Inorg. Chem. **2001,** *40,* 2582−2586

Robust, Alkali-Stable, Triscarbonyl Metal Derivatives of Hexametalate Anions, $[M_6O_{19}\{M'(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; M′ = Mn, Re; *n* = 1, 2)

Alexei V. Besserguenev, Michael H. Dickman, and Michael T. Pope*

Department of Chemistry, Box 571227, Georgetown University, Washington, D.C. 20057-1227

Received September 13, 2000

Ten 1:1 and 2:1 complexes of $[Mn(CO)_3]^+$ and $[Re(CO)_3]^+$ with $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ have been isolated as potassium salts in good yields and characterized by elemental analysis, ^{17}O NMR and infrared spectroscopy, and single-crystal X-ray structure determinations. Crystal data for **1** (*t*-Re_2Ta_6): empirical formula, $K_4Na_2Re_2C_6Ta_6O_{35}H_{20}$, monoclinic, space group, *C*2/*m*, $a = 17.648(3)$ Å, $b = 10.056(1)$ Å, $c = 13.171(2)$ Å, $\beta = 112.531(2)$°, $Z = 2$. **2** (*t*-Re_2Nb_6): empirical formula, $K_6Re_2C_6Nb_6O_{38}H_{26}$, monoclinic, space group, *C*2/*m*, $a = 17.724(1)$ Å, $b = 10.0664(6)$ Å, $c = 13.1965(7)$ Å, $\beta = 112.067(1)$°, $Z = 2$. **3** (*t*-Mn_2Nb_6): empirical formula, $K_6Mn_2C_6Nb_6O_{37}H_{24}$, monoclinic, space group, *C*2/*m*, $a = 17.812(2)$ Å, $b = 10.098(1)$ Å, $c = 13.109(2)$ Å, $\beta = 112.733(2)$°, $Z = 2$. **4** (*c*-Mn_2Nb_6): empirical formula, $K_6Mn_2C_6Nb_6O_{50}H_{50}$, triclinic, space group, $P\bar{1}$, $a = 10.2617(6)$ Å, $b = 13.4198(8)$ Å, $c = 21.411(1)$ Å, $\alpha = 72.738(1)$°, $\beta = 112.067(1)$°, $\gamma = 83.501(1)$°, $Z = 2$. **5** (*c*-Re_2Nb_6): empirical formula, $K_6Re_2C_6Nb_6O_{54}H_{58}$, monoclinic, space group, $P2_1/c$, $a = 21.687(2)$ Å, $b = 10.3085(9)$ Å, $c = 26.780(2)$ Å, $\beta = 108.787(1)$°, $Z = 4$. The complexes contain $M(CO)_3$ groups attached to the surface bridging oxygen atoms of the hexametalate anions to yield structures of nominal C_{3v} (1:1), D_{3d} (trans 2:1), and C_{2v} (cis 2:1) symmetry. The syntheses are carried out in aqueous solution or by aqueous hydrothermal methods, and the complexes have remarkably high thermal, redox, and hydrolytic stabilities**.** The Re-containing compounds are stable to 400−450 °C, at which point CO loss occurs. The Mn compounds lose CO at temperatures above 200 °C. Cyclic voltammetry of all complexes in 0.1 M sodium acetate show no redox behavior, except an irreversible oxidation process at ~1.0 V vs Ag/AgCl. In contrast to the parent hexametalate anions that are stable only in alkaline (pH >10) solution, the new complexes are stable, at least kinetically, between pH 4 and pH ~12.

Introduction

Polyoxometalates constitute a large class of inorganic complexes of great versatility and variety that are receiving much current attention.[1] We have recently been investigating polyoxotungstate complexes with lanthanides and actinides in connection with possible applications in the sequestration and immobilization of these species in nuclear wastes. Although polytungstates are thermally stable and radiation-resistant, their instability in highly alkaline solutions renders them inappropriate for certain waste streams, e.g., alkaline tank wastes at Hanford, WA.[2] In contrast, polyoxoanions of niobium and tantalum are stable only in basic media (pH >10). We report here the high-yield synthesis and characterization of very stable derivatives of these anions with $Mn(CO)_3^+$ and $Re(CO)_3^+$. The new complexes can be regarded as surrogates for corresponding technetium species, which will be reported elsewhere, and can provide routes to a solution of the problems associated with immobilization of ^{99}Tc ($t_{1/2}$ ~2 × 10^5 yr)[3].

With the exception of polyoxoanions incorporating Nb or Ta atoms in place of one or more W atoms,[4] there are very few reported examples of heteropolyniobates[5] and no reported examples of heteropolytantalates. Flynn determined the structure of $[Mn(Nb_6O_{19})_2]^{12-}$ and the Ni(IV) analog[6] and described complexes believed to be $[Co(en)(H_2O)(Nb_6O_{19})]^{5-}$ and $[Cr(en)(H_2O)(Nb_6O_{19})]$.[5−7] A large composite polyoxoanion containing hexaniobate subunits, $[\{Eu_3O(OH)_3(OH_2)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$, has been reported by Yamase.[8]

Experimental Section

Syntheses. Potassium hexaniobate, $K_7HNb_6O_{19}\cdot 13H_2O$ (Nb_6) and potassium hexatantalate, $K_8Ta_6O_{19}\cdot 17H_2O$ (Ta_6) were prepared by literature methods[9] and characterized by infrared spectroscopy and ^{17}O NMR spectroscopy. Nb_6 IR (cm^{-1}): 856 (vs), 777 (s), 669 (s), 528 (s), 418 (vs). ^{17}O NMR (ppm): 26 (O(M_6), A); 395 (O(M_2), B); 600

---

* To whom correspondence should be addressed. Phone: (202)687-6253. Fax: (202)687-6209. E-mail: popem@georgetown.edu.

