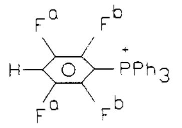


Figure 1. Labeling scheme for $Ph_3(4\text{-}C_6F_4H)P^+$.

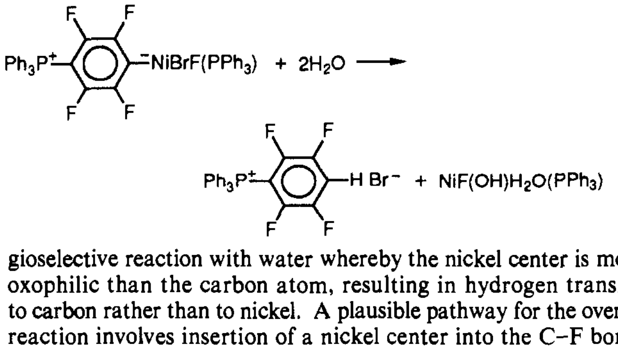
with the PANIC spectral simulation program[3] gives the following coupling constants: $^3J(PF^b)$ = 6.05 Hz, $^3J(F^aF^b)$ = 9.00 Hz, $^3J(HF^a)$ = 10.30 Hz, $^4J(PF^a)$ = 0.05 Hz, $^4J(HF)$ = 9.20 Hz, $^5J(F^aF^b)$ = −13.50 Hz, $^4J(F^aF^a)$ = −1.75 Hz, $^4J(F^bF^b)$ = 9.00 Hz.[3] The labeling scheme is shown in Figure 1.

The compound $[Ph_3(4\text{-}C_6F_4H)P]Br$ reacts with aqueous NaOH at ambient temperature to give quantitative conversion to triphenylphosphine oxide and 1,2,4,5-tetrafluorobenzene (eq 3). The

$$[Ph_3(4\text{-}C_6F_4H)P]Br + NaOH \rightarrow Ph_3PO + 1,2,4,5\text{-}C_6F_4H_2 + NaBr \quad (3)$$

^1H and ^{19}F NMR spectra of the product 1,2,4,5-tetrafluorobenzene correspond with those given in the literature.[4] If an aqueous solution of NaOD in D_2O is used, the *monodeuterated* compound $1,2,4,5\text{-}C_6F_4HD$ is obtained. This monodeuterated compound is also obtained upon treating the fusion product with D_2O, followed by reaction of the resulting salt $[Ph_3(4\text{-}C_6F_4D)P]Br$ with NaOH in water. The ^1H NMR spectrum of 1,2,4,5-tetrafluoro-3-deuterobenzene shows a triplet of triplets centered at δ 7.03 ($^3J(HF)$, $^5J(HF)$: 9.7, 7.5 Hz). The ^{19}F NMR spectrum shows a multiplet centered at δ −139.3 for chemically equivalent but magnetically inequivalent fluorine nuclei. Reactions that allow the selective deuteration of equivalent positions are rather rare. The *doubly deuterated* product $1,2,4,5\text{-}C_6F_4D_2$ can also be synthesized by treatment of $[Ph_3(4\text{-}C_6F_4D)P]Br$ with a solution of NaOD in D_2O. The ^{19}F NMR spectrum shows a single peak at δ −138.4. No other isomers are observed.

In the formation of $[Ph_3(4\text{-}C_6F_4H)P]^+$ the selective cleavage of the C–F bond must occur in the fusion reaction with nickel bromide rather than in the subsequent hydrolysis step. Cleavage of the C–F bond in the hydrolysis step does not explain our results because a phosphonium ion substituent on the fluoro aromatic ring is expected to increase the susceptibility of the ring to *nucleophilic* attack. Such nucleophilic attack by water at $[Ph_3(C_6F_5)P]^+$ is expected to occur either at the 4-position of the perfluoro ring to give $[Ph_3(4\text{-}C_6F_4OH)P]^+$[5] or at phosphorus to give phosphine oxide.[6] The only reasonable explanation for this unusual chemistry is that C–F cleavage occurs in the reaction with nickel bromide and that the melt contains an organonickel complex of a phosphonium salt. On the basis of the precedent in ref 1, we propose a structure of the type $Ph_3(4\text{-}C_6F_4(NiBrF(PPh_3)^-))P^+$ for the organonickel complex formed after reductive elimination of Br_2. Hydrolysis of this complex results in the formation of $[Ph_3(4\text{-}C_6F_4H)P]Br$ and uncharacterized nickel-containing products (eq 4). This phosphonium product results from a regioselective reaction with water whereby the nickel center is more oxophilic than the carbon atom, resulting in hydrogen transfer to carbon rather than to nickel. A plausible pathway for the overall reaction involves insertion of a nickel center into the C–F bond. The C–F bond in the 4-position is the sterically favored one, and recent examples of similar C–F oxidative additions have been reported.[7] This pathway is attractive because it explains why, under reaction conditions in an open container where the halogen formed in the reaction can escape, only small amounts of triphenylphosphine oxide are formed. Under sealed-tube conditions halogenation of triphenylphosphine occurs, and subsequent hydrolysis yields triphenylphosphine oxide as the major product.



