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# Synthesis and Structure of an Alkyne–Tetrabromoniobate(1−)

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*Summary: The unexpected formation of the anionic* $Nb^{III}$ *complex* $[Nb(F_3CC{\equiv}CCF_3)(py)Br_4]^-$ *(py = pyridine), containing a* $\eta^2$*-alkyne, from* $[Nb(CO)_6]^-$, $F_3CC{\equiv}CF_3$, *and [Hpy]Br, and the X-ray crystal structure of its* $[Et_4N]^+$ *salt are reported.*

Alkyne complexes of the early transition metals are of general interest in the context of their potential as intermediates in the catalysis of polymerization and oligomerization reactions. Low-valent niobium and tantalum compounds have also been discussed as intermediates in the selective reduction of alkynes to alkenes and one-to-two addition of alkynes to 1,3-dienes in the $MCl_5$/Zn/alkyne system[1,2] and in the $NbCl_3$(dme) promoted coupling of alkynes to 1,2-arylaldehydes.[3] While there is abundant information on molybdenum and tungsten complexes containing the alkyne ligand in the $\eta^2$-mode,[4] corresponding alkyne complexes of niobium and tantalum are scarce, and there are only a few reports on complexes where the metal does not contain a supporting cyclopentadienyl ligand. Examples are the $d^4$ complexes $Ta(ROC{\equiv}COR(dmpe)_2Cl$ ($R = SiMe_3$,[5a,b] H[5c]), $M(RC{\equiv}CR)(CO)_2L_2X$ (M = Nb,[6] Ta[7]), and $[Nb(RC{\equiv}CR')(CO)_2X]_2$[8] and the $d^2$ complexes $[Ta(PhC{\equiv}CPh)(py)Cl_4]^-$ [9] and $Nb(RC{\equiv}CR')L_nX_3$.[10] We have recently opened a novel route to $d^4$ Nb–alkyne complexes through the reactive, easily available precursors $[Nb_2(CO)_8(\mu\text{-}X)_3]^-$ [8] and $Nb(CO)_{3/4}(PR_3)_{3/2}X$.[6,11] Our explorations into a more direct route, starting from hexacarbonylniobate(1−), have now led, in a formally four-electron oxidation reaction, to an alkyne complex of $Nb^{III}$.

## Results and Discussion

When a THF solution of $[Et_4N][Nb(CO)_6]$ is reacted with [Hpy]Br in the presence of phosphines $p_n$, neutral, seven-coordinated complexes of composition $Nb(CO)_{6-n}p_nBr$ (n = 2–4) are formed.[11] This reaction, accompanied by an oxidation of $Nb^{1-}$ to $Nb^1$, probably proceeds in three steps through (i) oxidative addition of a proton to the Nb center and formation of a hydridoniobium compound {HNb(CO)},[12] (ii) exchange of hydride by bromide ({HNb(CO)} + HBr → {BrNb(CO)} + $H_2$) and formation of a dinuclear anion of composition $[Nb_2(CO)_8(\mu\text{-}Br)_3]^-$,[13] and (iii) rearrangement, by concomittant partial exchange of CO for the phosphine, to $Nb(CO)_{6-n}p_nBr$. If the phosphine is replaced by hexafluoro-2-butyne, $F_3CC{\equiv}CCF_3$, oxidation proceeds further, and the brick-red $Nb^{III}$ complex $[Et_4N][Nb(F_3CC{\equiv}CCF_3)(py)Br_4]$ forms, in which the alkyne is bonded in the $\eta^2$-mode and the sixth ligand, pyridine, stems from the reactant [Hpy]Br. The possibility of CO substitution by pyridine has been established for, inter alia, $Ta(CO)_4(dppe)Cl$.[14] A dinuclear, bromide-bridged carbonylniobium complex is a likely intermediate in this reaction as well, since the reaction leading to the alkyne complex is preferably carried out in two consecutive steps according to eq 1, each of which involves the transfer of two electrons

