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Polyazides

Coordination Adducts of Niobium(V) and Tantalum(V) Azide $M(N_3)_5$ ($M = Nb$, Ta) with Nitrogen Donor Ligands and their Self-Ionization[**]

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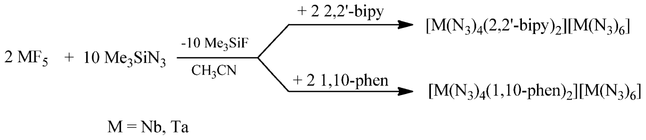
Abstract: *Several new donor–acceptor adducts of niobium and tantalum pentaazide with N-donor ligands have been prepared from the pentafluorides by fluoride–azide exchange with Me_3SiN_3 in the presence of the corresponding donor ligand. With 2,2′-bipyridine and 1,10-phenanthroline, the self-ionization products $[MF_4(2,2'\text{-bipy})_2]^+[M(N_3)_6]^-$, $[M(N_3)_4(2,2'\text{-bipy})_2]^+[M(N_3)_6]^-$ and $[M(N_3)_4(1,10\text{-phen})_2]^+[M(N_3)_6]^-$ were obtained. With the donor ligands 3,3′-bipyridine and 4,4′-bipyridine the neutral pentaazide adducts $(M(N_3)_5)_2{\cdot}L$ ($M =$ Nb, Ta; $L =$ 3,3′-bipy, 4,4′-bipy) were formed.*

Azides and polyazides are viable candidates for high-energy-density materials (HEDM) and have received considerable attention in recent years.[1] Polyazido compounds have great potential as energetic materials due to their highly positive heats of formation. However, the synthesis of molecules with a high number of azido groups is very challenging due to their shock sensitivity and explosive nature. Despite these obstacles, several binary transition metal azido complexes have been reported recently.[1c,2] In general, polyazido compounds can be obtained from the corresponding covalent fluorides by treatment with Me_3SiN_3 in a suitable solvent.[3] Neutral binary polyazides are often highly explosive but their sensitivity can be greatly reduced by either anion or adduct formation which increases the ionicity of the azido ligands making the breaking of an N–N bond less favorable and raises the activation energy barrier towards fatal N_2 elimination.[1a]

We recently reported the syntheses of the neutral group(V) metal polyazides $V(N_3)_4$, $Nb(N_3)_5$, and $Ta(N_3)_5$.[2f] These neutral polyazides are very shock sensitive, but can be stabilized through the formation of the corresponding anions $[V(N_3)_6]^{2-}$, $[Nb(N_3)_6]^-$, $[Nb(N_3)_7]^{2-}$, $[Ta(N_3)_6]^-$, and $[Ta(N_3)_7]^{2-}$.[2c,e,f] Here, we report the synthesis and characterization of neutral coordination adducts of $Nb(N_3)_5$ and $Ta(N_3)_5$ with N-donor ligands.

The reactions of NbF_5 and TaF_5 with an excess of Me_3SiN_3 in the presence of two equivalents of 2,2′-bipyridine (2,2′-bipy) or 1,10-phenanthroline (1,10-phen) in acetonitrile solution at ambient temperature results in self-ionization and fluoride/azide exchange (Scheme 1) leading to the formation of products containing a $[M(N_3)_6]^-$ anion as well as a $[M(N_3)_4L_2]^+$ cation ($M = Nb$, Ta, $L =$ 2,2′-bipy, 1,10-phen). The 2,2′-bipyridine adducts $[M(N_3)_4(2,2'\text{-bipy})_2][M(N_3)_6]$ were isolated as dark orange solids, while the corresponding 1,10-phenanthroline adducts $[M(N_3)_4(1,10\text{-phen})_2][M(N_3)_6]$ were found to be yellow (Nb) to off-white (Ta) solids.



Scheme 1. Reactions of niobium and tantalum pentafluoride with an excess of Me_3SiN_3 in the presence of 2,2′-bipyridine or 1,10-phenanthroline.