(4)

The subsequent reaction of $[Ph_3(4\text{-}C_6F_4H)P]Br$ with hydroxide ion follows an atom-transfer regioselectivity whereby the oxygen migrates to phosphorus and the hydrogen to carbon. We observe no formation of phenols, or of compounds that contain P–H bonds, resulting from the opposite selectivity.

Acknowledgment. We thank the Louisiana Board of Regents for support. We thank Mark Fink for helpful discussions.

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[4] *Aldrich Library of NMR Spectra*; Aldrich: Milwaukee, WI, 1983.

[5] Banks, R. E. *Fluorocarbons and Their Derivatives*, 2nd ed.; MacDonald; London, 1970; pp 218–221.

[6] We find that $[Ph_2(C_6F_5)MeP]^+$ reacts with OH^- to give primarily $Ph_2(C_6F_5)PO$.

[7] Richmond, T. G.; Osterberg, C. E.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 8091–8092. Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.* **1984**, *23*, 2968–2973.

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Novel Cubane-Type Molybdenum–Tin Cluster Complexes $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ and $Mo_3SnS_4(aq)^{6+}$

The sulfur-bridged incomplete cubane-type aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$ (A) reacts not only with metallic tin but also with tin(II) ion to give $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ (B) and $Mo_3SnS_4(aq)^{6+}$ (C), respectively. Although the aqua ion A reacts with metallic iron,[1] nickel,[2] copper,[3] mercury,[4] and magnesium,[5] it does not react with any 2+ ion of the metals.

Compounds containing both molybdenum and tin are relatively rare, though some very interesting reports have appeared.[6] No cubane-type compounds with a Mo_3SnS_4 core, to our knowledge, have been reported so far. We describe here the preparation, electronic spectra, and electrochemistry of B and C, together with the X-ray structure of the *p*-toluenesulfonate salt of B.

The preparation of $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9](CH_3C_6H_4SO_3)_8\cdot 26H_2O$ (B′) is as follows: All the experiments were carried out under a dinitrogen atmosphere. Addition of tin metal (3 g) to A (0.15 M per Mo, 25 mL in 2 M HCl) rapidly changed the color of the solution from green to red-purple. After a couple of days at room temperature, the unreacted metal was removed from the solution and Dowex 50W-X2 column chromatography was used (2 × 85 cm). The resin was washed with 0.5 M HCl, and a small amount of yellow-green single-cubane C was eluted with 1 M HCl. A small amount of unreacted A may follow this species. A red-purple solution of B was obtained by use of 2 M

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[1] Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342–1343.

[2] Shibahara, T.; Kuroya, H. *Abstracts of Papers*, 1987 International Miniconference for Young Chemists in Tokyo—Macrocyclic and Coordination Chemistry, Tokyo, July 1987; Japan Society of Young Coordination Chemists: Tokyo, 1987; Abstract D13. Shibahara, T.; Kuroya, H. *J. Coord. Chem.* **1988**, *18*, 233–236.

[3] Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1988**, *110*, 3313–3314.

[4] Akashi, H.; Shibahara, T. *Abstracts of Papers*, XXVI International Conference on Coordination Chemistry, Porto, Portugal, Aug 1988; Universidade do Porto and Sociedade Portuguesa de Química: Porto, Portugal, 1988; Abstract A27.

[5] Shibahara, T.; Yamamoto, T.; Kanadani, H.; Kuroya, H. *J. Am. Chem. Soc.* **1987**, *109*, 3495–3496.

[6] For example, $Mo_2(Sn(SnMe_3)_3)_2(NMe_2)_4$: Chisholm, M. H.; Chiu, H.-T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097–4102.