(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: New York, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) *Polyoxometalates. From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994. (d) *Chem. Rev.* **1998**, *98*, 1−387.

(2) Bunker, B.; Virden, J.; Kuhn, B.; Quinn, R. Nuclear Materials, Radioactive Tank Wastes. *Encyclopedia of Energy Technology and Environment*; Wiley: New York, 1995; p 2023.

(3) Yoshihara, K. Technetium in the Environment. In *Topics in Current Chemistry*; Dunitz, J. D., Hafner, K., Ito, S., Lehn, J.-M., Raymond, K. N., Rees, C. W., Thiem, J., Vögtle, F., Eds.; Springer-Verlag: New York, 1996; Vol. 176, p 17. (b) Boyd, G. E. *J. Chem. Educ.* **1959**, *36*, 3. (c) Schwochau, K. *Angew. Chem.* **1964**, *76*, 9.

(4) Dabbabi, M.; Boyer, M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1011−1014. (b) Klemperer, W. G.; Schwartz, C. *Inorg. Chem.* **1985**, *24*, 4459. (c) Hurrup, M. K.; Kim, G. S.; Zeng, H.; Johnson, R. P.; Vanderveer, D.; Hill, C. L. *Inorg. Chem.* **1998**, *37*, 5550. (d) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692. (e) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (f) Pohl, M.; Lyon, D. K.; Mizuno, N.; Nomiya, K.; Finke, R. G. *Inorg. Chem.* **1995**, *34*, 1413.

(5) Flynn, C. M., Jr. Ph.D. Thesis, University of Illinois, 1967.

(6) Flynn, C. M., Jr.; Stucky, G. A. *Inorg. Chem.* **1969**, *8*, 332, 335. (b) Dale, B. W.; Pope, M. T. *Chem. Commun.* **1967**, 792. (c) Dale, B. W.; Buckley, J. M.; Pope, M. T. *J. Chem. Soc. A* **1969**, 301.

(7) Flynn, C. M., Jr.; Stucky, G. A. *Inorg. Chem.* **1969**, *8*, 178.

(8) Yamase, T.; Naruke, H.; Sasaki, Y. *Inorg. Chem.* **1994**, *33*, 409.

(9) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93.

10.1021/ic001031y CCC: $20.00

(O(M), C). Ta_6 IR (cm^{-1}): 854 (s), 837 (s), 700 (s), 536 (s). ^{17}O NMR (ppm): −34 (O(M_6), A); 331 (O(M_2), B); 483 (O(M), C). Sodium salt of Nb_6 was obtained from a solution of the potassium salt by precipitation with 5 M NaCl. Dirhenium decacarbonyl, $Re_2(CO)_{10}$, and pentacarbonylbromomanganese, $Mn(CO)_5Br$, were purchased from Aldrich and used without further purification. Pentacarbonylbromorhenium, $Re(CO)_5Br$, triscarbonyltrisacetonitrilerhenium perchlorate, $[Re(CO)_3(CH_3CN)_3]ClO_4$, and triscarbonyltrisacetonitrilemanganese perchlorate, $[Mn(CO)_3(CH_3CN)_3]ClO_4$, were prepared by literature methods[10] and characterized by infrared spectroscopy and ^{17}O NMR spectroscopy. $Re(CO)_5Br$ IR (cm^{-1}): 2151 (m), 2059 (vs), 2035 (vs), 1974 (vs), 1964 (vs), 1122 (m), 1109 (w), 1004 (vw), 939 (vw), 912 (vw), 588 (vs), 553 (m). ^{17}O NMR (CD_3CN) (ppm): 357(sh), 356, 338 (C*O*). $[Re(CO)_3(CH_3CN)_3]ClO_4$ IR (cm^{-1}): 2364 (w), 2327 (w), 2298 (w), 2045 (vs), 1934 (vs), 1419 (w), 1369 (w), 1143 (sh), 1091 (vs), 1035 (w), 910 (w), 648 (sh), 625 (s), 588 (m), 540 (w), 482 (w). ^{17}O NMR (CD_3CN) (ppm): 342 (C*O*). $[Mn(CO)_3(CH_3CN)_3]ClO_4$ IR (cm^{-1}): 2364 (w), 2327 (w), 2300 (w), 2057 (vs), 1959 (vs), 1423 (w), 1373 (w), 1093 (vs), 1037 (m), 681 (m), 625 (s), 528 (m), 457 (m). ^{17}O NMR (CD_3CN) (ppm): 389 (C*O*).

