REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 16-03-2006	**2. REPORT TYPE** Journal Article	**3. DATES COVERED** *(From - To)*
4. TITLE AND SUBTITLE **Polyazide Chemistry: Synthesis and Properties of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$ (PREPRINT)**		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Ralf Haiges, Muhammed Yousufuddin, & Karl Christe (USC); Jerry Boatz (AFRL/PRSP)		**5d. PROJECT NUMBER**
		5e. TASK NUMBER 23030423
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680		**8. PERFORMING ORGANIZATION REPORT NUMBER** AFRL-PR-ED-JA-2006-102
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**10. SPONSOR/MONITOR'S ACRONYM(S)**
		11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2006-102

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-082)

13. SUPPLEMENTARY NOTES

Submitted to Angewandte Chemie.

14. ABSTRACT

During the last decade, inorganic polyazido compounds have received much attention.[1-3] Besides being of academic interest, azides and polyazides are viable candidates for high energy-density materials (HEDM). The azido group is very energetic and polyazides are highly endothermic compounds, whose energy content increases with an increasing number of azido ligands. It is, therefore, not surprising that the synthesis of molecules with a high number of azido groups is very challenging due to their explosive nature and shock sensitivity. Despite such obstacles, a number of pentaazido and anionic hexaazido compounds had been reported.[4] Very recently, unprecedented neutral hexaazido species $M(N_3)_6$ (M = Mo, W) have been prepared, and in case of $W(N_3)_6$ also structurally characterized. Treatment of $M(N_3)_6$ (M = Mo, W) with ionic azides yielded the first binary heptaazido compounds.[5]

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr. Scott A. Shackelford
a. REPORT **Unclassified**	**b. ABSTRACT** **Unclassified**	**c. THIS PAGE** **Unclassified**	A	39	**19b. TELEPHONE NUMBER** *(include area code)* N/A

Polyazide Chemistry: Synthesis and Properties of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$[**] (Preprint)

Ralf Haiges[*], Jerry A. Boatz, Muhammed Yousufuddin, and Karl O. Christe[*]

Dedicated to Professor Kurt Dehnicke on the occasion of his 75th birthday

During the last decade, inorganic polyazido compounds have received much attention.[1-3] Besides being of academic interest, azides and polyazides are viable candidates for high energy-density materials (HEDM). The azido group is very energetic and polyazides are highly endothermic compounds, whose energy content increases with an increasing number of azido ligands. It is, therefore, not surprising that the synthesis of molecules with a high number of azido groups is very challenging due to their explosive nature and shock sensitivity. Despite such obstacles, a number of pentaazido and anionic hexaazido compounds had been reported.[4] Very recently, unprecedented neutral hexaazido species $M(N_3)_6$ (M = Mo, W) have been prepared, and in case of $W(N_3)_6$ also structurally characterized. Treatment of $M(N_3)_6$ (M = Mo, W) with ionic azides yielded the first binary heptaazido compounds.[5]

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[**] This work was funded by the Air Force Office of Scientific Research, the Office of Naval Research and the National Science Foundation. We thank Prof. Dr. G. A. Olah for his steady support, and Prof. Dr. R. Bau and Drs. T. Schroer, S. Schneider and R. Wagner for their help and stimulating discussions.
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

However, due to their high sensitivity, the crystal structures of these heptaazides could not be determined and they were solely characterized by Raman spectroscopy. In this paper, we wish to communicate the synthesis and characterization of the heptaazido dianions, $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$. In addition, we want to report the crystal structures of $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$ and $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$, the first structurally characterized transition metal heptaazides. After completion of this work,[6] the crystal structures of the first actinide heptazide trianion, $[U(N_3)_7]^{3-}$, were published by Crawford, Ellern and Mayer.[7]

While the reactions of $Nb(N_3)_5$ and $Ta(N_3)_5$ with one equivalent of ionic azide, such as $[PPh_4]N_3$, yielded the corresponding hexaazido metalates,[4p] it was now found that the reactions with two equivalents of ionic azide in CH_3CN solution can produce salts of the heptaazido metalates $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$, respectively, [Eq. (1) (M = Nb, Ta].

$$M(N_3)_5 \; + \; 2\,[PPh_4]N_3 \xrightarrow{CH_3CN} [P(C_6H_5)_4]_2[M(N_3)_7]\cdot CH_3CN \qquad (1)$$

The heptaazido metalates of niobium and tantalum were isolated as yellow-orange and pale yellow solids, respectively, that are surprisingly stable. The compounds were characterized by the observed material balances, vibrational spectroscopy, and by their crystal structures.[8,9]

Because of the presence of two large counter-ions which serve as inert spacers and suppress detonation propagation, these salts are much less shock sensitive than neat $Nb(N_3)_5$ and $Ta(N_3)_5$, and are thermally surprisingly stable. While the heptaazido salts of molybdenum and tungsten $[PPh_4]^+[M(N_3)_7]^-$ (M = Mo, W) are also extremely shock sensitive solids that explode violently when warmed towards room temperature and decompose in solution,[5] no such decomposition could be observed for $[PPh_4]_2[Nb(N_3)_7]$ or $[PPh_4]_2[Ta(N_3)_7]$ at room temperature.

The structure of heptaazides is of particular interest, because three different ligand arrangements are possible for heptacoordinated transition metal complexes which differ only little in energy.[10] They are derived from a pentagonal bipyramid (1/5/1 arrangement), a monocapped trigonal prism (1/4/2 arrangement), and a monocapped octahedron (1/3/3 arrangement) (see Figure 1). Whereas for main group elements, the pentagonal bipyramidal 1/5/1 arrangement is preferred because the bonding involves the orthogonal *p* orbitals, the *d* orbital transition metal heptafluoride anions, MoF_7^- and WF_7^-, exhibit a monocapped octahedral 1/3/3 arrangement,[10h] and the *f* orbital actinide heptaazide trianion, $[U(N_3)_7]^{3-}$, can crystallize either in the monocapped octahedral 1/3/3 or the pentagonal bipyramidal 1/5/1 arrangements.[7] Recently, we had explored for $[W(N_3)_7]^-$ the relative energies of these three arrangements at the B3LYP(3)/SBKJ+(d) level of theory. Two stable minimum energy configurations, a 1/5/1 and a 1/4/2 structure, were located, with the former being favored by 3.3 kcal/mol.[5] We now repeated these calculations for the $[Ta(N_3)_7]^{2-}$ anion. At the B3LYP(5)/SBKJ+(d) level of theory, the 1/4/2 arrangement is favored by 1.0 kcal/mol. However, at the MP2/SBKJ+(d) level of theory, the 1/5/1 arrangement is lower in energy by 2.9 kcal/mol. In view of the small energy differences and the sensitivity to the level of theory used, theoretical predictions do not allow the reliable prediction of a preferred structure, even for the free gaseous species. In the solid state, small differences in packing energies could further complicate this situation. Therefore, experimental crystal structures are needed for distinguishing between the different possible arrangements.

Single crystals of $[P(C_6H_5)_4]_2[Nb(N_3)_7]\cdot CH_3CN$ and $[P(C_6H_5)_4]_2[Ta(N_3)_7]\cdot CH_3CN$ were grown by recrystallization from CH_3CN by slowly evaporating the solvent at reduced pressure. The two salts are isostructural and crystallize in the triclinic space group $P\overline{1}$. Their crystal structure analyses[8,9] reveal well separated units of $[PPh_4]^+$ and $[M(N_3)_7]^{2-}$ ions and CH_3CN, with no significant cation-anion, anion-anion and ion-CH_3CN interactions (Figure 2). The closest Nb···N and N···N contacts between neighboring anions are 7.11 Å and 4.02 Å, respectively.[4p]

In these $[P(C_6H_5)_4]_2[M(N_3)_7]\cdot CH_3CN$ salts, the anions (Figure 3) are only slightly distorted from the ideal 1/4/2 arrangement, favored by the density functional calculations for the free gaseous anions, and are similar to one of the two structures predicted for $[Mo(N_3)_7]^-$ and $[W(N_3)_7]^-$.[5] The average Nb-N distance of 2.125(28) Å in $[Nb(N_3)_7]^{2-}$ is considerably larger than those of 1.997(37) Å and 2.028(30) Å found[4p] for $CH_3CN{\cdot}Nb(N_3)_5$ and $[Nb(N_3)_6]^-$, respectively, as expected from the higher negative charge in the former which increases the ionic character of the azide ligands. The average Nb-N-N bond angle in $[Nb(N_3)_7]^{2-}$ amounts to 127.5°.

The observed infrared and Raman spectra of $[PPh_4]_2[Nb(N_3)_7]{\cdot}CH_3CN$ and $[PPh_4]_2[Ta(N_3)_7]{\cdot}CH_3CN$ are shown in Figures 4 and 5, respectively, and the observed and calculated frequencies and intensities are listed in Table 1. The observed frequencies and intensities are in fair agreement with those calculated. The vibrations due to the azido ligands occur in clusters of seven, one in-phase and six out-of-phase combinations, with the in-phase one being readily identified by its higher Raman intensity. The MN_7 skeletal modes were treated as ideal 1/4/2 structures of C_{2v} symmetry, in accord with the vibrational analysis of Beuter, Kuhlmann and Sawodny for heptafluorides.[11] Compared to the neutral pentaazides and hexaazido anions, the addition of a negatively charged N_3^- anion increases the ionicity of the metal-azide bonds and the ionic character of the azide ligands in the $[M(N_3)_7]^{2-}$ anions. With increasing ionic character, the M-N bonds are weakened and both the triple and the single N-N bonds of the covalent azides adopt more double bond character. This decreases the N≡N (antisymmetric) N_3 ligand and the MN_7 skeletal stretching frequencies and increases the N-N (symmetric) N_3 ligand stretching frequencies, which is clearly observed in our spectra.

In conclusion, $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$, the first examples of heptaazido dianions, have been prepared. They were structurally characterized and shown to possess monocapped prismatic 1/4/2 structures. Although the azido ligand can be considered to be a pseudohalide, it appears that the structures of these transition metal heptaazide dianions differ from those of the corresponding heptafluoride ions, which are monocapped octahedra, and the actinide heptaazido trianion, $[U(N_3)_7]^{3-}$, which can crystallize either as a monocapped octahedron or a pentagonal bipyramid.

