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Icosaniobate: A New Member of the Isoniobate Family

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Icosaniobate $[Nb_{20}O_{54}]^{8-}$ was synthesized by reacting $[H_4Nb_6O_{19}]^{4-}$ with NO in tetrahydrofuran or $MeNO_2$. A single-crystal X-ray diffraction study of its *n*-tetrabutylammonium salt [$a = 17.7284(18)$ Å, $b = 33.542(3)$ Å, $c = 34.316(2)$ Å, $Z = 4$, and space group $P22_12_1$] revealed a dimeric structure where two decaniobate ions are condensed sharing two terminal O atoms. Unlike that in $[(NbW_5O_{18})_2O]^{4-}$, the Nb–O–Nb bridges in icosaniobate are bent. The nonlinear bridging reduces the maximum possible symmetry of the dimeric anion to *mm*2, which it closely approximates.

The formation of polyniobate has been known for over a century.[1] The structure of hexaniobate, $[Nb_6O_{19}]^{8-}$, was determined as early as 1952.[2] In fact, it was one of the first polyoxometalates structurally characterized. Despite this long history, our knowledge of the polyniobate chemistry is still very limited and sketchy. Even today, hexaniobate and decaniobate, $[Nb_{10}O_{28}]^{6-}$, remain to be the only isopolyniobates isolated and structurally characterized,[3,4] although some other species have been proposed to exist in solution.[5,6] Here we report the synthesis and structural characterization of the third isopolyniobate, icosaniobate.

The icosaniobate $[Nb_{20}O_{54}]^{8-}$ is prepared as a colorless, crystalline, tetra-*n*-butylammonium (TBA) salt by bubbling NO gas through a tetrahydrofuran (THF) or $MeNO_2$ solution of $TBA_4[H_4Nb_6O_{19}]$[7,8] for several minutes, filtering a small amount of solids off, and adding ethyl acetate to the filtrate.[9]

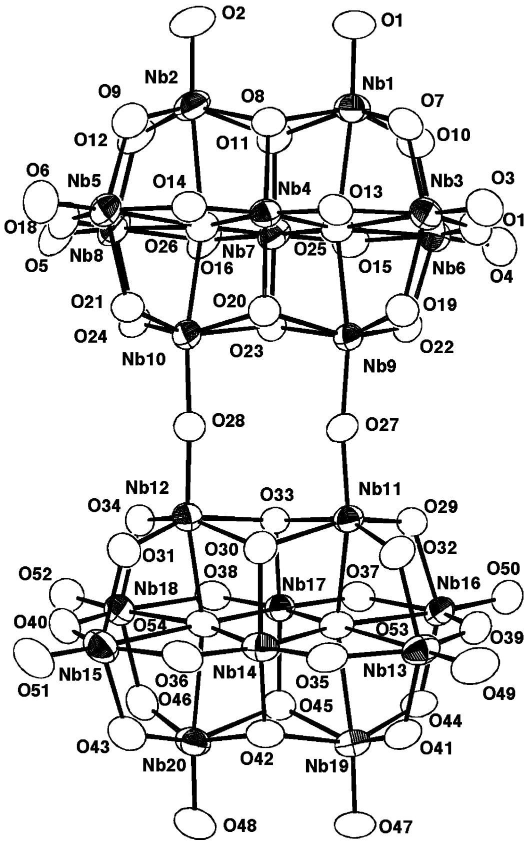

Figure 1. Perspective drawing of the $[Nb_{20}O_{54}]^{8-}$ anion. Displacement ellipsoids are scaled to enclose 50% probability levels.

X-ray structural analysis of crystalline $TBA_8[Nb_{20}O_{54}]$ revealed the presence of discrete $[Nb_{20}O_{54}]^{8-}$ anions of the dimeric structure shown in Figure 1.[10] Here two decaniobate anions form a dimer by sharing two terminal O atoms, O27 and O28. Unlike the Nb−O−Nb bridge in $[(NbW_5O_{18})_2O]^{4-}$,[11,12] which is linear, the bridges in the current anion are

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(1) Marignac, C. *Ann. Chim. Phys.* **1866**, *8*, 5−75.

(2) Lindqvist, I. *Ark. Kemi* **1952**, *5*, 247−250.

(3) Ozeki, T.; Yamase, T.; Naruke, H.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3249−3253.

(4) Graeber, E. J.; Morosin, B. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2137−2143.

(5) Larbi, S. S.; Bodiot, D.; Spinner, B. *Rev. Chim. Miner.* **1977**, *13*, 497−507.