$K_7[Re(CO)_3Nb_6O_{19}]$ ($ReNb_6$). Deionized water was used throughout all syntheses. One millimole (0.4067 g) of $Re(CO)_5Br$ was added to a solution of 1.37 g (1 mmol) of Nb_6 in 2 mL of water contained in a Teflon-lined Parr acid digestion bomb, the bomb was sealed, and the mixture was heated to 130 °C for 17 h. After being cooled, the resulting mixture, about 10 mg of insoluble unreacted $Re(CO)_5Br$, was filtered off and addition of 15 mL of ethanol to the filtrate ($V_{\text{adjusted}} = 5$ mL) yielded 1.19 g (71%) of crude product. The impurity, about 10% of *trans*-$K_6[\{Re(CO)_3\}_2Nb_6O_{19}]$ (*t*-Re_2Nb_6) was removed by dissolving the solid in 2.5 mL of water and adding 3 mL 5 M NaCl to precipitate pure $ReNb_6$. Anal. Calcd for $Na_7[Re(CO)_3Nb_6O_{19}]\cdot 9H_2O$: Na, 12.1 (11.06); Re, 12.7 (12.8); Nb, 37.3 (38.3); C, 2.52 (2.47).

$K_7[Re(CO)_3Ta_6O_{19}]$ ($ReTa_6$). One-half millimole (0.1809 g) of $[Re(CO)_3(CH_3CN)_3]ClO_4$ was dissolved into a solution of 1.0038 g (0.5 mmol) of Ta_6 in 10 mL of water, which had previously been deaerated with a stream of N_2 for 20 min. The reaction mixture, in a 100-mL single-necked flask fitted with a reflux condenser, was heated to 60 °C under a positive pressure of N_2 for 2.5 h. After being cooled, 60 mg of white insoluble material was filtered off, and addition of 15 mL of ethanol to the filtrate ($V_{\text{adjusted}} = 15$ mL) yielded 0.70 g (64%) of product. Anal. Calcd for $K_7[Re(CO)_3Ta_6O_{19}]\cdot 9H_2O$: K, 12.7 (13.1); Re, 9.10 (8.90); Ta, 50.2 (51.8); C, 2.10 (1.72).

$K_7[Mn(CO)_3Ta_6O_{19}]$ ($MnTa_6$). The procedure for $ReTa_6$ was repeated using $[Mn(CO)_3(CH_3CN)_3]ClO_4$. After being heated, 20 mg of insoluble material was filtered off, and the yellow product (0.57 g, 55%) was recovered from the filtrate ($V_{\text{adjusted}} = 15$ mL) by precipitation with 15 mL of ethanol. Anal. Calcd for $K_7[Mn(CO)_3Ta_6O_{19}]\cdot 15H_2O$: K, 13.22 (13.21); Mn, 2.67 (2.65); C, 1.76 (1.74); Ta, 52.30 (52.39).

$K_7[Mn(CO)_3Nb_6O_{19}]$ ($MnNb_6$). The procedure for $ReTa_6$ was repeated using $[Mn(CO)_3(CH_3CN)_3]ClO_4$ and $Na_7HNb_6O_{19}\cdot 15H_2O$. After the reaction mixture ($V = 40$ mL) was heated at 90 °C for 3 h, a small amount of insoluble material was filtered off, and the volume of the filtrate was reduced to 15 mL on a rotary evaporator. The yellow product (1.00 g, 70%) was obtained by precipitation with 15 mL of ethanol. Anal. Calcd for $K_7[Mn(CO)_3Nb_6O_{19}]\cdot 12H_2O$: K, 17.51 (17.79); Mn, 3.25 (3.57); C, 2.30 (2.34); Nb, 37.24 (36.24).

***trans*/*cis*-$K_6[\{Mn(CO)_3\}_2Nb_6O_{19}]$ (*t*/*c*-Mn_2Nb_6).** The procedure for $ReTa_6$ was repeated using 2 mmol (0.72 g) of $[Mn(CO)_3(CH_3CN)_3]ClO_4$ and 1 mmol (1.37 g) of $K_7HNb_6O_{19}\cdot 13H_2O$. After the reaction mixture ($V = 40$ mL) was stirred at room temperature for 4.5 h, a small amount of insoluble material was filtered off. The volume of the filtrate was reduced to 20 mL using a rotary evaporator, and 20 mL of ethanol was added to the filtrate to produce a yellow precipitate (0.48 g, 29%; 75% *t*-Mn_2Nb_6, 25% *c*-Mn_2Nb_6). The resulting filtrate, still yellow, was evaporated to 5 mL, and pale yellow material ($KClO_4$) was filtered off. *c*-Mn_2Nb_6 (0.43 g, 25%) was precipitated with 7 mL of ethanol.

The relative amounts of trans vs cis isomers are influenced by synthesis temperature. When the previously described procedure was repeated by refluxing the reaction mixture at 80 °C for 3 h, first precipitation with ethanol afforded 0.89 g of yellow product (51%; 25% *t*-Mn_2Nb_6, 75% *c*-Mn_2Nb_6).

Crystals suitable for X-ray study were grown, for example, by dissolving 480 mg of *t*-Mn_2Nb_6 in 2.5 mL of water and adding ethanol by vapor diffusion in the refrigerator. Two types of crystals appeared after 2−3 weeks of storage at 7 °C. Small yellow crystals of *t*-Mn_2Nb_6 (0.17 g) formed. In addition, 0.06 g of large, yellow, needle-type crystals of *c*-Mn_2Nb_6 was recovered. Anal. Calcd for $K_6[\{Mn(CO)_3\}_2Nb_6O_{19}]\cdot 8H_2O$: K, 15.60 (15.46); Mn, 7.20 (7.24); C, 5.10 (4.74); Nb, 36.2 (36.7). A total of 430 mg of *c*-Mn_2Nb_6 was dissolved in 2.5 mL of water. Large, needle-type, yellow crystals of *c*-Mn_2Nb_6 (0.16 g) formed after 2−3 weeks of storage in a refrigerator at 7 °C. Anal. Calcd for $K_6[\{Mn(CO)_3\}_2Nb_6O_{19}]\cdot 23H_2O$: K, 13.30 (13.12); Mn, 6.25 (6.15); C, 4.15 (4.03); Nb, 29.9 (31.2).