The four self-ionization products $[M(N_3)_4L_2]^+[M(N_3)_6]^-$ ($M = Nb$, Ta; $L =$ 2,2′-bipy, 1,10-phen) were characterized by vibrational spectroscopy (see Supporting Information), the observed material balances and, for $[Nb(N_3)_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$, $[Ta(N_3)_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ and $[Nb(N_3)_4(1,10\text{-phen})_2][Nb(N_3)_6]$ by their crystal structures.[4]

The reaction of NbF_5 and TaF_5 with three equivalents of Me_3SiN_3 in the presence of two equivalents of 2,2′-bipyridine in acetonitrile solution results again in self-ionization and the formation of a hexaazidometalate salt. While with an excess of Me_3SiN_3 fully azido-substituted salts containing tetraazido cations $[M(N_3)_4(2,2'\text{-bipy})_2]^+$ are obtained, the use of Me_3SiN_3 in a molar ratio of 1:3, results in the formation of a partially azido-substituted salt containing the tetrafluorometal cation $[MF_4(2,2'\text{-bipy})_2]^+$ and a hexaazido-substituted anion (Scheme 2).

The partially azido-substituted hexaazidoniobates and -tantalates $[MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$ were isolated as orange solids that were characterized by their crystal structures,[4]

$$2\,MF_5 \;+\; 6\,Me_3SiN_3 \xrightarrow[-6\,Me_3SiF]{+2\ 2,2'\text{-bipy}} [MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$$

$M = Nb$, Ta

Scheme 2. Reactions of niobium and tantalum pentafluoride with three equivalents of Me_3SiN_3 in the presence of 2,2′-bipyridine.

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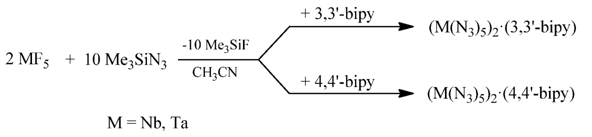
vibrational and NMR spectra, and the observed material balances (see Supporting Information).

When the fluoride/azide exchange reactions between the metal pentafluorides and excess trimethylsilyl azide were carried out in the presence of 3,3′-bipyridine (3,3′-bipy) or 4,4′-bipyridine (4,4′-bipy), respectively, only 2:1 adducts of the metal pentaazide with the corresponding bipyridine ligand could be isolated (Scheme 3). No evidence for the formation of a self-ionization product was found, not even when a large excess of 3,3′-bipy or 4,4′-bipy was used in the reaction. This difference in reaction behavior can be rationalized by the increased bite angles of 3,3′- and 4,4′-bipyridine compared to 2,2′-bipyridine or 1,10-phenanthroline.



Scheme 3. Reactions of niobium and tantalum pentafluoride with Me_3SiN_3 in the presence of 3,3′- and 4,4′-bipyridine.

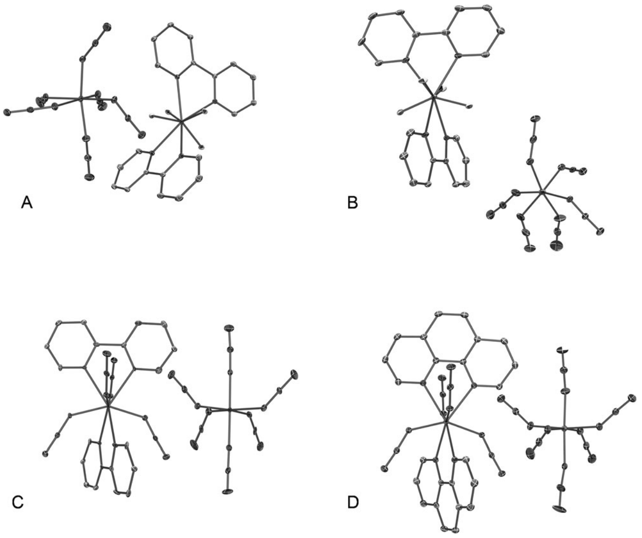


Figure 1. Crystal structures of $[NbF_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$ (**A**), $[TaF_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ (**B**), $[Nb(N_3)_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$ (**C**), and $[Nb(N_3)_4(\text{phen})_2][Nb(N_3)_6]$ (**D**). Ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.