(6) Rozantsev, G. M.; Dotsenko, O. I.; Taradina, G. V. *Russ. J. Coord. Chem.* **2000**, *26*, 247−253.

(7) Crude $TBA_4H_4[Nb_6O_{19}]\cdot 7H_2O$ was prepared by dissolving $K_7H[Nb_6O_{19}]\cdot 13H_2O$ (1.0 g, 7.3×10^{-4} mol) in 10 mL of H_2O, filtering any undissolved solids off, adding 1.0 M HCl (7.0 mL, 7.0×10^{-3} mol) to the filtrate, collecting the precipitate that formed by filtration, washing it with 4 × 30 mL of H_2O, drying it in vacuo over P_2O_5, reacting the dried precipitate with aqueous 0.4 M TBAOH (2.7 mL, 1.1×10^{-3} mol) at 80 °C for 24 h, filtering undissolved solids off, evaporating the filtrate to dryness, and drying the colorless solid obtained in vacuo over P_2O_5 for 24 h (0.50 g, 2.5×10^{-4} mol, 34%). Crystallization was accomplished by dissolving 0.10 g of the crude material in 1.5 mL of THF, adding 1.5 mL of Et_2O to the solution, and allowing the mixture to stand at ambient temperature for 18 h (60 mg, 3.1×10^{-5} mol, 20% over all yield). Anal. Calcd for $C_{64}H_{162}N_4Nb_6O_{26}$: C, 39.19; H, 8.32; N, 2.86; Nb, 28.4. Found: C, 39.40; H, 8.18; N, 2.83; Nb, 27.2. IR (ATR, 400−1000 cm^{-1}): 425 (s), 498 (s), 526 (s), 548 (sh), 580 (w), 697 (sh), 730 (vs), 784 (s), 885 (vs).

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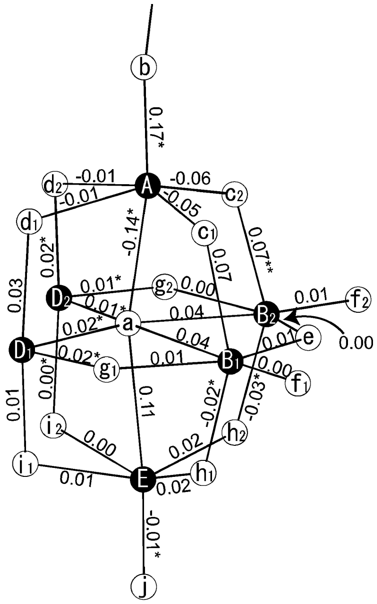

Figure 2. Asymmetric unit of the *mm*2-idealized $[Nb_{20}O_{54}]^{8-}$ anion. Figures indicate the differences of the bond lengths in angstroms from corresponding Nb−O bonds in $[Nb_{10}O_{28}]^{6-}$. The estimated standard deviation is 0.01 Å for the values indicated with * and 0.03 Å for that with **. For all others, the estimated standard deviation is 0.02 Å.

distinctively bent [Nb9−O27−Nb11 = 158.7(4)°, Nb10−O28−Nb12 = 160.3(4)°]. Although the icosaniobate anion has no rigorous crystallographic symmetry, it closely approximates its maximum possible symmetry *mm*2 (C_{2v}).

Figure 2 shows the asymmetric unit of the idealized $[Nb_{20}O_{54}]^{8-}$ anion of *mm*2 symmetry. The figure given along each Nb−O bond is the difference between the Nb−O bond lengths in $[Nb_{20}O_{54}]^{8-}$ and $[Nb_{10}O_{28}]^{6-}$. The corresponding *mmm* (D_{2h}) averaged bond length in $[Nb_{10}O_{28}]^{6-}$ was subtracted from each *mm*2 averaged bond length in $[Nb_{20}O_{54}]^{8-}$. Here both local and nonlocal effects of dimerization are clearly visible. The largest change is observed around the bridging oxygen O(b). The Nb(A)−O(b) bond has lost its double-bond nature completely and is lengthened by as much as 0.17 Å. The trans bond influence of this lengthening would make the Nb(A)−O(a) bond shorter, and it actually is shortened as expected. The trans bond-length alternation pattern[13] can be followed one step further to O(a)−Nb(E). However, the pattern fades beyond this point, and the change in Nb(E)−O(j) is very small.

In addition to the clearly visible trans influence, the elongation of the Nb(A)−O(b) bond seems to have some influence also on the bonds cis to it. The Nb(A)−O(c) bonds are shortened significantly. Here again we can follow the trans bond-length alternation pattern to Nb(E), although the lengthening of the Nb(E)−O(h_1) bond is very small.