***cis*-$K_6[\{Mn(CO)_3\}_2Ta_6O_{19}]$ (*c*-Mn_2Ta_6).** The procedure for $ReTa_6$ was repeated using 0.56 mmol (0.2006 g) of $[Mn(CO)_3(CH_3CN)_3]ClO_4$ and 0.56 mmol (1.15 g) of $MnTa_6$. Several drops of 3 M KOH were added to adjust the pH of water to 11 before $MnTa_6$ was dissolved. After the reaction mixture ($V = 10$ mL) was refluxed at 100 °C for 2 h, about 60 mg of insoluble material was filtered off, and the yellow product (0.60 g, 49%) was recovered from the filtrate ($V_{\text{adjusted}} = 10$ mL) by precipitation with 15 mL of ethanol. Anal. Calcd for $K_6[\{Mn(CO)_3\}_2Ta_6O_{19}]\cdot 16H_2O$: K, 10.52 (10.71); Mn, 5.21 (5.02); C, 3.22 (3.29); Ta, 48.4 (49.6).

***trans*/*cis*-$K_6[\{Re(CO)_3\}_2Nb_6O_{19}]$ (*t*/*c*-Re_2Nb_6).** The procedure for $ReNb_6$ was repeated using 1 mmol (1.37 g) of Nb_6 and 2 mmol (0.82 g) of $Re(CO)_5Br$. After the resulting mixture was cooled, 0.84 g (44%) of a white precipitate (mostly *t*-Re_2Nb_6 with impurity of unreacted $Re(CO)_5Br$) was recovered. *t*-Re_2Nb_6 was purified by dissolving in 2 mL of water, filtering off 10 mg of unreacted $Re(CO)_5Br$, and precipitating *t*-Re_2Nb_6 with ethanol. To the filtrate left from hydrothermal synthesis, 5 mL of ethanol was added, producing 0.49 g (25%) of white precipitate (∼75% *c*-Re_2Nb_6, ∼25% *t*-Re_2Nb_6).

Crystals suitable for X-ray study were obtained similarly to the manganese compounds. A total of 810 mg of *t*-Re_2Nb_6 was dissolved in 5 mL of water. A total of 720 mg of colorless block crystals of *t*-Re_2Nb_6 was recovered after storage in a refrigerator for 8 weeks at 7 °C. Anal. Calcd for $K_6[\{Re(CO)_3\}_2Nb_6O_{19}]\cdot 15H_2O$: K, 12.42 (12.31); Re, 19.55 (19.53); C, 3.81 (3.78); Nb, 29.23 (29.24). A total of 620 mg of *c*-Re_2Nb_6 was dissolved in 3 mL of water. A total of 340 mg of large, colorless needle crystals of *c*-Re_2Nb_6 was recovered after being refrigerated for 6−8 weeks at 7 °C. Anal. Calcd for $K_6[\{Re(CO)_3\}_2Nb_6O_{19}]\cdot 19H_2O$: K, 11.83 (11.86); Re, 18.72 (18.82); C, 3.62 (3.64); Nb, 28.11 (28.18).

Alternative Procedure for *trans*-$K_6[\{Re(CO)_3\}_2Nb_6O_{19}]$ (*t*-Re_2Nb_6). The procedure for $ReTa_6$ was repeated using 1 mmol (1.37 g) of Nb_6 and 2 mmol (0.99 g) of $[Re(CO)_3(CH_3CN)_3]ClO_4$. After the reaction mixture ($V = 40$ mL) was heated at 60 °C for 1.5 h, a small amount of insoluble material was filtered off. The volume of the filtrate was reduced to 20 mL using a rotary evaporator, and 0.95 g (50%) of white *t*-Re_2Nb_6 was recovered after precipitation with 20 mL of ethanol.

***trans*-$K_4Na_2[\{Re(CO)_3\}_2Ta_6O_{19}]$ (*t*-Re_2Ta_6).** The procedure for *c*-Mn_2Ta_6 was repeated using 0.32 mmol (0.71 g) of potassium salt of $ReTa_6$ and 0.32 mmol (0.1591 g) of $[Re(CO)_3(CH_3CN)_3]ClO_4$. Several drops of 3 M NaOH were added to adjust the pH of water to >10 before dissolving $ReTa_6$. After the reaction mixture ($V = 12$ mL) was refluxed at 100 °C for 1 h, 0.53 g (68%) of white *t*-Re_2Ta_6 was recovered by precipitation with 12 mL of ethanol. Single crystals were grown using the same procedure as for *t*-Mn_2Nb_6 and *t*-Re_2Nb_6. Anal. Calcd for $K_4Na_2[\{Re(CO)_3\}_2Ta_6O_{19}]\cdot 11H_2O$: K, 7.31 (6.71); Na, 1.98 (1.97); Re, 15.7 (16.0); C, 3.23 (3.09); Ta, 45.32 (46.58).