$$2[Et_4N][Nb(CO)_6] + 4[Hpy]Br \rightarrow [Et_4N][Nb_2(CO)_8Br_3] + 2H_2 + [Et_4N]Br + 4py + 4CO \quad (1a)$$

$$[Et_4N][Nb_2(CO)_8Br_3] + [Et_4N]Br + 4[Hpy]Br + 4F_3CC{\equiv}CCF_3 \rightarrow 2[Et_4N][Nb(F_3CC{\equiv}CCF_3)(py)Br_4] + 2F_3CH{=}CHCF_3 + 2py + 8CO \quad (1b)$$

per Nb. The extremely electron-deficient bis(trifluoromethyl)acetylene may well be the driving force for the unexpected second step (eq 1b); this reaction path has not been observed with alkyl- or phenylacetylenes. Rather, if the anion $[Nb_2(CO)_8Br_3]^-$ is reacted with these alkynes, the dinuclear complexes $\{Nb(CO)_2(\eta^2\text{-alkyne})\}_2(\mu\text{-}Br)_2$ form.[8] In eq 1b, hexafluorobutyne is the electron acceptor (the formation of hexafluorobutene has been detected by GC–MS), a reaction which is reminiscent of the reduction of alkynes to alkenes by $NbCl_5$/Zn.[1,2]

Figure 1 shows an ORTEP drawing of the anion $[Nb(F_3CC{\equiv}CCF_3)(py)Br_4]^-$. Atomic coordinates and isotropic thermal parameters are listed in Table I; bonding parameters, in Table II. The coordination geometry of this complex anion is best described by an octahedron, with pyridine and the side-on coordinating alkyne forming the axis and the four bromo ligands in the octahedral plane.

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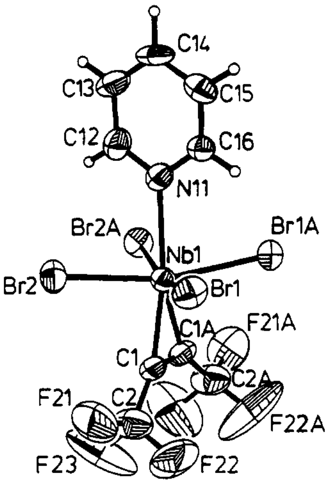

**Figure 1.** ORTEP drawing and labeling scheme of the anion $[Nb(F_3CC{\equiv}CCF_3)(py)Br_4]^-$.

**Table I. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Factors of the Non-Hydrogen Atoms ($pm^2 \times 10^{-1}$) for $[Nb(CF_3C{\equiv}CCF_3)(py)Br_4]^-$**

| | *x* | *y* | *z* | *U*(eq), Å$^2$ |
|---|---|---|---|---|
| Nb(1) | 2051(1) | 1143(1) | 7500 | 35(1) |
| Br(1) | 850(1) | 2074(1) | 6531(1) | 50(1) |
| Br(2) | 3823(1) | 475(1) | 6542(1) | 51(1) |
| C(1) | 331(10) | 341(6) | 7158(6) | 42(4) |
| C(2) | −585(17) | −25(10) | 6580(9) | 73(6) |
| F(21) | −76(11) | 68(6) | 5931(5) | 106(4) |
| F(22) | −2020(10) | 177(9) | 6567(6) | 187(7) |
| F(23) | −544(17) | −824(6) | 6641(6) | 179(7) |
| N(11) | 4113(13) | 2159(8) | 7500 | 42(5) |
| C(12) | 5639(16) | 1965(10) | 7500 | 51(7) |
| C(13) | 6862(18) | 2527(11) | 7500 | 57(7) |
| C(14) | 6469(19) | 3316(12) | 7500 | 54(7) |
| C(15) | 4929(19) | 3517(10) | 7500 | 47(6) |
| C(16) | 3819(17) | 2944(9) | 7500 | 36(5) |
| N(20) | 4229(14) | 7500 | 0 | 48(5) |
| C(21) | 3215(14) | 8165(8) | 321(7) | 69(5) |
| C(22) | 2088(17) | 8550(9) | −223(8) | 108(7) |
| C(23) | 5234(15) | 7811(8) | −607(7) | 68(5) |
| C(24) | 6338(16) | 8493(10) | −405(8) | 100(7) |