Experimental Section

Caution! *Covalent azides are potentially hazardous and can decompose explosively under various conditions! They should be handled only on a scale of less than 1 mmol. Because of the high energy content and high detonation velocities of these azides, their explosions are particularly violent and can cause, even on a one mmol scale, significant damage. The use of appropriate safety precautions (safety and face shields, leather gloves, protective clothing, such as heavy leather welding suits and ear plugs) is mandatory. Teflon containers should be used, whenever possible, to avoid hazardous shrapnel formation. The manipulation of these materials is facilitated by handling them, whenever possible, in solution to avoid detonation propagation, the use of large inert counter-ions as spacers, and anion formation which increases the partial negative charges on the terminal* N_γ *atoms and thereby reduces the* N_β-N_γ *triple bond character.* ***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. All reaction vessels were passivated with ClF_3 prior to use. Nonvolatile materials were handled in the dry argon atmosphere of a glove box.

Raman spectra were recorded at –80 °C directly in the Teflon reactors in the range 3500–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrophotometer, using a Nd-YAG laser at 1064 nm with power levels less than 50 mW(!). Infrared spectra were recorded in the range 4000-400 cm^{-1} on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample.

The starting materials NbF_5, TaF_5 (both Ozark Mahoning) and $[P(C_6H_5)_4]I$ (Aldrich) were used without further purification. $(CH_3)_3SiN_3$ (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $Nb(N_3)_5$ and $Ta(N_3)_5$ was freshly prepared from Me_3SiN_3 and NbF_5 and TaF_5, respectively, prior to use.[4p] $[P(C_6H_5)_4]N_3$ was obtained from $[P(C_6H_5)_4]Cl$ by anion-exchange in aqueous solution.[12]

Preparation of $[M(N_3)_7]^{2-}$ salts (M = Nb, Ta): Neat PPh_4N_3 (0.40 mmol) was added to a frozen solution of $M(N_3)_5$ (0.20 mmol) in CH_3CN (25 mmol) at –78 °C. The reaction mixture was warmed to -25 °C and occasionally agitated. After 30 minutes, all volatiles were removed at -20 °C in a dynamic vacuum, leaving behind solid $[M(N_3)_7]^{2-}$ salts.

$[P(C_6H_5)_4]_2[Nb(N_3)_7]\cdot CH_3CN$: orange solid, 0.193 g, expected for 0.20 mmol: 0.221 g.

$[P(C_6H_5)_4]_2[Ta(N_3)_7]\cdot CH_3CN$: pale yellow solid, 0.242 g, expected for 0.20 mmol: 0.239 g.

Computational Methods: The molecular structures and harmonic vibrational frequencies were calculated using previously described methods and basis sets.[5]

Received: , 2006

Keywords: Crystal structure, heptaazidoniobate(V), heptaazidotantalate(V), vibrational spectra, binary Group 5 azides, theoretical calculations

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[8] Crystal data for $C_{50}H_{43}N_{22}NbP_2$: M_r = 1106.91, triclinic, space group P-1, a = 10.7669(10), b = 11.2290(10), c = 24.053(2) Å, α = 83.196(2), β = 81.576(2), γ = 61.5450(10)°, V = 2525.2(4) Å^3, $F(000)$ = 1136, $\rho_{calcd.}$ (Z = 2) = 1.456 g·cm^{-3}, μ = 0.363 mm^{-1}, approximate crystal dimensions 0.32 x 0.25 x 0.09 mm^3, θ range = 1.71 to 27.45°, index ranges $-13 \leq h \leq 13$, $-14 \leq k \leq 10$, $-25 \leq l \leq 31$, Mo$_{K\alpha}$ (λ = 0.71073 Å), T = 133(2) K, 15500 measured data (Bruker 3-circle, SMART APEX CCD with χ-axis fixed at 54.74°, using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 10839 (R_{int} = 0.0275) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2001), transmission factors min/max ratio = 0.803. Structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2, data to parameters ratio: 16.0 : 1, final R indices [$I>2\sigma(I)$]: $R1$ = 0.0436, $wR2$ = 0.0976, R indices (all data): $R1$ = 0.0647, $wR2$ = 0.1039, GOF on F^2 = 1.024. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 269626.

[9] Crystal data for $C_{50}H_{43}N_{22}P_2Ta$: M_r = 1194.95, triclinic, space group P-1, a = 10.7596(9), b = 11.2429(10), c = 24.043(2) Å, α = 83.1580(10), β = 81.5910(10), γ = 61.6170(10)°, V

= 2527.3(4) Å^3, *F(000)* = 1200, $\rho_{calcd.}$ (Z = 2) = 1.570 g·cm^{-3}, μ = 2.299 mm^{-1}, approximate crystal dimensions 0.37 x 0.36 x 0.15 mm^3, θ range = 1.72 to 27.54°, index ranges $-10 \leq h \leq 13$, $-10 \leq k \leq 14$, $-31 \leq l \leq 31$, $\mathrm{Mo}_{K\alpha}$ (λ = 0.71073 Å), T = 123(2) K, 15609 measured data (Bruker 3-circle, SMART APEX CCD with χ-axis fixed at 54.74°, using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 10936 (R_{int} = 0.0207) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2001), transmission factors min/max ratio: 0.785. Structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2, data to parameters ratio = 16.0 : 1, final R indices [$I>2\sigma(I)$]: $R1$ = 0.0242, $wR2$ = 0.0635, R indices (all data): $R1$ = 0.0258, $wR2$ = 0.0641, GOF on F^2 = 1.041. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 269627.

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Figure 1. Possible arrangements for heptacoordinated transition metals: (1/5/1); (a) monocapped octahedron (1/3/3), (b) monocapped trigonal prism (1/4/2), and (c) pentagonal bipyramid (1/5/1) .

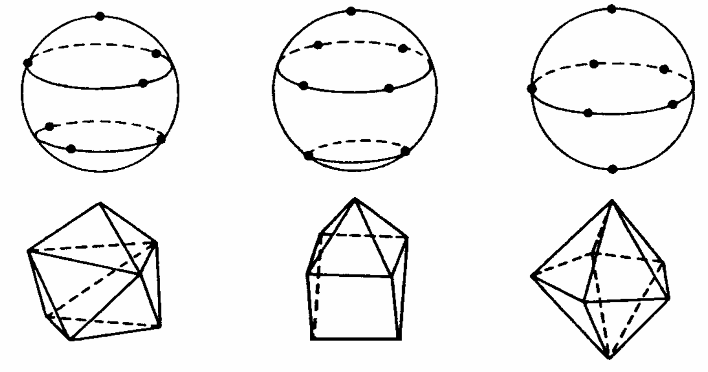

(a) (b) (c)

Figure 2. Packing diagram of $[P(C_6H_5)_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

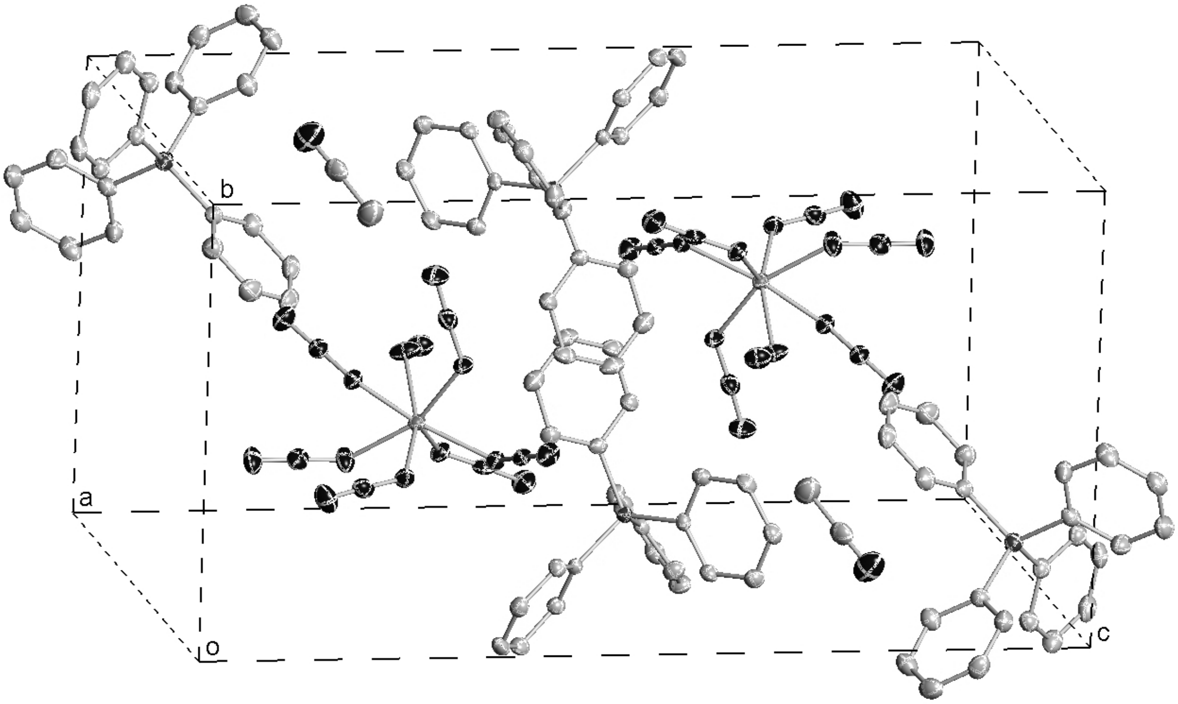


Figure 3. ORTEP drawing of the $[M(N_3)_7]^{-2}$ (M = Nb, Ta) di-anions. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: Nb-N1 2.121(2), Nb-N4 2.114(2), Nb-N7 2.091(2), Nb-N10 2.171(2), Nb-N13 2.140(2), Nb-N16 2.140(2), Nb-N19 2.096(2), N1-N2 1.209(3), N2-N3 1.140(3), N7-N8 1.217(3), N8-N9 1.138(3), N1-Nb-N4 74.21(9), N1-Nb-N7 84.02(10), N1-Nb-N10 79.50(9), N1-Nb-N13 90.63(10), N1-Nb-N16 126.23(9), N1-Nb-N19 157.34(10), Nb-N1-N2 130.2(2), N1-N2-N3 176.3(3).

Ta-N1 2096(2), Ta-N4 2.129(2), Ta-N7 2.164(2), Ta-N10 2.130(2), Ta-N13 2.107(2), Ta-N16 2.116(2), Ta-N19 2.087(2), N1-N2 1.210(3), N2-N3 1.139(3), N7-N8 1.202(3), N8-N9 1.146(3), N1-Ta-N4 80.88(9), N1-Ta-N7 78.19(8), N1-Ta-N10 75.13(8), N1-Ta-N13 124.62(8), N1-Ta-N16 156.92(9), N1-Ta-N19 96.11(9), Ta-N1-N2 125.89(18), N1-N2-N3 177.5(3).