^{17}O Enrichment. The procedure for synthesis of $ReNb_6$ and *t*/*c*-Re_2Nb_6 was followed using (instead of deionized water) a mixture of 1.5 mL of 99% D_2O and 1.0 g of 10% enriched water for $ReNb_6$ enrichment and a mixture of 2.5 mL of 99% D_2O and 0.53 g of 10% enriched water for *t*/*c*-Re_2Nb_6 enrichment.

Instrumental. An approximate sphere of data was collected on a Siemens SMART 1K CCD system. Crystal stability was monitored by

---

(10) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1985**, *23*, 44. (b) Edwards, D. A.; Marshalsea, J. *J. Organomet. Chem.* **1977**, *131*, 73.

Table 1. Oxygen-17 NMR Chemical Shifts

compound	terminal	bridging	central	carbonyl
Nb_6	600	395	26	
Ta_6	483	331	−34	
$MnNb_6$	615, 633	128, 410, 428	35	378
$ReNb_6$	629, 645	156, 408, 435	40	333
$MnTa_6$	497, 516	91, 346, 357	−21	380
$ReTa_6$	502, 521	121, 349, 361	−17	334
c-Mn_2Nb_6	?[a], 659, 697	145, ?, 447, 454	47	382, 383
c-Re_2Nb_6	659, 675, 719	178, 190, 457, 465	54	334, 336
c-Mn_2Ta_6	?, 541, ?	103, ?, 367, 371	?	384, 386
t-Mn_2Nb_6	663	143, 447	46	382
t-Re_2Nb_6	679	169, 458	53	335
t-Re_2Ta_6	553	133, 379	?	336

[a] A question mark (?) indicates that the signal was not reliably observed.

recollection of the first 50 frames after data collection was finished. No significant decay was observed. Crystallographic data are in Table 2. The structures were solved by direct methods using SHELXTL.[11] Hydrogen atoms were not included in the models.

^{17}O NMR spectra were collected on a Bruker AM 300 spectrometer. The offset frequency was 40.687 MHz, the bandwidth was 50 kHz, and the repetition rate was 10 Hz. All spectra were collected in deuterated water, except for the spectra of $Re(CO)_5Br$, $Re(CO)_3(CH_3CN)_3ClO_4$, and $Mn(CO)_3(CH_3CN)_3ClO_4$, which were collected in deuterated acetonitrile. Collection time for unenriched samples was about 20 h.

IR spectra were obtained on a Nicolet 7000 spectrometer with a resolution of 2 cm^{-1}. All samples were prepared as KBr pellets. TGA curves were obtained from room temperature to 950 °C under nitrogen atmosphere on a TGA 2050 analyzer made by TA Instruments. Alumina pans were used for all measurements. DSC curves were obtained from room temperature to 725 °C under nitrogen atmosphere on a DSC 2910 calorimeter made by TA Instruments. Platinum pans were used for all measurements.

Cyclic voltammetry curves were obtained for all compounds in aqueous solution. A total of 0.1 g of the corresponding compound was dissolved in 10 mL of deaerated water, forming ~0.02 M solution. A total of 0.1 M $Na(CH_3COO)$ was used as a supporting electrolyte. Platinum wire was used as a counting electrode, glassy carbon was used as a working electrode, and Ag/AgCl saturated electrode was used as a reference electrode. Chemical analyses were performed by Kanti Technologies, Inc., 43 Old Falls Blvd., N. Tonawanda, NY 14120.

Results and Discussion

The first examples of organometallic groups attached to hexametalate oxoanions were reported by Klemperer several years ago,[12] and all organometallic derivatives of polyoxometalates have been reviewed recently.[13] Of direct relevance to the present work are the anions $[Nb_2W_4O_{19}\{M(CO)_3\}]^{3-}$ (M = Mn, Re)[12] and $[P_2Nb_3W_{15}O_{62}\{Re(CO)_3\}]$,[8−14] isolated as tetra-*n*-butylammonium salts from acetonitrile solution. The greater surface-charge densities of $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$ as compared to $[Nb_2W_4O_{19}]^{4-}$ and $[P_2Nb_3W_{15}O_{62}]^{9-}$ result in an enhanced reactivity of the former anions toward the binding of the organometallic moieties.

The new niobate and tantalate derivatives reported here are easily prepared in good yield in aqueous solution, starting with $[M(CO)_3(CH_3CN)_3]^+$ or under hydrothermal conditions starting with $[M(CO)_5Br]$. The compositions and structures of the new complexes are established by elemental analysis, by infrared and ^{17}O NMR spectroscopy, and by single-crystal X-ray diffraction of five salts.

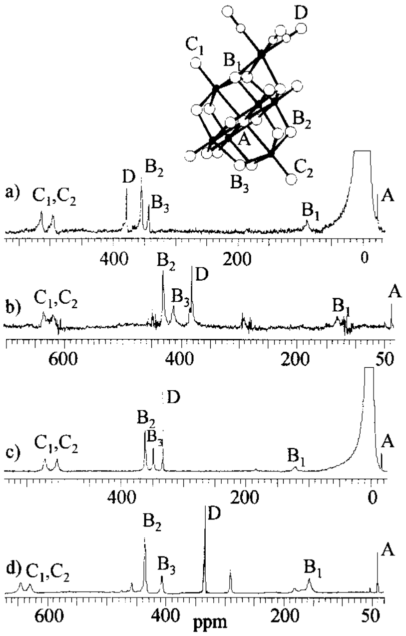

Figure 1. Oxygen-17 NMR spectra of (a) $MnTa_6$, (b) $MnNb_6$, (c) $ReTa_6$, and (d) $ReNb_6$.