**Table II. Selected Bond Lengths and Bond Angles for $[Nb(F_3CC{\equiv}CF_3)(py)Br_4]^-$**

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Nb(1)-Br(1) | 2.580(2) | C(1)-C(2) | 1.455(19) |
| C(2)-F(22) | 1.252(17) | C(2)-F(21) | 1.288(19) |
| Nb(1)-Br(2) | 2.573(2) | C(2)-F(22) | 1.252(17) |
| Nb(1)-N(11) | 2.420(12) | C(2)-F(23) | 1.333(19) |
| Nb(1)-C(1) | 2.066(9) | N(11)-C(12) | 1.322(18) |
| C(1)-C(1A) | 1.269(21) | N(11)-C(16) | 1.329(19) |
| | Bond Angles (deg) | | |
| Br(1)-Nb(1)-Br(2) | 90.2(1) | Br(2)-Nb(1)-N(11) | 83.5(2) |
| Br(1)-Nb(1)-C(1) | 84.2(3) | C(1)-Nb(1)-N(11) | 162.0(3) |
| Br(2)-Nb(1)-C(1) | 85.1(3) | C(1)-Nb(1)-C(1A) | 35.8(6) |
| Br(1)-Nb(1)-N(11) | 82.1(3) | C(2)-C(1)-Nb(1) | 150.1(9) |
| | | C(2)-C(1)-C(1A) | 137.6(7) |

**Table III. Crystallographic Data for $[Et_4N][Nb(F_3CC{\equiv}CCF_3)(py)Br_4]$**

| | |
|---|---|
| (a) Crystal Data | |
| formula | $C_{17}H_{25}Br_4F_6N_2Nb$ |
| *M* | 783.9 |
| cryst syst | orthorhombic |
| space group | *Pbcm* (No. 57) |
| *a*, Å | 8.407(2) |
| *b*, Å | 16.619(3) |
| *c*, Å | 18.570(4) |
| *Z* | 4 |
| *V*, Å$^3$ | 2594.5(10) |
| cryst dimens, mm | 0.29 × 0.34 × 0.42 |
| cryst color | light red |
| *D*(calc), g cm$^{-3}$ | 2.007 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 67 |
| *F*(000) | 1504 |
| (b) Data Collection | |
| diffractometer | Syntex $P2_1$ |
| radiation ($\lambda$, Å) | Mo K$\alpha$ (0.710 73) |
| monochromator | graphite |
| $2\theta$ scan range, deg | 4.5–55.0 |
| index ranges | $0 \leq h \leq 10, 0 \leq k \leq 21, 0 \leq l \leq 24$ |
| no. of rflns collcd | 2855 |
| indpt rflns ($R_{int}$ = 3.16%) | 2593 |
| obsvd rflns ($F > 4\sigma(F)$) | 1423 |
| weighting scheme | $w^{-1} = \sigma^2(F) + 0.0005F^2$ |
| (c) Refinement | |
| no. of params refined | 150 |
| *R*, % | 5.44 |
| $R_w$, % | 5.09 |
| $\Delta/\sigma$ (max, min) | 0.071, 0.004 |
| largest diff peak, e Å$^{-3}$ | 0.70 |
| largest diff hole, e Å$^{-3}$ | 0.71 |