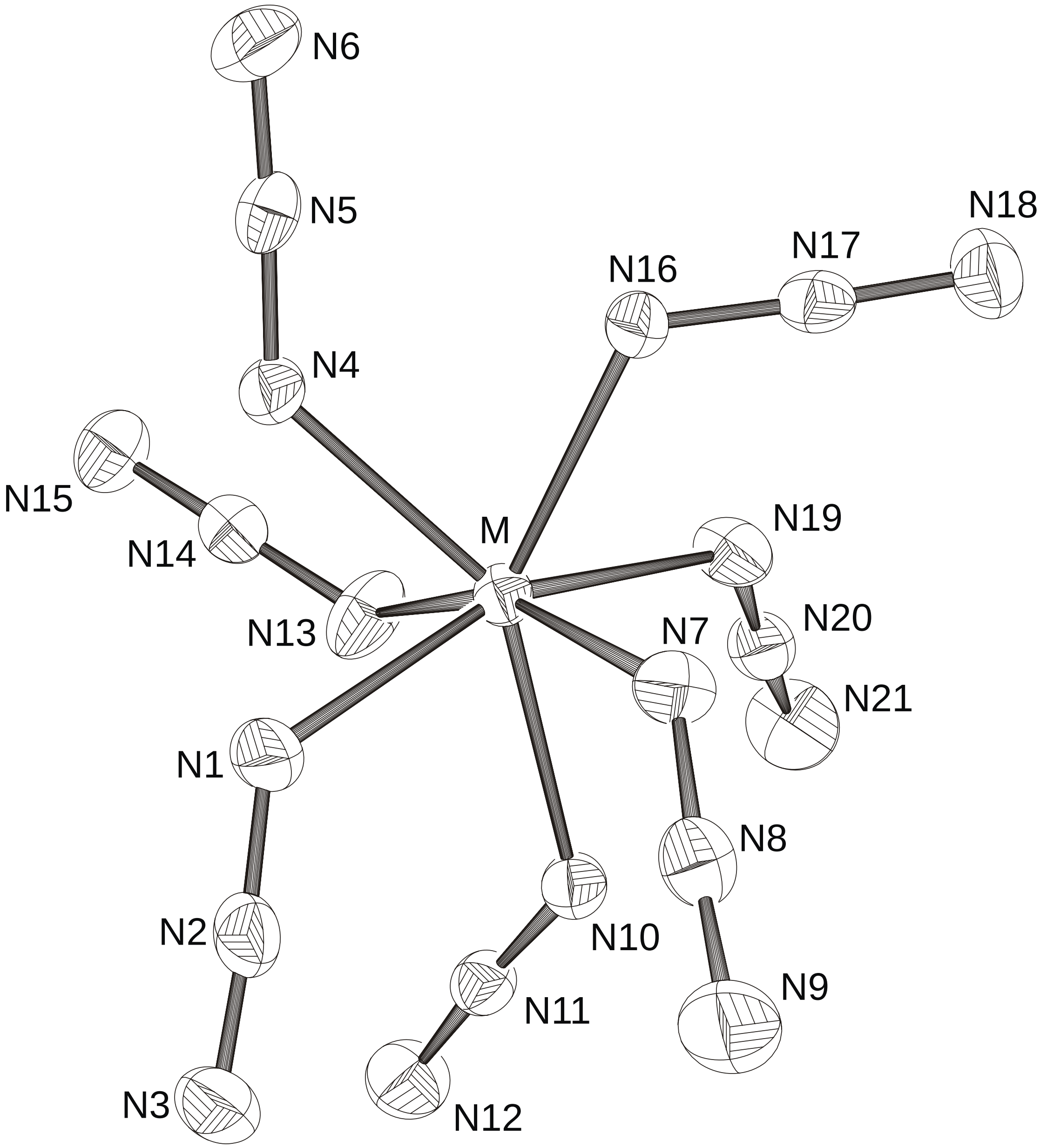


Figure 4. IR and Raman spectra of solid $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$. The bands belonging to the $[Nb(N_3)_7]^{2-}$ anion are marked by asterisks (*).The band marked with a diamond (♦) is due to the Teflon-FEP sample tube.

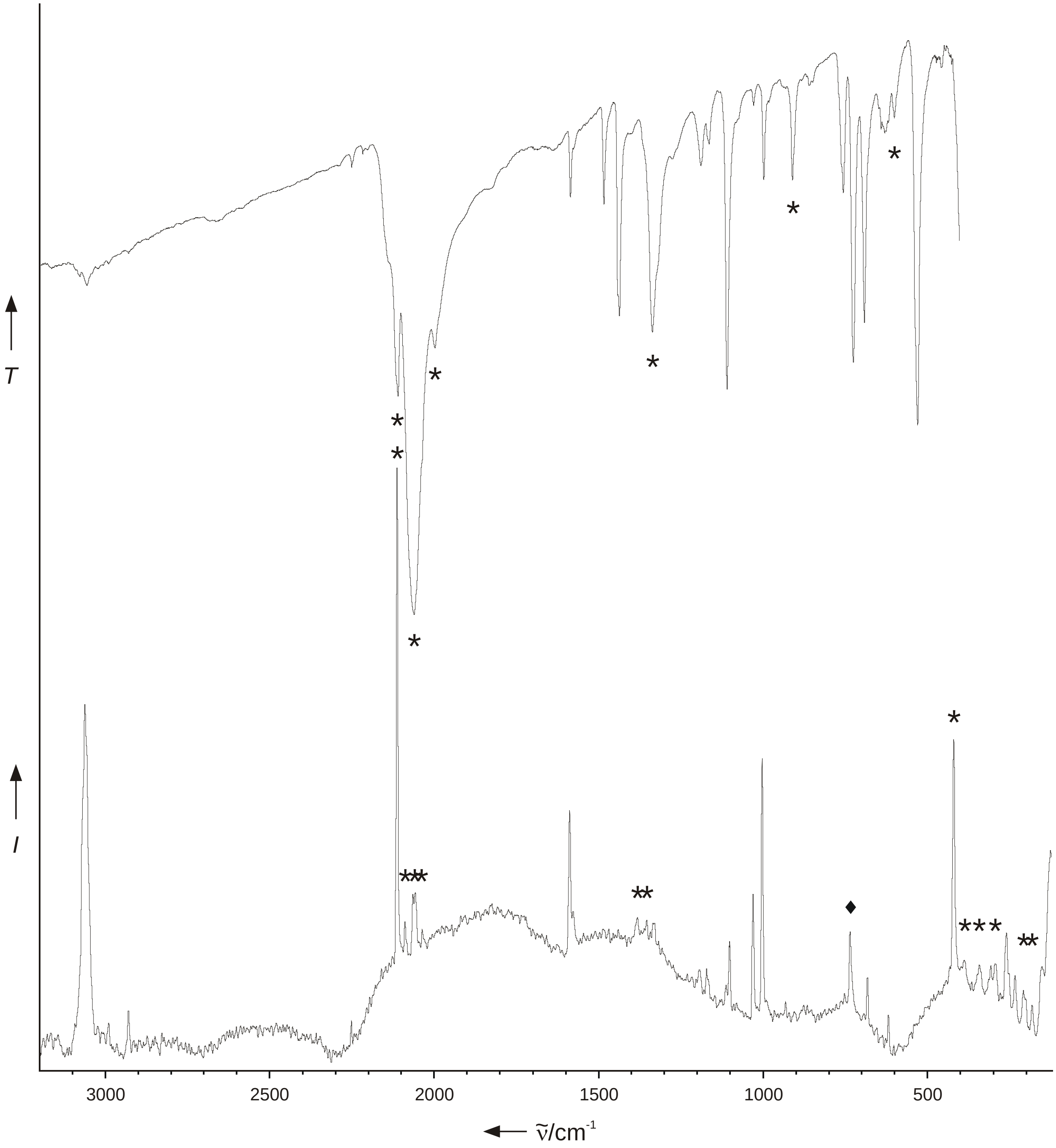


Figure 5. IR and Raman spectra of solid $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$. The bands belonging to the $[Ta(N_3)_7]^{2-}$ anion are marked by asterisks (*). The band marked by a diamond (♦) is due to the Teflon-FEP sample tube.

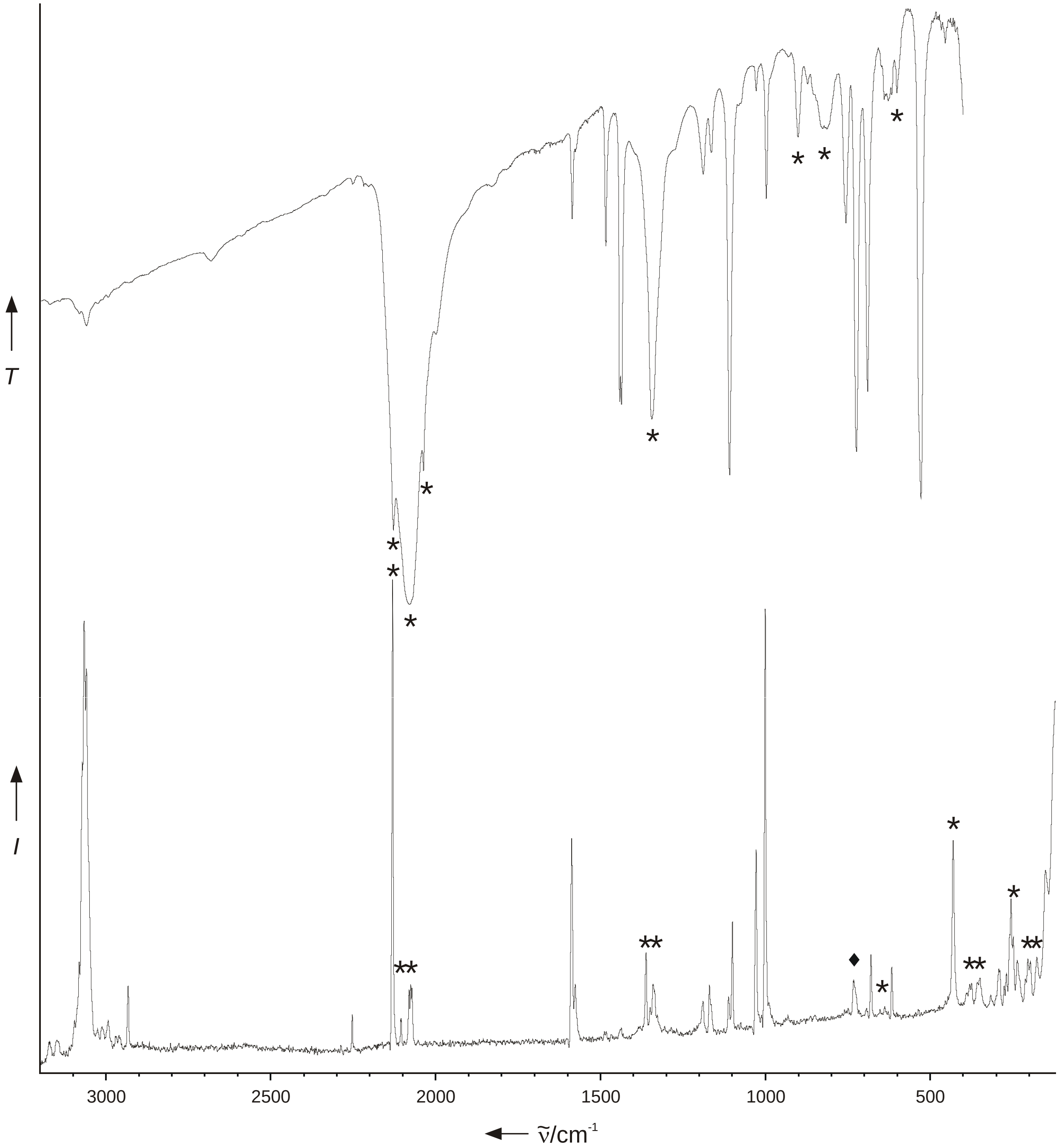


Table 1. Comparison of observed and unscaled calculated[a] vibrational frequencies [cm^{-1}] and intensities[b] of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$.