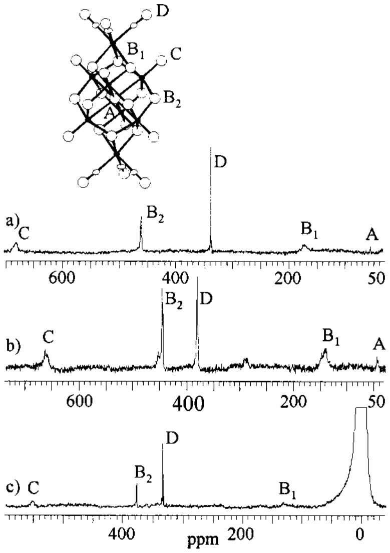

Figure 2. Oxygen-17 NMR spectra of trans isomers of (a) Re_2Nb_6, (b) Mn_2Nb_6, and (c) Re_2Ta_6.

^{17}O NMR spectroscopy proved to be the simplest way to confirm the structures of the product anions (see Figures 1−3 and Table 1. The salts were soluble enough to allow accumulation of spectra of unenriched samples within 20 h. All symmetry-distinct oxygen atoms could be detected, and assignments are shown in the figures. All assignments were made on the basis of peak intensities and proximity of peaks to corresponding peaks of Nb_6 and Ta_6.[9] Some spectra revealed the presence of ClO_4^- (δ ~290 ppm) as an impurity, and spectra of enriched samples of $ReNb_6$ showed signals from traces of *c*- and *t*-Re_2Nb_6. The formation of 2:1 complexes and the existence of both cis and trans isomers were first deduced from the NMR spectra.

X-ray analysis of single crystals of potassium salts of trans isomers of Re_2Nb_6, Mn_2Nb_6, and Re_2Ta_6 and of cis isomers of Mn_2Nb_6 and Re_2Nb_6 are summarized in Tables 2 and 3. The

---

(11) Sheldrick, G. M. *SHELXTL*; Bruker AXS Inc.: Madison, WI, 1997.

(12) Besecker, C. J.; Klemperer W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Inorg. Chem.* **1985**, *24*, 44.

(13) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77.

(14) Nagata, T.; Pohl, M.; Weiner, H.; Finke, R. G. *Inorg. Chem.* **1997**, *36*, 1366.

Table 2. Crystal Data

	t-Re_2Ta_6, **1**	*t*-Re_2Nb_6, **2**	*t*-Mn_2Nb_6, **3**	*c*-Mn_2Nb_6, **4**	*c*-Re_2Nb_6, **5**
emp. form.	$K_4Na_2Re_2C_6Ta_6O_{35}H_{20}$	$K_6Re_2C_6Nb_6O_{38}H_{26}$	$K_6Mn_2C_6Nb_6O_{37}H_{24}$	$K_6Mn_2C_6Nb_6O_{50}H_{50}$	$K_6Re_2C_6Nb_6O_{54}H_{58}$
fw	2312.70	1870.76	1590.19	1824.40	2158.98
space group	*C*2/*m* (No. 12)	*C*2/*m* (No. 12)	*C*2/*m* (No. 12)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell, Å, deg	$a = 17.648(3)$ $b = 10.0561(14)$ $c = 13.1714(19)$ $\beta = 112.531(2)$	$a = 17.724(1)$ $b = 10.0664(6)$ $c = 13.1965(7)$ $\beta = 112.067(1)$	$a = 17.812(2)$ $b = 10.098(1)$ $c = 13.109(2)$ $\beta = 112.733(2)$	$a = 10.2617(6)$ $b = 13.4198(8)$ $c = 21.411(1)$ $\alpha = 72.738(1)$ $\beta = 85.591(1)$ $\gamma = 83.501(1)$	$a = 21.867(2)$ $b = 10.3085(9)$ $c = 26.780(2)$ $\beta = 108.787(1)$
vol, Å^3	2159.1(5)	2182.0(2)	2174.7(5)	2794.7(3)	5714.8(9)
Z	2	2	2	2	4
T, °C	−102	−102	−102	−102	−102
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
calcd density, g/cm^3	3.557	2.853	2.428	2.168	2.509
μ	21.217	7.718	2.760	2.179	5.931
R^a	0.0588	0.0307	0.0484	0.0583	0.0574
$wR_2{}^b$	0.1764	0.0826	0.1338	0.1927	0.1676

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ includes $I > 2.00\ \sigma(I)$. [b] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)]^2/\sum[w(F_o)^2]^2\}^{0.5}$, includes all I.