The niobium and tantalum pentaazide donor adducts $(M(N_3)_5)_2{\cdot}L$ (L = 3,3′-bipy, 4,4′-bipy) were isolated as orange (Nb) or off-white (Ta) solids that were characterized by their crystal structures,[4] vibrational and NMR spectra, and the observed material balances (see Supporting Information).

The niobium and tantalum azido compounds of this work are moderately moisture sensitive. While the compounds decompose when exposed to moisture for several minutes or when dissolved in moist solvents, short-time air exposure of a few seconds did not result in hydrolysis.

The details of the crystallographic data collection and refinement parameters for all structurally investigated compounds are given in the Supporting Information. The crystal structures of the partially azido-substituted complexes $[NbF_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$ and $[TaF_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ consist of isolated and well separated $[MF_4(2,2'\text{-bipy})_2]^+$ cations and pseudo octahedral $[M(N_3)_6]^-$ anions (Figure 1 A,B). In the cations, the central metal atom is coordinated by a total of four fluoride ligands as well as four N-atoms from the two coordinated 2,2′-bipy ligands. This results in a pseudo-square antiprismatic environment around the metal atom in which each of the squares is composed of two fluoride ligands and two N-atoms from two different 2,2′-bipy ligands. Both squares are elongated along the N,N diagonal. The observed M−F bond distances in the $[MF_4(2,2'\text{-bipy})_2]^+$ cations (Nb: 1.884(1)–1.800(1) Å, Ta: 1.886(5)–1.812(5) Å) are slightly shorter than the ones found in the cations $[MF_4(\text{pyridine})_4]^+$ (Nb: 1.898(2)–1.803(2) Å, Ta: 1.903(2)–1.910(2) Å)[5] but are in the region of the M−F distances of the parent compounds M_4F_{20} (Nb: 1.75(5)–1.77(2) Å, Ta: 1.797(9)–1.773(8) Å).[6]

The structures of the complexes $[Nb(N_3)_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$, $[Ta(N_3)_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$, and $[Nb(N_3)_4(1,10\text{-phen})_2][Nb(N_3)_6]$ consist of well separated $[M(N_3)_6]^-$ anions and $[Nb(N_3)_4L_2]^+$ cations (Figure 1 C,D). The M−N bonds in the $[M(N_3)_4L_2]^+$ cations are 0.01 to 0.02 Å longer than the distances found for the $[M(N_3)_6]^-$ anions. The observed structural parameters of the $[M(N_3)_6]^-$ anions in the compounds $[MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$, $[M(N_3)_4(2,2'\text{-bipy})_2][M(N_3)_6]$, and $[Nb(N_3)_4(1,10\text{-phen})_2][Nb(N_3)_6]$ are in good agreement with the ones previously reported for $[PPh_4][M(N_3)_6]$.[2f]

The crystal structures of the neutral metal pentaazide 3,3′-bipy and 4,4′-bipy adducts consist of individual $(M(N_3)_5)_2{\cdot}L$ (M = Nb, Ta; L = 3,3′-bipy, 4,4′-bipy) molecules (Figure 2). The closest intermolecular M−N contacts are 4.029(6) Å (Nb) and 4.042(12) Å (Ta) in the 3,3′-bipyridine adducts and 3.920(3) Å (Nb) and 3.955(12) Å (Ta) for the 4,4′-bipyridine adducts. The closest intermolecular N−N contacts are 2.970(6) and 2.889(3) Å (Nb) and 2.979(12) and 2.905(4) Å (Ta). It is interesting to note that $[NbF_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$ crystallizes in the monoclinic space group $P2_1/c$ while the