		$[Nb(N_3)_7]^{2-}$ [c]				$[Ta(N_3)_7]^{2-}$ [d]			
	appr. mode	observed		calculated (IR) [Ra]		observed		calculated (IR) [Ra]	
	Description[e]	IR	Ra	B3LYP(5)	MP2	IR	Ra	B3LYP(5)	MP2
ν_1		2113 s	2115 [10.0]	2182 (328) [1042]	2175 (139) [25]	2130 s	2131 [10.0]	2209 (234) [868]	2202 (657) [24]
ν_2			2090 [2.3]	2148 (3032) [63]	2171 (595) [23]		2105 [1.2]	2174 (2962) [57]	2198 (638) [18]
ν_3	$\nu_{as}N_3$,	2065 vs	2066 [2.6]	2142 (1516) [117]	2161 (526) [112]	2081 vs		2154 (3248) [66]	2197 (503) [21]
ν_4	1 in-phase,			2140 (1773) [143]	2161 (1473) [16]		2081[1.7]	2151 (799) [120]	2184 (896) [37]
ν_5	6 out-of-phase			2137 (2395) [67]	2157 (1571) [32]	2037 s		2151 (2297) [52]	2180 (729) [24]
ν_6			2058 [2.6]	2135 (16) [209]	2148 (947) [27]		2076 [1.9]	2149 (244) [127]	2173 (956) [9.2]
ν_7		2000 m	2038 [2.1]	2121 (20) [108]	2131 (71) [826]	1999 m	2072 [1.8]	2138 (139) [113]	2160 (165) [219]
ν_8			1381 [2.0]	1396 (28) [38]	1282 (68) [39]		1362 [2.5]	1432 (17) [95]	1292 (42) [37]
ν_9				1386 (280) [9.8]	1279 (107) [5.9]		1350 [1.4]	1420 (289) [19]	1290 (39) [64]
ν_{10}	ν_sN_3,		1353 [1.9]	1382 (79) [22]	1277 (9.1) [117]		1341 [1.8]	1394 (25) [53]	1284 (46) [62]
ν_{11}	1 in-phase,			1380 (193) [5.8]	1275 (52) [74]		1336 [1.7]	1386 (248) [9.5]	1281 (64) [105]
ν_{12}	6 out-of-phase			1377 (16) [21]	1272 (28) [76]	1346 s		1386 (277) [7.4]	1275 (60) [64]
ν_{13}		1337 m		1375 (291) [4.1]	1260 (72) [59]		1328 [1.2]	1385 (37) [21]	1267 (66) [62]
ν_{14}				1372 (62) [14]	1257 (49) [70]			1384 (85) [20]	1265 (44) [67]
ν_{15}				635 (6.8) [1.1]	612 (4.5) [1.5]		652 [1.3]	629 (6.0) [1.1]	602 (3.7) [2.8]
ν_{16}		640 w		631 (14) [1.0]	610 (2.5) [2.6]	641 w		626 (13) [0.3]	597 (2.9) [1.0]
ν_{17}	δN_3 in-plane,	627 w		629 (11) [0.9]	608 (8.5) [2.8]		638 [1.4]	625 (4.1) [1.0]	594 (7.2) [2.4]
ν_{18}	1 in-phase,			628 (3.8) [1.0]	606 (2.1) [2.4]	627 w		623 (7.6) [0.4]	592 (6.3) [5.2]
ν_{19}	6 out-of-phase			625 (3.3) [1.1]	605 (4.9) [4.6]			623 (3.5) [1.0]	580 (6.3) [2.2]
ν_{20}		598 w		612 (9.3) [1.5]	594 (48) [5.5]	602 w		609 (11) [0.3]	573 (3.4) [4.2]
ν_{21}				607 (20) [1.7]	590 (1.5) [22]			604 (1.5) [0.2]	568 (1.0) [0.1]
ν_{22}				599 (7.6) [0.7]	558 (1.5) [0.8]			602 (16) [0.4]	563 (2.0) [0.9]
ν_{23}				598 (6.6) [1.0]	555 (1.7) [2.2]			601 (2.4) [0.2]	560 (1.3) [2.3]
ν_{24}	δN_3 out-of-plane,			591 (6.8) [0.7]	550 (1.6) [1.3]			599 (0.6) [0.5]	558 (8.0) [2.8]
ν_{25}	1 in-phase,			588 (1.7) [0.5]	545 (1.9) [1.0]			597 (7.9) [2.5]	549 (1.9) [0.8]
ν_{26}	6 out-of-phase			588 (9.3) [0.2]	540 (1.0) [0.9]			591 (13) [0.4]	541 (5.3) [1.3]
ν_{27}				585 (5.1) [0.2]	539 (1.9) [0.4]			583 (6.7) [0.3]	525 (2.5) [0.5]
ν_{28}				581 (5.5) [0.4]	537 (2.8) [0.7]			579 (5.6) [0.6]	505 (0.4) [0.3]
ν_{29}			418 [5.5]	382 (9.6) [93]	406 (339) [10]		431 [4.7]	388 (0.1) [77]	410 (1.3) [92]
ν_{30}	νMN_7,			377 (353) [4.2]	400 (404) [1.9]		389 [1.6]	361 (20) [11]	382 (162) [4.0]
ν_{31}	3 A_1		384 [1.9]	371 (305) [7.2]	397 (375) [11]		380 [1.8]	359 (10) [12]	379 (236) [7.8]
ν_{32}	1 A_2			366 (292) [0.7]	391 (51) [201]		375 [1.9]	346 (161) [1.2]	366 (239) [9.7]
ν_{33}	2 B_1		339 [1.8]	337 (10) [10]	355 (3.7) [28]		357 [1.9]	343 (169) [0.2]	343 (48) [22]
ν_{34}	1 B_2			329 (21) [14]	347 (13) [34]		349 [2.0]	335 (283) [2.7]	329 (8.1) [13]
ν_{35}			305 [1.9]	306 (1.5) [1.9]	331 (4.9) [27]			315 (1.8) [1.6]	316 (17) [12]
ν_{36}				278 (64) [3.3]	272 (52) [6.6]			262 (49) [6.1]	287 (48) [3.4]
ν_{37}				270 (58) [2.4]	269 (22) [2.9]			260 (49) [3.5]	286 (90) [6.9]
ν_{38}	δMN_7,			269 (23) [2.1]	265 (37) [4.6]			255 (132) [1.7]	258 (26) [15]
ν_{39}	3 A_1			260 (13) [3.9]	259 (32) [3.9]		248 [2.8]	253 (94) [6.9]	251 (44) [3.5]
ν_{40}	2 A_2		230 [1.7]	242 (8.1) [5.9]	246 (13) [2.5]			238 (25) [1.7]	248 (30) [4.5]
ν_{41}	3 B_1			215 (3.4) [5.8]	222 (3.1) [2.7]			220 (2.5) [4.2]	236 (15) [18]
ν_{42}	3 B_2		206 [1.5]	210 (2.5) [13]	219 (2.3) [2.6]		204 [2.4]	212 (2.5) [3.7]	226 (28) [3.4]
ν_{43}				203 (0.1) [2.3]	213 (1.7) [12]			200 (4.2) [1.4]	219 (26) [5.1]
ν_{44}				196 (1.4) [8.0]	211 (2.9) [7.4]		196 [2.3]	195 (4.0) [16]	209 (7.1) [9.5]
ν_{45}			179 [1.3]	155 (1.2) [33]	149 (7.2) [3.6]		177 [2.4]	163 (0.5) [26]	147 (3.6) [7.7]
ν_{46}				137 (5.9) [5.6]	146 (6.1) [12]			148 (2.9) [1.4]	137 (5.3) [6.3]
ν_{47}				135 (5.1) [2.2]	135 (0.5) [38]			144 (4.4) [2.9]	113 (7.1) [8.5]
ν_{48}				95 (1.9) [7.2]	98 (2.2) [9.4]			94. (1.6) [5.7]	92 (0.0) [7.4]
ν_{49}				89 (0.6) [11]	94 (3.9) [4.8]			90 (2.5) [4.8]	82 (2.6) [5.3]
ν_{50}				85 (1.7) [14]	77 (1.8) [11]			88 (2.4) [9.7]	68 (2.2) [12]
ν_{51}				82 (2.1) [3.1]	76 (1.2) [12]			87 (0.4) [16]	65 (7.1) [10]
ν_{52}				78 (1.6) [3.8]	75 (4.0) [9.3]			83 (3.4) [5.2]	63 (2.4) [19]
ν_{53}	torsional			64 (0.2) [15]	70 (0.8) [26]			77 (0. 8) [13]	56 (0.7) [13]
ν_{54}	modes			49 (1.1) [14]	52 (0.3) [6.0]			51 (4.6) [1.6]	52 (0.3) [8.5]
ν_{55}				46 (0.0) [21]	47 (3.4) [16]			44 (2.5) [15]	45 (2.5) [11]
ν_{56}				43 (2.9) [4.0]	43 (1.3) [17]			39 (0.3) [22]	45 (1.2) [5.8]
ν_{57}				32 (0.2) [14]	35 (0.3) [16]			32 (0.7) [9.9]	40 (0.2) [24]
ν_{58}				31 (0.3) [7.3]	33 (0.3) [17]			21 (1.5) [2.9]	26 (0.6) [2.5]
ν_{59}				23 (0.3) [6.2]	26 (0.3) [8.4]			20 (0.2) [11]	21 (0.5) [5.3]
ν_{60}				17 (0.6) [2.6]	21 (0.7) [2.3]			6 (0.1) [1.3]	17 (0.9) [4.9]

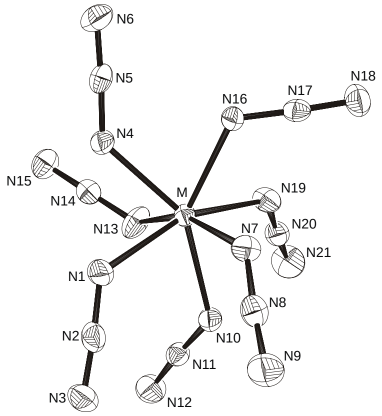
[a] Calculated at the B3LYP(5)/SBKJ+(d) level of theory. [b] Calculated IR intensities are given in parentheses (km mol^{-1}), and Raman intensities in brackets [Å^4 amu^{-1}]. [c] As $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$. In addition to the bands listed in this table, bands belonging to CH_3CN were observed in the Raman spectrum at 2933 [1.1] and 2257 [0.6] cm^{-1}. [d] As $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$. In addition to the bands listed in this table, bands belonging to CH_3CN were observed in the Raman spectrum at 2934 [1.8] and 2253 [1.3] cm^{-1}. [e] The mode assignments for the MN_7 skeletons were made assuming an ideal 1/4/2 arrangement of C_{2v} symmetry.