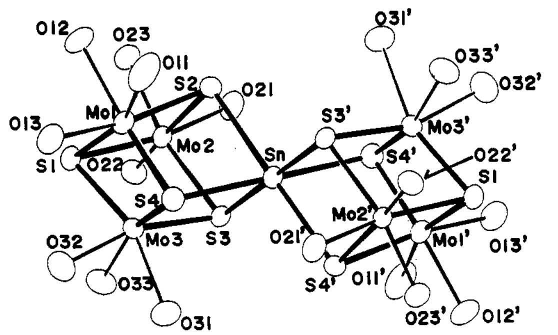


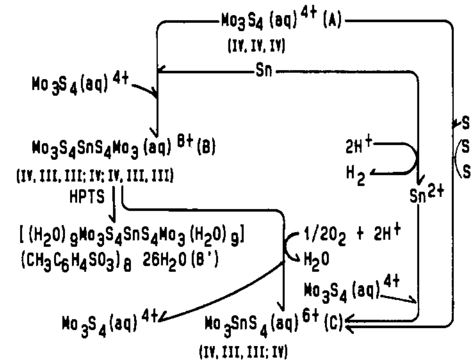
Figure 1. Perspective view of the $[(H_2O)_9Mo_3S_4SnS_4Mo_3(H_2O)_9]^{8+}$ cation with selected atomic distances (Å): Mo1–Mo2 = 2.680 (2); Mo1–Mo3 = 2.694 (2); Mo2–Mo3 = 2.691 (2); Mo1–S1 = 2.338 (3); Mo1–S2 = 2.344 (4); Mo1–S4 = 2.345 (4); Mo2–S1 = 2.339 (3); Mo2–S2 = 2.341 (4); Mo2–S3 = 2.338 (3); Mo3–S1 = 2.334 (3); Mo3–S3 = 2.339 (3); Mo3–S4 = 2.344 (4); Mo1–Sn = 3.739(1); Mo2–Sn = 3.729 (1); Mo3–Sn = 3.670(1); Sn–S2 = 2.659 (3); Sn–S3 = 2.608 (3); Sn–S4 = 2.613 (3); Mo–O(average) = 2.177 [20]. The primed atoms are related to the unprimed ones by a center of symmetry.

HCl; yield 80%. The solution was absorbed on the cation exchanger again and eluted with 4 M HPTS (*p*-toluenesulfonic acid). The resultant solution was kept in a refrigerator, and dark brown crystals of B′ were obtained in a few days;[7] yield 40% based on A. The crystals lose some of the water of crystallization easily: Thermal analysis made clear that 22 H_2O's are lost at 68 °C under an argon stream. The aqua ion B is very air-sensitive, giving A and C in the ratio 1:1 on exposure to air. The compound B′ dissolves in some organic solvents—fairly soluble in methanol, ethanol, and acetone, slightly soluble in acetonitrile and ethyl acetate and insoluble in carbon tetrachloride—the stability and reactivity of the compounds being under investigation.

The single-cubane-type aqua ion C can also be prepared easily by the addition of solid tin(II) chloride dihydrate or tin(II) oxide ($Sn:Mo_3$ = 1.2:1) to A (0.2 M per Mo, 20 mL, in 2 M HCl), which immediately changed the color of the solution from green to yellow-green. Then, Dowex 50W-X2 column chromatography was used (1 M HCl) and the yellow-green solution was collected. The solution was absorbed on the cation exchanger again and eluted with 3 M HPTS. The aqua ion C is fairly air-stable in contrast to the air-sensitiveness of the aqua ion B. Only a few percent change of absorbance per day was observed when C was exposed to air. Although we have not yet succeeded in isolating a solid sample of C, we have prepared a derivative complex of C, $K_3[Mo_3SnS_4(Hnta)_3Cl_3]\cdot 3H_2O$ (D). The preparation of D is as follows: Solid $SnCl_2\cdot 2H_2O$ ($Sn:Mo_3$ = 1.2:1) and then nitrilotriacetic acid ($H_3nta:Mo_3Sn$ = 4.8:1) were added to A (25 mL, 0.05 M per Mo, 2 M HCl), where H_3nta had been dissolved in a minimum amount of 10 M KOH. The pH of the solution was adjusted to 1.2 by the addition of 10 M KOH. The solution was filtered and allowed to stand for 1 day, which gave grayish green powder precipitates.[8] The spectrum of D dissolved in 1 M HCl is very similar to that of C.

The X-ray crystal structure analysis[9] of B′ revealed the existence of a heterometal double-cubane-type $Mo_3S_4SnS_4Mo_3$ core in B′. The ORTEP drawing is shown in Figure 1 together with selected atomic distances. The Mo–Mo distance is the shortest of complexes with the cubane-type Mo_3MS_4[1-5,10,11] or incomplete cubane-type Mo_3S_4[12] core reported so far. The Mo–Sn distance is far longer than that described in ref 6 (2.77 Å).

Scheme I. Formation of B and C in 2 M HCl[a]



[a] The assumed formal oxidation states of Mo and Sn are noted under the respective chemical formulas.