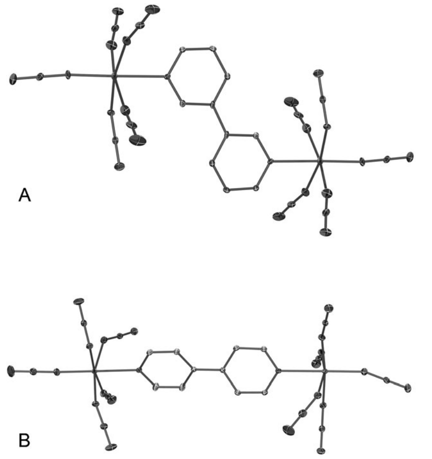


Figure 2. Crystal structures of $(Nb(N_3)_5)_2{\cdot}(3,3'\text{-bipy})$ (**A**) and $(Nb(N_3)_5)_2{\cdot}(4,4'\text{-bipy})$ (**B**). Ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity.

corresponding compound $[TaF_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ crystallizes in the triclinic space group *P*-1 while the two corresponding compounds in the pairs $[Nb(N_3)_4(2,2'\text{-bipy})_2][Nb(N_3)_6]$ and $[Ta(N_3)_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$, $(Nb(N_3)_5)_2\cdot(3,3'\text{-bipy})$ and $(Nb(N_3)_5)_2\cdot(3,3'\text{-bipy})$, as well as $(Nb(N_3)_5)_2\cdot(4,4'\text{-bipy})$ and $(Ta(N_3)_5)_2\cdot(4,4'\text{-bipy})$ are isostructural. Previously, the related pairs of compounds $[NbF_4(\text{pyridine})_4][NbF_6]$ and $[TaF_4(\text{pyridine})_4][TaF_6]$,[5] $[NbF_4(\text{dppe})_2][NbF_6]\cdot\frac{1}{2}CH_3CN$ and $[TaF_4(\text{dppe})_2][TaF_6]\cdot\frac{1}{2}CH_3CN$,[5] $[PPh_4][Nb(N_3)_6]$ and $[PPh_4][Ta(N_3)_6]$,[2f] as well as $[PPh_4]_2[Nb(N_3)_7]$ and $[PPh_4]_2[Ta(N_3)_7]$[2e] have been found to be isostructural.

The thermal stability of each polyazido compound was determined using differential thermal analysis (DTA) scans. The results of these scans are summarized in Table 1. As can be expected for binary polyazides, none of the investigated compounds showed a smooth decomposition upon heating at a rate of 5 °C min^{-1}. Instead, all compounds exploded. The niobium azides were found to have explosion temperatures between 120 and 141 °C. The tantalum azides are thermally somewhat more stable than the corresponding niobium azides and explode between 155 and 165 °C.

Table 1: Thermal stability of the polyazido adducts.

Compound	$T_{\text{explosion}}$	
	M = Nb	M = Ta
$[MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$	141 °C	165 °C
$[M(N_3)_4(2,2'\text{-bipy})_2][M(N_3)_6]$	120 °C	155 °C
$[M(N_3)_4(1,10\text{-phen})_2][M(N_3)_6]$	131 °C	161 °C
$(M(N_3)_5)_2\cdot 3,3'\text{-bipy}$	133 °C	155 °C
$(M(N_3)_5)_2\cdot 4,4'\text{-bipy}$	129 °C	163 °C

In summary, several new donor–acceptor adducts of niobium and tantalum pentaazide with N-donor ligands have been prepared from the pentafluorides by fluoride–azide exchange with Me_3SiN_3 and the corresponding donor ligand in CH_3CN solution. With 2,2′-bipyridine and 1,10-phenanthroline as donor ligands, the adducts $[M(N_3)_4L_2]^+[M(N_3)_6]^-$ were obtained. The formation of these self-ionization products proceeds stepwise and for L = 2,2′-bipy, it was possible the isolate the intermediates $[MF_4L_2]^+[M(N_3)_6]^-$. With the donor ligands 3,3′-bipyridine and 4,4′-bipyridine no evidence for the formation of an self-ionization product was found. Instead, the neutral pentaazide adducts $(M(N_3)_5)_2\cdot L$ (M = Nb, Ta; L = 3,3′-bipy, 4,4′-bipy) were obtained.