Synopsis

R. Haiges*, Jerry A. Boatz, Muhammed Yousufuddin, K. O. Christe*

Polyazide Chemistry: Synthesis and Properties of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$

Does the azide ligand behave as a true pseudo-halogen? Not necessarily, according to the authors who used doubly charged anions and bulky counter-ions to prepare and structurally characterize for the first time transition metal heptaazides. Contrary to the isolobal heptafluorides MoF_7^- and WF_7^-, the $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$ anions have trigonal prismatic 2/4/1 and not monocapped octahedral 1/3/3 structures.



Supplementary Material

Polyazide Chemistry: Synthesis and Properties of $[Nb(N_3)_7]^{2-}$ and $[Ta(N_3)_7]^{2-}$ [**]

Ralf Haiges[*], Jerry A. Boatz, Muhammed Yousufuddin, and Karl O. Christe[*]

Table S1. Crystal data and structure refinement for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Table S3. Bond lengths and angles for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Table S4. Anisotropic displacement parameters for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Table S5. Crystal data and structure refinement for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

Table S6. Atomic coordinates and equivalent isotropic displacement parameters for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

Table S7. Bond lengths and angles for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

Table S8. Anisotropic displacement parameters for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

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[**] This work was funded by the Air Force Office of Scientific Research, the Office of Naval Research and the National Science Foundation. We thank Prof. Dr. G. A. Olah for his steady support, and Prof. Dr. R. Bau and Drs. T. Schroer, S. Schneider and R. Wagner for their help and stimulating discussions.

Table S1. Crystal data and structure refinement for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Empirical formula	$C_{50}H_{43}N_{22}NbP_2$	
Formula weight	1106.91	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7669(10) Å	α = 83.196(2)°
	b = 11.2290(10) Å	β = 81.576(2)°
	c = 24.053(2) Å	γ = 61.5450(10)°
Volume	2525.2(4) $Å^3$	
Z	2	
Density (calculated)	1.456 Mg/m^3	
Absorption coefficient	0.363 mm^{-1}	
F(000)	1136	
Crystal size	0.32 x 0.25 x 0.09 mm^3	
Theta range for data collection	1.71 to 27.45°	
Index ranges	-13<=h<=13, -14<=k<=10, -25<=l<=31	
Reflections collected	15500	
Independent reflections	10839 [R(int) = 0.0275]	
Completeness to theta = 27.45°	93.8 %	
Transmission factors	min/max: 0.803	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10839 / 0 / 677	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0436, wR2 = 0.0976	
R indices (all data)	R1 = 0.0647, wR2 = 0.1039	
Largest diff. peak and hole	0.537 and -0.461 e.Å-3	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Nb(1)	7038(1)	5813(1)	7205(1)	19(1)
P(1)	7587(1)	565(1)	5837(1)	17(1)
P(2)	931(1)	2028(1)	9237(1)	22(1)
N(1)	5331(3)	7172(2)	7746(1)	32(1)
N(2)	5177(2)	7197(2)	8253(1)	29(1)
N(3)	4960(3)	7279(3)	8729(1)	38(1)
N(4)	5390(2)	7017(2)	6690(1)	24(1)
N(5)	5388(2)	7356(2)	6196(1)	24(1)
N(6)	5329(3)	7720(3)	5732(1)	36(1)
N(7)	8179(2)	6652(2)	7491(1)	26(1)
N(8)	8289(2)	6823(2)	7968(1)	28(1)
N(9)	8454(3)	6987(3)	8404(1)	43(1)
N(10)	7537(2)	4688(2)	8010(1)	24(1)
N(11)	6859(2)	4224(2)	8310(1)	24(1)
N(12)	6267(3)	3751(3)	8617(1)	37(1)
N(13)	6006(3)	4585(2)	7217(1)	35(1)
N(14)	4980(2)	4885(2)	6976(1)	24(1)
N(15)	4019(3)	5128(3)	6751(1)	33(1)
N(16)	8012(2)	6358(2)	6448(1)	22(1)
N(17)	9292(3)	5865(2)	6344(1)	23(1)
N(18)	10495(3)	5424(2)	6229(1)	34(1)
N(19)	8806(3)	3991(2)	6963(1)	29(1)
N(20)	9087(2)	2886(2)	7195(1)	27(1)
N(21)	9396(3)	1824(3)	7396(1)	45(1)
N(22)	5015(4)	192(3)	8223(1)	57(1)
C(1)	5919(3)	938(3)	6254(1)	17(1)
C(2)	5692(3)	-117(3)	6528(1)	21(1)
C(3)	4417(3)	172(3)	6852(1)	26(1)
C(4)	3352(3)	1498(3)	6884(1)	25(1)
C(5)	3556(3)	2541(3)	6603(1)	25(1)
C(6)	4836(3)	2277(3)	6285(1)	22(1)

C(7)	7438(3)	2129(3)	5493(1)	20(1)
C(8)	7418(3)	3084(3)	5826(1)	23(1)
C(9)	7184(3)	4344(3)	5590(1)	28(1)
C(10)	6981(3)	4659(3)	5025(1)	30(1)
C(11)	7017(3)	3721(3)	4692(1)	27(1)
C(12)	7252(3)	2448(3)	4928(1)	23(1)
C(13)	7868(3)	-641(2)	5342(1)	17(1)
C(14)	6824(3)	-322(3)	4989(1)	20(1)
C(15)	7004(3)	-1228(3)	4605(1)	24(1)
C(16)	8213(3)	-2481(3)	4587(1)	26(1)
C(17)	9230(3)	-2821(3)	4950(1)	25(1)
C(18)	9076(3)	-1897(3)	5321(1)	21(1)
C(19)	9068(3)	-171(3)	6247(1)	20(1)
C(20)	9227(3)	-1217(3)	6651(1)	26(1)
C(21)	10473(3)	-1925(3)	6906(1)	29(1)
C(22)	11557(3)	-1582(3)	6772(1)	27(1)
C(23)	11395(3)	-523(3)	6381(1)	27(1)
C(24)	10169(3)	166(3)	6109(1)	24(1)
C(25)	-721(3)	3112(3)	9625(1)	23(1)
C(26)	-1132(3)	2624(3)	10141(1)	30(1)
C(27)	-2445(3)	3420(3)	10425(1)	34(1)
C(28)	-3325(3)	4678(3)	10201(1)	30(1)
C(29)	-2913(3)	5172(3)	9695(1)	33(1)
C(30)	-1603(3)	4386(3)	9403(1)	27(1)
C(31)	1532(3)	3024(3)	8749(1)	22(1)
C(32)	2482(3)	3430(3)	8891(1)	29(1)
C(33)	2885(3)	4235(3)	8510(1)	36(1)
C(34)	2351(3)	4643(3)	7996(1)	36(1)
C(35)	1413(3)	4241(3)	7851(1)	31(1)
C(36)	1000(3)	3431(3)	8232(1)	28(1)
C(37)	687(3)	909(3)	8843(1)	23(1)
C(38)	1816(3)	84(3)	8464(1)	27(1)
C(39)	1699(3)	-868(3)	8197(1)	31(1)
C(40)	476(3)	-998(3)	8296(1)	35(1)
C(41)	-653(3)	-166(3)	8659(1)	32(1)
C(42)	-560(3)	792(3)	8934(1)	27(1)

C(43)	2177(3)	1039(3)	9741(1)	23(1)
C(44)	2920(3)	-367(3)	9729(1)	27(1)
C(45)	3829(3)	-1108(3)	10133(1)	31(1)
C(46)	4030(3)	-468(3)	10539(1)	33(1)
C(47)	3301(3)	933(3)	10549(1)	29(1)
C(48)	2359(3)	1688(3)	10161(1)	26(1)
C(49)	5613(3)	733(3)	7990(1)	34(1)
C(50)	6369(4)	1438(4)	7703(2)	50(1)

Table S3. Bond lengths [Å] and angles [°] for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$.