The electronic spectra of A, B, and C in HPTS are shown in Figure 2 (supplementary material), where B [λ_{max}, nm (ϵ, M^{-1} cm^{-1} per Mo) 545 (2514), 960 (142)] has a intense peak in the visible region and a medium peak in the near-infrared region, while C [560 (115), 644 sh (109)] has no peak in the near-infrared region. The electronic spectrum of B in 2 M HCl [545 (2424), 1010 (133)] is not so different from that of B in HPTS, whereas the electronic spectrum of C in 1 M HCl [590 (116), 673 (149)] is considerably different from that of C in HPTS. The explanation of this difference is as follows: The aqua molecules attached to the tin atom of C are easily displaced by chloride ions; however, the tin atom of B is sandwiched between two Mo_3S_4 groups and the access of chloride ions to the tin atom is prevented.

The reactions of A with tin metal and tin(II) ion are summarized in Scheme I. The driving force for the formation of both single- (C) and double-cubane-type (B) mixed-metal ions is, we presume, that both tin metal and tin(II) ion can reduce $Mo^{IV}{}_3$ to $Mo^{IV}Mo^{III}{}_2$, the two-electron reduction being effective.

A cyclic voltammogram of B in 2 M HCl shows two quasi-reversible waves (E_{pc} = −485 and −710 mV and E_{pa} = −360 and −590 mV vs Ag/AgCl (3 M NaCl)), whereas that of C in 0.5 M HCl shows a quasi-reversible wave (E_{pc} = −438 and E_{pa} = −344 mV), a glassy-carbon working electrode being used. We tentatively assign the formal oxidation states of B and C in the cyclic voltammetry: (IV, III, III; IV; IV, III, III) ↔ (IV, III, III; II; IV, III, III) ↔ (III, III, III; II; III, III, III) for the core (Mo, Mo, Mo; Sn; Mo, Mo, Mo) of B and (IV, III, III; IV) ↔ (IV, III, III; II) for the core (Mo, Mo, Mo; Sn) of C. No peak was observed in the cyclic voltammogram of A in 2 M HCl in the −0.2 to −1.0 V region, the same working electrode being used.[13]

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Supplementary Material Available: Tables of atomic coordinates and thermal parameters and of atomic distances and angles and figures of cyclic voltammograms and of electronic spectra of B and C in HPTS and HCl (7 pages). Ordering information is given on any current masthead page.

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(7) Anal. Calcd for B′: C, 21.60; H, 4.66. Found: C, 21.64; H, 3.27.

(8) Anal. Calcd for D: N, 3.04; C, 15.66; H, 1.97. Found: N, 3.05; C, 15.75; H, 1.64.

(9) Crystal data: triclinic system, space group $P\bar{1}$, a = 14.499 (4) Å, b = 18.517 (6) Å, c = 13.746 (5) Å, α = 105.16 (3)°, β = 119.92 (2)°, γ = 72.59 (3)°, V = 3023.8 (18) $Å^3$, Z = 1. The structure was solved by direct methods (MULTAN) and refined by least squares to a current R value of 0.0484 for 5135 reflections ($F_o > 8\sigma(F_o)$). Details will be reported elsewhere.

(10) Cu: Wu, X.-T.; Lu, S.-F.; Zu, L.-Y.; Wu, Q.-J.; Lu, J. *Inorg. Chim. Acta* **1987**, *133*, 39–42.

(11) Sb: Lu, S.-F.; Huang, J.-Q.; Lin, Y.-H.; Huang, J. L. *Acta Chim. Sin.* **1987**, *45*, 666–675.

(12) For example: (a) 2.775 [8] Å ($[Mo_3S_4(CN)_9]^{5-}$): Muller, A.; Jostes, R.; Eltzner, W.; Nie, C.-S.; Diemann, E.; Bogge, H.; Zimmermann, M.; Dartmann, M.; Reinsch-Vogell, U.; Che, S.; Cyvin, S. J.; Cyvin, B. N. *Inorg. Chem.* **1985**, *24*, 2872–2884. (b) 2.754 [11] Å ($[Mo_3S_4(ida)_3]^{2-}$): Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357–361. (c) 2.766 (4) Å ($[Mo_3S_4(dmpe)_3]^-$): Cotton, F. A.; Llusar, R. *Polyhedron* **1987**, *6*, 1741–1745. (d) 2.766 [24] Å ($[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$: Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *Chem. Lett.* **1987**, 2025–2028.

(13) If a hanging-mercury-drop electrode is used as a working electrode, reduction and oxidation peaks are obtained.[12b]