Experimental Section

Caution! Polyazides are extremely shock-sensitive and can explode violently upon the slightest provocation. They should be handled only on a scale using appropriate safety precautions.[2e] **Ignoring safety precautions can lead to serious injuries!**

Materials and Apparatus: All reactions were carried out in Teflon-FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a Pyrex glass vacuum line. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. The starting materials NbF_5, TaF_5 (Ozark Mahoning), 2,2′-bipyridine (2,2′-bipy), 4,4′-bipyridine (4,4′-bipy), and 1,10-phenanthroline (1,10-phen) (Aldrich) were used without further purification. 3,3′-Bipyridine (3,3′-bipy) was prepared from 3-bromopyridine using a literature method.[7] Solvents were dried by standard methods and freshly distilled prior to use.

Crystal structure determinations: The single-crystal X-ray diffraction data of $[Nb(N_3)_4(1,10\text{-phen})_2][Nb(N_3)_6]$ and $[Ta(N_3)_4(2,2'\text{-bipy})_2][Ta(N_3)_6]$ were collected on a Bruker SMART APEX diffractometer with the χ-axis fixed at 54.74° and using $Mo_{K\alpha}$ radiation (graphite monochromator) from a fine-focus tube. The diffractometer was equipped with an APEX CCD detector and an LT-3 apparatus for low-temperature data collection. All other single crystal diffraction data were collected on a Bruker SMART APEX DUO diffractometer with the χ-axis fixed at 54.74° and using $Mo_{K\alpha}$ radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an APEX II CCD detector and an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. A complete hemisphere of data was scanned on omega and phi (0.5°) at a detector resolution of 512 × 512. The frames were then integrated using the SAINT[8] algorithm to give the hkl files corrected for Lp/decay. The absorption correction was performed using the SADABS program.[9] The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package.[10] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[11]

Preparation of $[MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$ (M = Nb, Ta): A sample of MF_5 (1.00 mmol) and 2,2′-bipyridine (156 mg, 1.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of Me_3SiN_3 (345 mg, 3.00 mmol) and CH_3CN (1.5 mL) in vacuum at −196 °C. The mixture was allowed to warm to ambient temperature. After 6 h, all volatile material was pumped off, leaving behind orange crystals of $[MF_4(2,2'\text{-bipy})_2][M(N_3)_6]$ in quantitative yield.

Preparation of $[M(N_3)_4L_2][M(N_3)_6]$ (M = Nb, Ta; L = 2,2′-bipy, 1,10-phen): A sample of MF_5 (1.00 mmol) and 2,2′-bipyridine (156 mg, 1.00 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of Me_3SiN_3 (691 mg, 6.00 mmol) and CH_3CN (1.5 mL) in vacuum at −196 °C. The mixture was allowed to warm to ambient temperature. After 6 h, all volatile material was pumped off, leaving behind red crystals of $[M(N_3)_4L_2][M(N_3)_6]$ in quantitative yield.

Preparation of $(M(N_3)_5)_2\cdot L$ (M = Nb, Ta; L = 3,3′-bipy, 4,4′-bipy): A sample of MF_5 (1.00 mmol) and bipyridine (78 mg, 0.50 mmol) was loaded into a Teflon-FEP ampule, followed by the addition of Me_3SiN_3 (691 mg, 6.00 mmol) and CH_3CN (1.5 mL) in vacuum at −196 °C. The mixture was allowed to warm to ambient temperature. After 6 h, all volatile material was pumped off, leaving behind yellow to orange (Nb) or off-white (Ta) crystals of $(M(N_3)_5)_2\cdot L$ in quantitative yield.

Further experimental details are given in the Supporting Information.

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