Nb(1)-N(7)	2.091(2)	C(4)-C(5)	1.374(4)	C(38)-C(39)	1.373(4)
Nb(1)-N(19)	2.096(2)	C(5)-C(6)	1.389(4)	C(39)-C(40)	1.377(4)
Nb(1)-N(4)	2.114(2)	C(7)-C(12)	1.384(4)	C(40)-C(41)	1.384(4)
Nb(1)-N(1)	2.121(2)	C(7)-C(8)	1.403(4)	C(41)-C(42)	1.377(4)
Nb(1)-N(16)	2.140(2)	C(8)-C(9)	1.379(4)	C(43)-C(44)	1.390(4)
Nb(1)-N(13)	2.140(2)	C(9)-C(10)	1.383(4)	C(43)-C(48)	1.400(4)
Nb(1)-N(10)	2.171(2)	C(10)-C(11)	1.381(4)	C(44)-C(45)	1.381(4)
P(1)-C(19)	1.793(3)	C(11)-C(12)	1.390(4)	C(45)-C(46)	1.376(4)
P(1)-C(7)	1.795(3)	C(13)-C(18)	1.391(3)	C(46)-C(47)	1.385(4)
P(1)-C(13)	1.796(2)	C(13)-C(14)	1.391(3)	C(47)-C(48)	1.374(4)
P(1)-C(1)	1.806(3)	C(14)-C(15)	1.381(4)	C(49)-C(50)	1.444(5)
P(2)-C(31)	1.790(3)	C(15)-C(16)	1.389(4)		
P(2)-C(37)	1.792(3)	C(16)-C(17)	1.382(4)	N(7)-Nb(1)-N(19)	96.26(9)
P(2)-C(25)	1.800(3)	C(17)-C(18)	1.382(4)	N(7)-Nb(1)-N(4)	119.73(9)
P(2)-C(43)	1.800(3)	C(19)-C(20)	1.392(4)	N(19)-Nb(1)-N(4)	123.66(9)
N(1)-N(2)	1.209(3)	C(19)-C(24)	1.393(4)	N(7)-Nb(1)-N(1)	84.02(10)
N(2)-N(3)	1.140(3)	C(20)-C(21)	1.384(4)	N(19)-Nb(1)-N(1)	157.34(10)
N(4)-N(5)	1.206(3)	C(21)-C(22)	1.380(4)	N(4)-Nb(1)-N(1)	74.21(9)
N(5)-N(6)	1.140(3)	C(22)-C(23)	1.383(4)	N(7)-Nb(1)-N(16)	76.22(9)
N(7)-N(8)	1.217(3)	C(23)-C(24)	1.389(4)	N(19)-Nb(1)-N(16)	75.33(9)
N(8)-N(9)	1.138(3)	C(25)-C(30)	1.380(4)	N(4)-Nb(1)-N(16)	73.57(9)
N(10)-N(11)	1.202(3)	C(25)-C(26)	1.395(4)	N(1)-Nb(1)-N(16)	126.23(9)
N(11)-N(12)	1.151(3)	C(26)-C(27)	1.387(4)	N(7)-Nb(1)-N(13)	158.58(10)
N(13)-N(14)	1.207(3)	C(27)-C(28)	1.370(4)	N(19)-Nb(1)-N(13)	80.85(10)
N(14)-N(15)	1.139(3)	C(28)-C(29)	1.379(4)	N(4)-Nb(1)-N(13)	78.23(9)
N(16)-N(17)	1.214(3)	C(29)-C(30)	1.389(4)	N(1)-Nb(1)-N(13)	90.63(10)
N(17)-N(18)	1.147(3)	C(31)-C(36)	1.381(4)	N(16)-Nb(1)-N(13)	122.73(10)
N(19)-N(20)	1.213(3)	C(31)-C(32)	1.398(4)	N(7)-Nb(1)-N(10)	79.61(9)
N(20)-N(21)	1.139(3)	C(32)-C(33)	1.380(4)	N(19)-Nb(1)-N(10)	78.27(9)
N(22)-C(49)	1.132(4)	C(33)-C(34)	1.374(4)	N(4)-Nb(1)-N(10)	144.76(9)
C(1)-C(2)	1.393(3)	C(34)-C(35)	1.386(4)	N(1)-Nb(1)-N(10)	79.50(9)
C(1)-C(6)	1.398(3)	C(35)-C(36)	1.391(4)	N(16)-Nb(1)-N(10)	141.67(9)
C(2)-C(3)	1.386(4)	C(37)-C(42)	1.394(4)	N(13)-Nb(1)-N(10)	79.01(9)
C(3)-C(4)	1.383(4)	C(37)-C(38)	1.403(4)	C(19)-P(1)-C(7)	109.13(12)

C(19)-P(1)-C(13)	108.05(12)	C(9)-C(8)-C(7)	119.6(3)	C(31)-C(36)-C(35)	120.0(3)
C(7)-P(1)-C(13)	112.07(12)	C(8)-C(9)-C(10)	120.1(3)	C(42)-C(37)-C(38)	120.2(2)
C(19)-P(1)-C(1)	113.09(12)	C(11)-C(10)-C(9)	120.7(3)	C(42)-C(37)-P(2)	121.1(2)
C(7)-P(1)-C(1)	107.58(12)	C(10)-C(11)-C(12)	119.5(3)	C(38)-C(37)-P(2)	118.6(2)
C(13)-P(1)-C(1)	106.97(11)	C(7)-C(12)-C(11)	120.2(2)	C(39)-C(38)-C(37)	119.5(3)
C(31)-P(2)-C(37)	107.92(13)	C(18)-C(13)-C(14)	119.7(2)	C(38)-C(39)-C(40)	120.1(3)
C(31)-P(2)-C(25)	110.12(12)	C(18)-C(13)-P(1)	121.3(2)	C(39)-C(40)-C(41)	120.7(3)
C(37)-P(2)-C(25)	109.90(12)	C(14)-C(13)-P(1)	118.86(19)	C(42)-C(41)-C(40)	120.3(3)
C(31)-P(2)-C(43)	112.37(13)	C(15)-C(14)-C(13)	120.4(2)	C(41)-C(42)-C(37)	119.2(3)
C(37)-P(2)-C(43)	109.14(13)	C(14)-C(15)-C(16)	119.5(3)	C(44)-C(43)-C(48)	119.7(3)
C(25)-P(2)-C(43)	107.37(13)	C(17)-C(16)-C(15)	120.4(2)	C(44)-C(43)-P(2)	120.6(2)
N(2)-N(1)-Nb(1)	130.2(2)	C(16)-C(17)-C(18)	120.2(3)	C(48)-C(43)-P(2)	119.6(2)
N(3)-N(2)-N(1)	176.3(3)	C(17)-C(18)-C(13)	119.8(2)	C(45)-C(44)-C(43)	119.6(3)
N(5)-N(4)-Nb(1)	132.76(19)	C(20)-C(19)-C(24)	119.2(3)	C(46)-C(45)-C(44)	120.6(3)
N(6)-N(5)-N(4)	177.0(3)	C(20)-C(19)-P(1)	120.3(2)	C(45)-C(46)-C(47)	119.9(3)
N(8)-N(7)-Nb(1)	130.20(19)	C(24)-C(19)-P(1)	119.8(2)	C(48)-C(47)-C(46)	120.4(3)
N(9)-N(8)-N(7)	176.5(3)	C(21)-C(20)-C(19)	120.2(3)	C(47)-C(48)-C(43)	119.7(3)
N(11)-N(10)-Nb(1)	127.63(18)	C(22)-C(21)-C(20)	120.4(3)	N(22)-C(49)-C(50)	178.7(3)
N(12)-N(11)-N(10)	176.3(3)	C(21)-C(22)-C(23)	119.7(3)		
N(14)-N(13)-Nb(1)	124.95(19)	C(22)-C(23)-C(24)	120.5(3)		
N(15)-N(14)-N(13)	177.9(3)	C(23)-C(24)-C(19)	119.9(3)		
N(17)-N(16)-Nb(1)	122.13(18)	C(30)-C(25)-C(26)	120.4(2)		
N(18)-N(17)-N(16)	177.8(3)	C(30)-C(25)-P(2)	120.5(2)		
N(20)-N(19)-Nb(1)	124.82(19)	C(26)-C(25)-P(2)	119.1(2)		
N(21)-N(20)-N(19)	177.2(3)	C(27)-C(26)-C(25)	119.4(3)		
C(2)-C(1)-C(6)	119.9(2)	C(28)-C(27)-C(26)	120.1(3)		
C(2)-C(1)-P(1)	119.82(19)	C(27)-C(28)-C(29)	120.6(3)		
C(6)-C(1)-P(1)	120.2(2)	C(28)-C(29)-C(30)	120.1(3)		
C(3)-C(2)-C(1)	119.7(2)	C(25)-C(30)-C(29)	119.4(3)		
C(4)-C(3)-C(2)	120.0(3)	C(36)-C(31)-C(32)	120.0(3)		
C(5)-C(4)-C(3)	120.5(3)	C(36)-C(31)-P(2)	118.7(2)		
C(4)-C(5)-C(6)	120.4(3)	C(32)-C(31)-P(2)	121.2(2)		
C(5)-C(6)-C(1)	119.3(3)	C(33)-C(32)-C(31)	119.5(3)		
C(12)-C(7)-C(8)	119.8(2)	C(34)-C(33)-C(32)	120.4(3)		
C(12)-C(7)-P(1)	122.3(2)	C(33)-C(34)-C(35)	120.6(3)		
C(8)-C(7)-P(1)	117.7(2)	C(34)-C(35)-C(36)	119.4(3)		

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4]_2[Nb(N_3)_7]\cdot CH_3CN$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Nb(1)	18(1)	16(1)	20(1)	0(1)	-2(1)	-8(1)
P(1)	18(1)	16(1)	18(1)	-1(1)	-2(1)	-8(1)
P(2)	19(1)	21(1)	23(1)	-2(1)	-1(1)	-8(1)
N(1)	26(1)	31(1)	25(1)	-2(1)	1(1)	-2(1)
N(2)	21(1)	24(1)	33(2)	1(1)	0(1)	-4(1)
N(3)	34(2)	37(2)	25(2)	-3(1)	4(1)	-5(1)
N(4)	21(1)	24(1)	25(1)	5(1)	-4(1)	-9(1)
N(5)	21(1)	15(1)	34(2)	0(1)	-7(1)	-7(1)
N(6)	40(2)	32(2)	31(2)	6(1)	-13(1)	-12(1)
N(7)	32(1)	28(1)	24(1)	-2(1)	-2(1)	-19(1)
N(8)	26(1)	26(1)	35(2)	-5(1)	0(1)	-15(1)
N(9)	45(2)	51(2)	35(2)	-16(1)	-2(1)	-23(2)
N(10)	22(1)	24(1)	23(1)	2(1)	-3(1)	-11(1)
N(11)	24(1)	23(1)	24(1)	1(1)	-5(1)	-9(1)
N(12)	40(2)	43(2)	35(2)	6(1)	-3(1)	-26(1)
N(13)	35(2)	26(1)	48(2)	12(1)	-19(1)	-17(1)
N(14)	28(1)	16(1)	27(1)	-1(1)	1(1)	-11(1)
N(15)	33(2)	32(2)	41(2)	0(1)	-11(1)	-19(1)
N(16)	19(1)	22(1)	22(1)	1(1)	-2(1)	-7(1)
N(17)	29(1)	19(1)	20(1)	4(1)	-3(1)	-10(1)
N(18)	23(1)	31(2)	41(2)	3(1)	2(1)	-9(1)
N(19)	33(1)	18(1)	27(1)	3(1)	2(1)	-7(1)
N(20)	25(1)	25(1)	26(1)	-5(1)	0(1)	-7(1)
N(21)	50(2)	20(1)	51(2)	3(1)	-1(1)	-7(1)
N(22)	72(2)	72(2)	49(2)	8(2)	-18(2)	-52(2)
C(1)	17(1)	21(1)	15(1)	-2(1)	-1(1)	-10(1)
C(2)	21(1)	17(1)	22(1)	-3(1)	-3(1)	-6(1)
C(3)	27(2)	25(2)	28(2)	-3(1)	0(1)	-15(1)
C(4)	23(1)	27(2)	25(2)	-7(1)	1(1)	-11(1)
C(5)	22(1)	21(1)	29(2)	-7(1)	0(1)	-6(1)
C(6)	23(1)	20(1)	23(2)	-3(1)	-4(1)	-11(1)
C(7)	18(1)	17(1)	25(2)	-1(1)	0(1)	-9(1)