Table 3. Selected Average Bond Lengths (Å) and Angles (deg)[a]

	t-Re_2Nb_6	*t*-Mn_2Nb_6	*t*-Re_2Ta_6	*c*-Re_2Nb_6	*c*-Mn_2Nb_6
M−O(terminal)	1.765(5)	1.776(5)	1.79(2)	1.765(6)	1.771(5)
M−O(M)	1.964(4)	1.971(4)	1.96(1)	1.920(6)−2.010(6)	1.931(1)−2.004(4)
M−O(M, M′)	2.048(4)	2.044(4)	2.06(1)	2.017(6)−2.092(6)	2.003(4)−2.066(4)
M−O(M_5)	2.3972(6)	2.3967(6)	2.397(1)	2.397(6)	2.386(4)
M′−C	1.894(7)	1.804(8)	1.88(3)	1.904(9)	1.793(8)
M′−O(M_2)	2.176(5)	2.085(5)	2.17(2)	2.178(6)	2.070(5)
CM′C	88.6(4)	88.8(4)	90(1)	89.4(4)	88.9(3)
OM′O	74.8(2)	79.2(2)	75.6(7)	74.9(2)	79.0(2)

[a] M = Nb, Ta; M′ = Mn, Re.

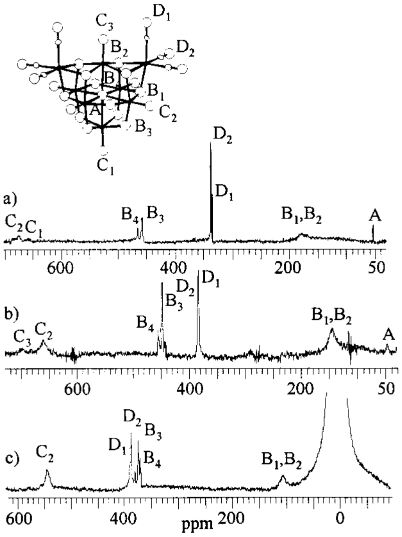

Figure 3. Oxygen-17 NMR spectra of cis isomers of (a) Re_2Nb_6, (b) Mn_2Nb_6, and (c) Mn_2Ta_6.

structures of trans and cis isomers are shown in polyhedral and thermal-ellipsoid representations in Figures 4 and 5. The metrical data listed in Table 3 are for the most part unexceptional. Attachment of $[M(CO)_3]^+$ to the anions results in a closing up of the three surface oxygen atoms involved. The nonbonded O⋯O contacts are ~0.2 Å shorter than those in corresponding O_3 sets that are not bonded to M (2.777−2.851 Å). This presumably reflects the reduction in charge density on the bonded oxygen atoms. At the same time, the O−M−O angles are reduced from an idealized 90 to 75−80°, a distortion dictated by the lengths of the M−O bonds.

The cis isomers of the 2:1 complexes have two open O_3 sets that could be used for attachment of additional $M(CO)_3$ groups.

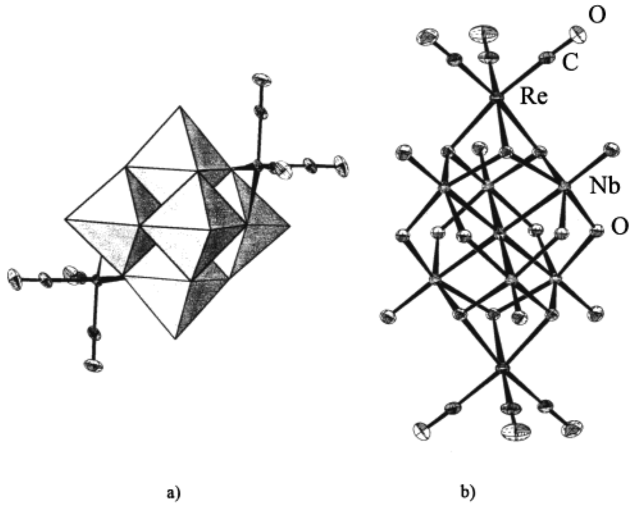

Figure 4. Structure of *trans*-$[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$ in (a) polyhedral and (b) thermal-ellipsoid (50%) representations.

All four such positions are occupied in the neutral species $[\{(C_5Me_5)Rh\}_4V_6O_{19}]$.[15] Attempts to introduce more than two $M(CO)_3$ groups to the niobate and tantalate systems have so far been unsuccessful.

Representative infrared spectra are shown in Figure 6, and these provide the quickest way to identify the three structural types. Vibrational frequencies for all the new complexes are listed in the Supporting Information. The simple metal−oxygen stretching pattern (400−900 cm^{-1}) of the original hexametalate anions[16] is split into more components by the lower symmetry of the $M(CO)_3$ derivatives, and a new weak band at ~460 cm^{-1}

---

(15) Chae, H. K.; Klemperer, W. G.; Day, V. W. *Inorg. Chem.* **1989**, *28*, 1423.

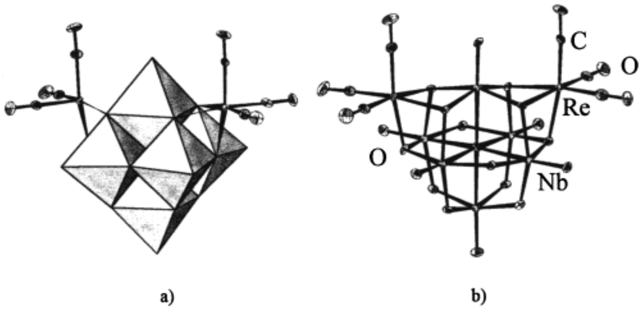

Figure 5. Structure of *cis*-$[Nb_6O_{19}\{Re(CO)_3\}_2]^{6-}$ in (a) polyhedral and (b) thermal-ellipsoid (50%) representations.