Niobium is displaced out of this plane by 0.325(6) Å toward the alkyne. A symmetry plane, containing the pyridine ring, cuts through the acetylene backbone. The overall arrangement is similar to that of $[Ta(PhC{\equiv}CPh)(py)Cl_4]^-$.[9] Metal—C and C—C bond lengths of the Nb complex compare to those of other Nb$^{III}$ and Ta$^{III}$ alkyne complexes. There are no significant differences in these parameters between the Nb$^{III}$ and Nb$^{I}$ alkynes. For the latter of composition $[Nb(RC{\equiv}CR)(CO)_2(diphos)X]$, the alkyne has been shown to act as a four-electron-donating ligand;[6] the same description should prevail for $[Nb(F_3CC{\equiv}CCF_3)Br_4(py)]^-$. In solution, the local symmetry of this anion is $C_{2v}$, as evidenced by only one signal for the $CF_3$ group in the $^{19}F$ and $^{13}C$ NMR.[15] There are no interatomic hydrogen bonds involving the fluorines on the one hand and pyridine or the counterion $[Et_4N]^+$ on the other hand.

## Experimental Section

All operations were carried out under an atmosphere of argon, using standard Schlenk techniques. Solvents were dried by conventional methods and distilled in a stream of argon prior to use. The starting material $[Et_4N][Nb(CO)_6]$ was prepared as described in the literature.[6,16] Hexafluorobutyne was purchased (Strem).

**$[(C_2H_5)_4N][Nb(F_3CC{\equiv}CCF_3)(C_5H_5N)Br_4]$.** A 0.391-g (1-mmol) sample of $[Et_4N][Nb(CO)_6]$ and 0.324 g (2 mmol) of [Hpy]Br dissolved in 20 mL of THF were stirred at room temperature for 12 h. The bordeau-red solution thus obtained, containing the anion $[Nb_2(CO)_8(\mu\text{-}Br)_3]^-$, was treated with excess hexafluorobutyne. Within 2 h of stirring, CO evolved and a brick-red solution of the alkyne complex formed. This was filtered to remove small amounts of a white precipitate, and the filtrate was concentrated to 10 mL in vacuo at room temperature. The viscous solution was allowed to stand at −26 °C overnight. Crystals separated, which were collected and dried. Yield: 0.360 g (46%). $[Et_4N][Nb(F_3CC{\equiv}CCF_3)(py)Br_4]$ is a brick-red, crystalline compound, which is sensitive to moisture and insoluble in pentane. Anal. Calcd for $C_{17}H_{25}Br_4F_6N_2Nb$: C, 26.05; H, 3.21; N, 3.57. Found: C, 26.15; H, 3.07; N, 3.51. One of the crystals was used for the X-ray analysis.

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(15) $^{19}F$ NMR (THF-$d_8$; $\delta$, ppm): −67.7. $^{13}C$ NMR [THF-$d_8$; $\delta$, ppm ($^1J_{FC}$, Hz)]: $CF_3$ 129 (266). No signal has been detected for the alkyne carbons, possibly as a consequence of intensity problems due to coupling to the $^{19}F$ *and* $^{93}Nb$ ($I = {}^9/_2$) nuclei. The NMR spectra were obtained at 75.3 MHz ($^{19}F$) and 90.6 MHz ($^{13}C$). $\delta$ values are given relative to $CFCl_3$ ($^{19}F$) and TMS ($^{13}C$).

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**X-ray Crystallography for [Et$_4$N][Nb(F$_3$CC≡CCF$_3$)(py)Br$_4$].** Crystal and data collection parameters are contained in Table III. The solution and refinement of the structure was carried out with the program system SHELXTL PLUS;[17] for an emperical absorption correction, the programm DIFABS was used.[18] The positions of the non-hydrogen atoms were located via direct methods. Hydrogen atoms were included in the later states of refinement for geometrical calculations and with fixed positions and thermal parameters.

**Supplementary Material Available:** For the compound [Et$_4$N][Nb(F$_3$CC≡CCF$_3$)(py)Br$_4$], a cell drawing and Schakal drawings with numbering schemes of the cation and the anion and full tables of bond distances and angles, anisotropic thermal parameters of the non-hydrogen atoms, and coordinates and isotropic thermal parameters of the hydrogen atoms (6 pages). Ordering information is given on any current masthead page.

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