C(8)	23(1)	20(1)	24(2)	-2(1)	0(1)	-9(1)
C(9)	25(2)	19(1)	37(2)	-5(1)	2(1)	-9(1)
C(10)	26(2)	20(2)	41(2)	6(1)	-3(1)	-10(1)
C(11)	24(2)	29(2)	28(2)	5(1)	-3(1)	-12(1)
C(12)	22(1)	21(1)	26(2)	-1(1)	-3(1)	-11(1)
C(13)	20(1)	19(1)	15(1)	-2(1)	1(1)	-12(1)
C(14)	19(1)	20(1)	21(1)	-2(1)	-1(1)	-8(1)
C(15)	26(2)	28(2)	21(2)	0(1)	-5(1)	-16(1)
C(16)	31(2)	24(2)	25(2)	-10(1)	5(1)	-16(1)
C(17)	23(1)	18(1)	29(2)	-3(1)	3(1)	-7(1)
C(18)	20(1)	20(1)	23(2)	-1(1)	-1(1)	-10(1)
C(19)	17(1)	21(1)	19(1)	-5(1)	-1(1)	-7(1)
C(20)	27(2)	27(2)	28(2)	1(1)	-6(1)	-17(1)
C(21)	35(2)	23(2)	27(2)	4(1)	-10(1)	-13(1)
C(22)	23(2)	30(2)	26(2)	-5(1)	-6(1)	-7(1)
C(23)	23(2)	37(2)	25(2)	-5(1)	-1(1)	-18(1)
C(24)	24(2)	26(2)	23(2)	2(1)	-3(1)	-12(1)
C(25)	18(1)	22(1)	27(2)	-5(1)	-1(1)	-9(1)
C(26)	29(2)	25(2)	32(2)	0(1)	1(1)	-10(1)
C(27)	32(2)	35(2)	31(2)	-7(1)	7(1)	-16(2)
C(28)	21(2)	32(2)	34(2)	-11(1)	1(1)	-9(1)
C(29)	28(2)	28(2)	33(2)	-5(1)	-8(1)	-2(1)
C(30)	28(2)	29(2)	20(2)	-1(1)	0(1)	-10(1)
C(31)	20(1)	19(1)	25(2)	-4(1)	4(1)	-6(1)
C(32)	31(2)	31(2)	28(2)	-1(1)	-4(1)	-15(1)
C(33)	35(2)	39(2)	42(2)	-5(2)	3(2)	-24(2)
C(34)	33(2)	33(2)	34(2)	0(1)	11(1)	-15(2)
C(35)	27(2)	32(2)	23(2)	0(1)	3(1)	-6(1)
C(36)	22(2)	31(2)	28(2)	-5(1)	1(1)	-10(1)
C(37)	23(1)	22(1)	24(2)	-1(1)	-3(1)	-10(1)
C(38)	22(2)	30(2)	28(2)	-5(1)	-3(1)	-9(1)
C(39)	31(2)	29(2)	29(2)	-7(1)	-6(1)	-8(1)
C(40)	48(2)	32(2)	31(2)	-1(1)	-11(2)	-23(2)
C(41)	35(2)	43(2)	30(2)	1(1)	-4(1)	-26(2)
C(42)	27(2)	31(2)	23(2)	-1(1)	-1(1)	-13(1)
C(43)	20(1)	24(2)	22(2)	-1(1)	1(1)	-9(1)

C(44)	25(2)	27(2)	27(2)	-5(1)	1(1)	-11(1)
C(45)	27(2)	30(2)	28(2)	2(1)	0(1)	-7(1)
C(46)	25(2)	42(2)	24(2)	2(1)	1(1)	-10(1)
C(47)	26(2)	42(2)	19(2)	-7(1)	1(1)	-17(1)
C(48)	24(2)	28(2)	24(2)	-2(1)	1(1)	-11(1)
C(49)	43(2)	35(2)	28(2)	-7(1)	-10(1)	-19(2)
C(50)	72(3)	58(2)	39(2)	-3(2)	-4(2)	-46(2)

Table S5. Crystal data and structure refinement for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

Empirical formula	$C_{50}H_{43}N_{22}P_2Ta$	
Formula weight	1194.95	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7596(9) Å	α = 83.1580(10)°
	b = 11.2429(10) Å	β = 81.5910(10)°
	c = 24.043(2) Å	γ = 61.6170(10)°
Volume	2527.3(4) Å^3	
Z	2	
Density (calculated)	1.570 Mg/m^3	
Absorption coefficient	2.299 mm^{-1}	
F(000)	1200	
Crystal size	0.37 x 0.36 x 0.15 mm^3	
Theta range for data collection	1.72 to 27.54°	
Index ranges	-10<=h<=13, -10<=k<=14, -31<=l<=31	
Reflections collected	15609	
Independent reflections	10936 [R(int) = 0.0207]	
Completeness to theta = 27.54°	93.8 %	
Transmission factors	min/max ratio:0.785	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10936 / 0 / 677	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0635	
R indices (all data)	R1 = 0.0258, wR2 = 0.0641	
Largest diff. peak and hole	1.192 and -0.618 e.Å^{-3}	

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ta(1)	7048(1)	5799(1)	7210(1)	17(1)
P(1)	7592(1)	560(1)	5838(1)	16(1)
P(2)	935(1)	2029(1)	9236(1)	20(1)
N(1)	8824(2)	3982(2)	6976(1)	26(1)
N(2)	9112(2)	2870(2)	7197(1)	25(1)
N(3)	9422(3)	1803(2)	7390(1)	41(1)
N(4)	6025(2)	4579(2)	7208(1)	30(1)
N(5)	4993(2)	4873(2)	6970(1)	22(1)
N(6)	4028(2)	5117(2)	6747(1)	30(1)
N(7)	7528(2)	4679(2)	8015(1)	21(1)
N(8)	6856(2)	4212(2)	8319(1)	23(1)
N(9)	6271(3)	3742(3)	8627(1)	33(1)
N(10)	8029(2)	6330(2)	6457(1)	21(1)
N(11)	9308(2)	5849(2)	6345(1)	21(1)
N(12)	10503(2)	5420(2)	6222(1)	31(1)
N(13)	5408(2)	7017(2)	6699(1)	23(1)
N(14)	5394(2)	7352(2)	6199(1)	22(1)
N(15)	5323(3)	7714(2)	5737(1)	33(1)
N(16)	5328(2)	7139(2)	7748(1)	30(1)
N(17)	5178(2)	7186(2)	8254(1)	27(1)
N(18)	4951(3)	7284(3)	8731(1)	36(1)
N(19)	8178(2)	6645(2)	7497(1)	25(1)
N(20)	8297(2)	6819(2)	7970(1)	26(1)
N(21)	8481(3)	6990(3)	8402(1)	40(1)
N(22)	5031(4)	184(4)	8216(1)	54(1)
C(1)	5923(2)	934(2)	6254(1)	17(1)
C(2)	4841(2)	2268(2)	6285(1)	20(1)
C(3)	3555(3)	2539(2)	6602(1)	23(1)
C(4)	3347(3)	1492(3)	6888(1)	24(1)
C(5)	4413(3)	161(3)	6853(1)	23(1)
C(6)	5696(2)	-124(2)	6533(1)	20(1)

C(7)	7869(2)	-640(2)	5344(1)	16(1)
C(8)	6816(2)	-310(2)	4988(1)	19(1)
C(9)	7002(3)	-1218(3)	4605(1)	23(1)
C(10)	8203(3)	-2474(3)	4587(1)	24(1)
C(11)	9226(3)	-2818(2)	4950(1)	23(1)
C(12)	9080(3)	-1897(2)	5326(1)	21(1)
C(13)	9083(2)	-184(2)	6248(1)	18(1)
C(14)	9231(3)	-1231(3)	6655(1)	23(1)
C(15)	10480(3)	-1936(3)	6911(1)	28(1)
C(16)	11568(3)	-1594(3)	6772(1)	26(1)
C(17)	11416(3)	-540(3)	6381(1)	26(1)
C(18)	10183(3)	157(3)	6111(1)	22(1)
C(19)	7446(2)	2127(2)	5499(1)	18(1)
C(20)	7252(2)	2448(3)	4929(1)	22(1)
C(21)	7019(3)	3720(3)	4698(1)	27(1)
C(22)	6982(3)	4660(3)	5031(1)	29(1)
C(23)	7199(3)	4335(3)	5595(1)	27(1)
C(24)	7433(3)	3070(2)	5831(1)	23(1)
C(25)	693(3)	909(2)	8842(1)	22(1)
C(26)	-551(3)	792(3)	8934(1)	26(1)
C(27)	-648(3)	-174(3)	8658(1)	31(1)
C(28)	486(3)	-1009(3)	8296(1)	33(1)
C(29)	1709(3)	-869(3)	8196(1)	30(1)
C(30)	1824(3)	92(3)	8465(1)	26(1)
C(31)	2179(2)	1041(3)	9740(1)	22(1)
C(32)	2359(3)	1693(3)	10158(1)	24(1)
C(33)	3305(3)	932(3)	10554(1)	28(1)
C(34)	4033(3)	-469(3)	10541(1)	30(1)
C(35)	3833(3)	-1107(3)	10132(1)	30(1)
C(36)	2921(3)	-363(3)	9727(1)	26(1)
C(37)	-712(2)	3108(2)	9623(1)	21(1)
C(38)	-1594(3)	4398(3)	9399(1)	26(1)
C(39)	-2907(3)	5181(3)	9691(1)	31(1)
C(40)	-3323(3)	4689(3)	10200(1)	28(1)
C(41)	-2444(3)	3415(3)	10424(1)	31(1)
C(42)	-1137(3)	2622(3)	10135(1)	28(1)

C(43)	1544(2)	3026(2)	8752(1)	22(1)
C(44)	2493(3)	3428(3)	8892(1)	28(1)
C(45)	2899(3)	4237(3)	8510(1)	35(1)
C(46)	2358(3)	4646(3)	7992(1)	33(1)
C(47)	1424(3)	4243(3)	7851(1)	30(1)
C(48)	1008(3)	3434(3)	8223(1)	26(1)
C(49)	5625(3)	725(3)	7986(1)	34(1)
C(50)	6377(4)	1445(4)	7703(1)	46(1)

Table S7. Bond lengths [Å] and angles [°] for $[PPh_4]_2[Ta(N_3)_7]\cdot CH_3CN$.