The dimerization has little effect on the central part of the $Nb_{10}O_{28}$ moiety. The bonds between Nb(D), O(d), and O(i) show very little or no change. The lengths of the bonds to these central atoms do not change significantly either. Other bonds that are not affected by dimerization are the terminal Nb(B)−O(f) bonds and the doubly bridging Nb(B)−O(e) and Nb(B)−O(g) bonds in the “equatorial” plane of the $Nb_{10}O_{28}$ moiety. It is interesting to note that Nb(B)−O(a) bonds are elongated. It seems that the Nb(A)−O(a) bond shortened so much that the lengthening of the Nb(E)−O(a) bond alone was not sufficient to maintain a constant valence at O(a).

The structure of the hexaniobate is robust, and it persists in solution even at a pH as high as 14.[14,15] It has sometimes been assumed that relatively severe reaction conditions such as hydrothermal processing are needed to break down the Nb_6O_{19} framework once it is formed.[16] The current study demonstrates that is not always the case, and a soft chemical approach to novel polyniobates is possible.

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Supporting Information Available: Crystallographic data for $TBA_8[Nb_{20}O_{54}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Filowitz, M.; Ho, R. K. C.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1979**, *18*, 93−103.

(9) NO was bubbled through a solution of $TBA_4H_4[Nb_6O_{19}]\cdot 7H_2O$ (1.0 g, 5.1×10^{-4} mol, in 20 mL of THF) for 6 min at ca. 100 mL min^{-1}. After a small amount of solids was filtered off, 0.8 mL of ethyl acetate was added to 1 mL of the filtrate. Crystals that appeared overnight from the mixture were collected by decantation, washed with 3 × 0.5 mL of ethyl acetate, and dried in vacuo over P_2O_5 for 1 h to yield 0.65 g of $TBA_8[Nb_{20}O_{54}]\cdot H_2O$ (1.4×10^{-4} mol, 92%). Anal. Calcd for $C_{128}H_{290}N_8Nb_{20}O_{55}$: C, 32.85; H, 6.25; N, 2.39; Nb, 39.7. Found: C, 33.10; H, 6.35; N, 2.37; Nb, 39.2. IR (ATR, 400−1000 cm^{-1}): 431 (s), 478 (w), 505 (s), 533 (vs), 540 (sh), 579 (m), 608 (m), 633 (sh), 644 (vs), 745 (s), 802 (vs), 884 (sh), 909 (vs), 924 (w), 930 (w). Single crystals suitable for X-ray diffraction were prepared by dissolving 100 mg of the crude crystals in 1.0 mL of CH_3CN, adding 5 mL of ethyl acetate to the solution, and allowing the mixture to stand at ambient temperature. A total of 56 mg of plate-shaped crystals appeared the next day. Reactions of $TBA_4H_4[Nb_6O_{19}]\cdot 7H_2O$ with HCl or $HClO_4$ yielded compounds that showed IR spectra indicative of icosaniobate. However, we could not isolate it in a pure form, probability because of a large amount of TBACl or $TBAClO_4$ produced as byproducts.

(10) Single crystals of $TBA_8[Nb_{20}O_{54}]\cdot 3CH_3COOC_2H_5$ are, at 150(1) K, orthorhombic, space group $P22_12_1$, with a = 17.7284(18) Å, b = 33.542(3) Å, c = 34.316(2) Å, V = 20406(3) Å^3, and Z = 4. A colorless crystal of dimensions 0.45 × 0.40 × 0.30 mm^3 was used for data collection. Diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer using Mo Kα radiation. The final agreement factors were $R = 0.061$ for 43 336 reflections with $F^2 > 2\sigma(F^2)$ and $wR(F^2) = 0.178$ for 45 939 unique reflections.

(11) Lu, Y.-J.; Lalancette, R.; Beer, R. H. *Inorg. Chem.* **1996**, *35*, 2524−2529.

(12) Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Havelock, J. *J. Chem. Soc., Dalton Trans.* **1996**, 681−690.

(13) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *Inorg. Chem.* **1985**, *24*, 4055−4062.

(14) Neumann, G. *Acta Chem. Scand.* **1964**, *18*, 278−280.

(15) Etxebarria, N.; Fernández, L. A.; Madariaga, J. M. *J. Chem. Soc., Dalton Trans.* **1994**, 3055−3059.

(16) Bonhomme, F.; Larentzos, J. P.; Alam, T. M.; Maginn, E. J.; Nyman, M. *Inorg. Chem.* **2005**, *44*, 1774−1785.