80 and refined by SHELX. Tables of atomic positions, thermal parameters, and bond lengths are available as supplementary material. Attempts to obtain crystals that diffract better are continuing.

(9) Correction for the diamagnetism of $5C_5H_5^-$ ($-50.9 \times 10^{-6} \times 5$), $6S^{2-}$ ($-38 \times 10^{-6} \times 6$), $2Ti^{4+}$ ($-5 \times 10^{-6} \times 2$), and $3Ti^{3+}$ ($-9.2 \times 10^{-6} \times 3$) gives a moment of 1.66 μ_β. See: Weiss, A.; Witte, H. "Magnetochemie"; Verlag Chemie: Weinheim, 1973; pp 93–95.

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Excited-State Chemistry of Tetrakis(μ-pyrophosphito)diplatinum(II). Photoinduced Addition of Aryl Bromides and Iodides to the Binuclear Complex and the Photoinduced Catalytic Conversion of Isopropyl Alcohol into Acetone and Hydrogen

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Aqueous solutions of the binuclear platinum(II) complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ show an intense absorption band at 367 nm (ϵ_{max} 3.45×10^4) and a corresponding emission at 514 nm.[1] This emission has been identified as a long-lived phosphorescence (τ = 9.8 (2) μs) originating from a triplet excited state.[2] Using a simplified MO treatment, the respective ground- and excited-state configurations of these binuclear d^8 complexes are represented as $(d_{z^2})^2(d^*_{z^2})^2$ and $(d_{z^2})^2(d_{z^2}^*)^1(p_z)^1$. The excited state $Pt_2(\mu\text{-}P_2O_5H_2)_4^{-*}$ undergoes efficient energy quenching with SO_2.[3] Quenching is also observed with electron-transfer reagents, and from experiments using different oxidants the electrode potential for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}/Pt_2(\mu\text{-}P_2O_5H_2)_4^{3-}$ has been estimated to be <−1 V.[2,4] This long microsecond lifetime for $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-*}$ makes it conceptually feasible to carry out reaction chemistry with this triplet excited state, and its strong reducing properties makes it a useful reagent for reaction with organic halides. This paper reports the first organometallic reactions of $Pt_2(P_2O_5H_2)_4^{4-*}$ and relates its redox behavior and radical character to the Gray MO model.

The complex $Pt_2(\mu\text{-}P_2O_5H_2)_4^{4-}$ undergoes thermal addition of halogens X_2 and methyl iodide to give the axially disubstituted Pt(III)–Pt(III) complexes $Pt_2(\mu\text{-}P_2O_5H_2)_4X_2^{4-}$ and $Pt_2(\mu\text{-}P_2O_5H_2)_4MeI^{4-}$.[5] Thermal addition of the higher homologues RI (R = Et, *n*-Pr, *i*-Pr, *n*-pent) also gives $Pt_2(\mu\text{-}P_2O_5H_2)_4RI^{4-}$, but the complex is contaminated with $Pt_2(\mu\text{-}P_2O_5H_2)_4I_2^{4-}$.[6] Aryl halides do not undergo thermal addition. Aryl bromides or iodides

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(6) UV-vis data for $Pt_2(\mu\text{-}P_2O_5H_2)_4RI^{4-}$: λ_{max} 352 (R = Et); 355 nm (R = *i*-Pr, *n*-Pr, *n*-pent). UV-vis data for $Pt_2(\mu\text{-}P_2O_5H_2)_4X_2^{4-}$: λ_{max} 338 (X = I), 305 nm (X = Br): from ref 5.

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