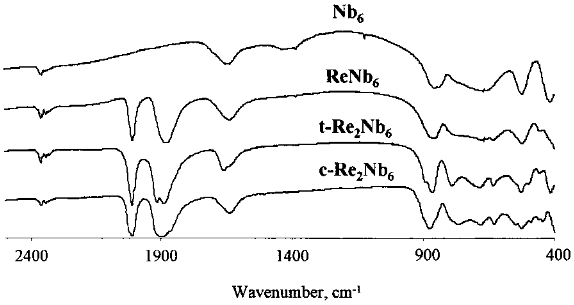

Figure 6. Infrared spectra of Nb_6, $ReNb_6$, *t*-Re_2Nb_6, and *c*-Re_2Nb_6.

is assigned to the Mn(Re)−C vibrations.[10b] In addition, two sets of CO stretching bands are seen at ca. 1900 and 2000 cm^{-1}. Similar bands are observed for a number of *fac*-$[M(CO)_3L_3]^+$ (M = Mn, Re) complexes.[17]

Unlike the underivatized hexametalates, which are stable only in strongly basic media[18] (precipitation of the oxides begins below pH ∼10), solutions of the Mn and Re derivatives show no sign of precipitation when the pH is lowered to 4. Cyclic voltammograms of all the compounds in 0.1 M sodium acetate show no redox features except an irreversible oxidation process at +1.5 V (Re) and +0.9 V (Mn). Similar features are observed in voltammograms of the corresponding $[M(CO)_3(CH_3CN)_3]^+$ cations.

Representative TGA curves for *t*-Mn_2Nb_6 and *t*-Re_2Nb_6 are shown in Figure 7. The other complexes behave similarly. The initial weight loss corresponds to the loss of water of crystallization. A second endothermic process starts at 400−450 °C for the Re compounds and at ∼200 °C for the Mn compounds and corresponds to the loss of the CO ligands. A third weight loss (Re compounds only) above 700 °C is assumed to be associated with the loss of Re_2O_7 formed by oxidation or disproportionation.

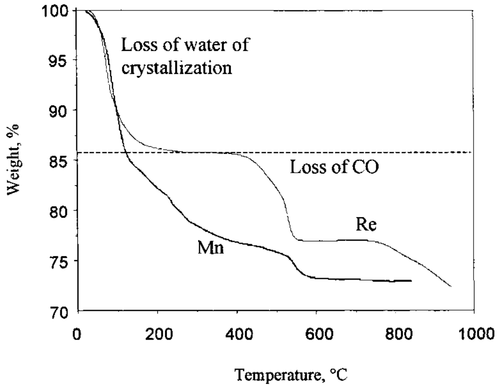

Figure 7. TGA curves of *t*-Mn_2Ta_6 (Mn) and *t*-Re_2Nb_6 (Re). Robust, alkali-stable, triscarbonyl metal derivatives of hexametalate anions, $[M_6O_{19}\{M'(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; M′ = Mn, Re; *n* = 1, 2).

Conclusion

The title complexes demonstrate the reactivity of the hexaniobate and hexatantalate anions toward binding of triscarbonyl metal groups and imply that other organometallic species can be attached in a similar fashion, pointing the way to soluble alkali-stable supported catalysts. Although both Nb and Ta anions could be derivatized, the tantalate required more forcing conditions, e.g., 100 °C for *t*-Mn_2Ta_6 vs room temperature for the corresponding niobate. The syntheses are straightforward and efficient, and the products are robust species, stable in aqueous solution over a broad pH range, including highly alkaline conditions. The Re compounds are thermally stable to ∼400 °C in the solid state and can be formed under hydrothermal conditions at 130 °C and pH ∼12. Such properties suggest that analogous complexes with $Tc(CO)_3^+$ could be employed for the sequestration and storage of ^{99}Tc wastes.

Acknowledgment. We thank the DOE for support of this work through the Office of Energy Research and Environmental Management Science Program, Grant DE-FG07-96ER14695.

Supporting Information Available: Table of infrared frequencies and X-ray crystallographic files, in CIF format, for the structure determinations of **1** (*t*-Re_2Ta_6), **2** (*t*-Re_2Nb_6), **3** (*t*-Mn_2Nb_6), **4** (*c*-Mn_2Nb_6), and **5** (*c*-Re_2Nb_6). This material is available free of charge via the Internet at http://pubs.acs.org.

IC001031Y

---

(16) Farrell, F. J.; Maron, V. A.; Spiro, T. G. *Inorg. Chem.* **1969**, *8*, 2638. (b) Rocchiccioli- Deltcheff, C.; Thouvenot, R.; Dabbabi, M. *Spectrochim. Acta* **1977**, *33A*, 143. (c) Mattes, R.; Bierbüsse, H.; Fuchs, J. *Z. Anorg. Allg. Chem.* **1971**, *385*, 230.

(17) Kirkham, W. J.; Osborne, A. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc.* **1965**, 551. (b) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501. (c) Kraihansel C. S.; Maples P. K. *J. Organomet. Chem.* **1976**, *117*, 159.

(18) Etxebarria, N.; Fernandez, L. A.; Madariaga, J. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3055.