Ta(1)-N(19)	2.087(2)	C(5)-C(6)	1.389(3)	C(40)-C(41)	1.383(4)
Ta(1)-N(1)	2.096(2)	C(7)-C(12)	1.395(3)	C(41)-C(42)	1.388(4)
Ta(1)-N(13)	2.107(2)	C(7)-C(8)	1.402(3)	C(43)-C(44)	1.390(4)
Ta(1)-N(16)	2.116(2)	C(8)-C(9)	1.380(3)	C(43)-C(48)	1.409(3)
Ta(1)-N(4)	2.129(2)	C(9)-C(10)	1.389(4)	C(44)-C(45)	1.387(4)
Ta(1)-N(10)	2.130(2)	C(10)-C(11)	1.386(4)	C(45)-C(46)	1.386(4)
Ta(1)-N(7)	2.1644(19)	C(11)-C(12)	1.392(3)	C(46)-C(47)	1.377(4)
P(1)-C(7)	1.793(2)	C(13)-C(18)	1.394(3)	C(47)-C(48)	1.379(4)
P(1)-C(19)	1.797(2)	C(13)-C(14)	1.400(3)	C(49)-C(50)	1.451(4)
P(1)-C(13)	1.799(2)	C(14)-C(15)	1.387(3)		
P(1)-C(1)	1.804(2)	C(15)-C(16)	1.382(4)	N(19)-Ta(1)-N(1)	96.11(9)
P(2)-C(43)	1.789(3)	C(16)-C(17)	1.383(4)	N(19)-Ta(1)-N(13)	118.83(8)
P(2)-C(25)	1.794(3)	C(17)-C(18)	1.392(3)	N(1)-Ta(1)-N(13)	124.62(8)
P(2)-C(37)	1.795(2)	C(19)-C(20)	1.395(3)	N(19)-Ta(1)-N(16)	84.52(9)
P(2)-C(31)	1.798(2)	C(19)-C(24)	1.395(3)	N(1)-Ta(1)-N(16)	156.92(9)
N(1)-N(2)	1.210(3)	C(20)-C(21)	1.388(4)	N(13)-Ta(1)-N(16)	73.58(8)
N(2)-N(3)	1.139(3)	C(21)-C(22)	1.383(4)	N(19)-Ta(1)-N(4)	159.49(9)
N(4)-N(5)	1.208(3)	C(22)-C(23)	1.386(4)	N(1)-Ta(1)-N(4)	80.88(9)
N(5)-N(6)	1.141(3)	C(23)-C(24)	1.384(4)	N(13)-Ta(1)-N(4)	78.34(8)
N(7)-N(8)	1.202(3)	C(25)-C(26)	1.390(4)	N(16)-Ta(1)-N(4)	90.46(10)
N(8)-N(9)	1.146(3)	C(25)-C(30)	1.400(3)	N(19)-Ta(1)-N(10)	76.33(8)
N(10)-N(11)	1.215(3)	C(26)-C(27)	1.389(4)	N(1)-Ta(1)-N(10)	75.13(8)
N(11)-N(12)	1.144(3)	C(27)-C(28)	1.386(4)	N(13)-Ta(1)-N(10)	73.63(8)
N(13)-N(14)	1.215(3)	C(28)-C(29)	1.381(4)	N(16)-Ta(1)-N(10)	126.95(8)
N(14)-N(15)	1.137(3)	C(29)-C(30)	1.384(4)	N(4)-Ta(1)-N(10)	121.71(9)
N(16)-N(17)	1.209(3)	C(31)-C(36)	1.392(4)	N(19)-Ta(1)-N(7)	80.07(8)
N(17)-N(18)	1.144(3)	C(31)-C(32)	1.398(3)	N(1)-Ta(1)-N(7)	78.13(8)
N(19)-N(20)	1.210(3)	C(32)-C(33)	1.390(3)	N(13)-Ta(1)-N(7)	144.50(8)
N(20)-N(21)	1.140(3)	C(33)-C(34)	1.388(4)	N(16)-Ta(1)-N(7)	79.27(8)
N(22)-C(49)	1.126(4)	C(34)-C(35)	1.380(4)	N(4)-Ta(1)-N(7)	79.45(8)
C(1)-C(2)	1.397(3)	C(35)-C(36)	1.384(4)	N(10)-Ta(1)-N(7)	141.87(7)
C(1)-C(6)	1.402(3)	C(37)-C(42)	1.392(3)	C(7)-P(1)-C(19)	112.45(11)
C(2)-C(3)	1.390(3)	C(37)-C(38)	1.396(3)	C(7)-P(1)-C(13)	107.79(10)
C(3)-C(4)	1.387(4)	C(38)-C(39)	1.392(4)	C(19)-P(1)-C(13)	108.94(11)

C(4)-C(5)	1.389(3)	C(39)-C(40)	1.385(4)	C(7)-P(1)-C(1)	106.97(11)
C(19)-P(1)-C(1)	107.39(11)	C(10)-C(11)-C(12)	120.4(2)	C(38)-C(37)-P(2)	120.30(19)
C(13)-P(1)-C(1)	113.37(10)	C(11)-C(12)-C(7)	119.2(2)	C(39)-C(38)-C(37)	119.2(2)
C(43)-P(2)-C(25)	108.37(12)	C(18)-C(13)-C(14)	119.7(2)	C(40)-C(39)-C(38)	120.3(2)
C(43)-P(2)-C(37)	110.06(11)	C(18)-C(13)-P(1)	119.79(18)	C(41)-C(40)-C(39)	120.6(2)
C(25)-P(2)-C(37)	110.05(12)	C(14)-C(13)-P(1)	120.02(18)	C(40)-C(41)-C(42)	119.6(3)
C(43)-P(2)-C(31)	111.99(12)	C(15)-C(14)-C(13)	119.7(2)	C(41)-C(42)-C(37)	120.1(2)
C(25)-P(2)-C(31)	108.99(11)	C(16)-C(15)-C(14)	120.3(2)	C(44)-C(43)-C(48)	119.9(2)
C(37)-P(2)-C(31)	107.36(11)	C(15)-C(16)-C(17)	120.2(2)	C(44)-C(43)-P(2)	121.79(19)
N(2)-N(1)-Ta(1)	125.89(18)	C(16)-C(17)-C(18)	120.1(2)	C(48)-C(43)-P(2)	118.3(2)
N(3)-N(2)-N(1)	177.5(3)	C(17)-C(18)-C(13)	119.8(2)	C(45)-C(44)-C(43)	119.7(3)
N(5)-N(4)-Ta(1)	125.96(17)	C(20)-C(19)-C(24)	120.2(2)	C(46)-C(45)-C(44)	120.1(3)
N(6)-N(5)-N(4)	178.3(3)	C(20)-C(19)-P(1)	121.73(19)	C(47)-C(46)-C(45)	120.4(3)
N(8)-N(7)-Ta(1)	128.66(16)	C(24)-C(19)-P(1)	117.94(18)	C(46)-C(47)-C(48)	120.6(3)
N(9)-N(8)-N(7)	176.4(2)	C(21)-C(20)-C(19)	119.5(2)	C(47)-C(48)-C(43)	119.3(3)
N(11)-N(10)-Ta(1)	123.47(16)	C(22)-C(21)-C(20)	120.2(2)	N(22)-C(49)-C(50)	178.4(3)
N(12)-N(11)-N(10)	177.6(2)	C(21)-C(22)-C(23)	120.4(2)		
N(14)-N(13)-Ta(1)	133.26(17)	C(24)-C(23)-C(22)	120.1(2)		
N(15)-N(14)-N(13)	176.9(3)	C(23)-C(24)-C(19)	119.7(2)		
N(17)-N(16)-Ta(1)	130.36(18)	C(26)-C(25)-C(30)	120.7(2)		
N(18)-N(17)-N(16)	175.8(3)	C(26)-C(25)-P(2)	120.93(19)		
N(20)-N(19)-Ta(1)	130.97(18)	C(30)-C(25)-P(2)	118.25(19)		
N(21)-N(20)-N(19)	175.9(3)	C(27)-C(26)-C(25)	119.2(2)		
C(2)-C(1)-C(6)	119.8(2)	C(28)-C(27)-C(26)	120.2(3)		
C(2)-C(1)-P(1)	120.44(18)	C(29)-C(28)-C(27)	120.5(3)		
C(6)-C(1)-P(1)	119.77(17)	C(28)-C(29)-C(30)	120.2(2)		
C(3)-C(2)-C(1)	119.8(2)	C(29)-C(30)-C(25)	119.2(2)		
C(4)-C(3)-C(2)	120.2(2)	C(36)-C(31)-C(32)	120.1(2)		
C(3)-C(4)-C(5)	120.2(2)	C(36)-C(31)-P(2)	120.5(2)		
C(6)-C(5)-C(4)	120.1(2)	C(32)-C(31)-P(2)	119.39(19)		
C(5)-C(6)-C(1)	119.9(2)	C(33)-C(32)-C(31)	119.6(2)		
C(12)-C(7)-C(8)	120.3(2)	C(34)-C(33)-C(32)	119.9(2)		
C(12)-C(7)-P(1)	121.12(18)	C(35)-C(34)-C(33)	120.2(2)		
C(8)-C(7)-P(1)	118.59(17)	C(34)-C(35)-C(36)	120.6(3)		
C(9)-C(8)-C(7)	119.7(2)	C(35)-C(36)-C(31)	119.6(2)		
C(8)-C(9)-C(10)	120.2(2)	C(42)-C(37)-C(38)	120.2(2)		

C(11)-C(10)-C(9)	120.2(2)	C(42)-C(37)-P(2)	119.40(19)

Table S8. Anisotropic displacement parameters ($Å^2$x 10^3) for $[PPh_4]_2[Ta(N_3)_7]{\cdot}CH_3CN$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + \ldots\ + 2\, h\, k\, a^*\, b^*\, U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta(1)	16(1)	15(1)	17(1)	1(1)	-3(1)	-6(1)
P(1)	17(1)	15(1)	15(1)	0(1)	-3(1)	-7(1)
P(2)	17(1)	20(1)	20(1)	-1(1)	-2(1)	-7(1)
N(1)	26(1)	18(1)	25(1)	2(1)	2(1)	-6(1)
N(2)	24(1)	22(1)	22(1)	-2(1)	-1(1)	-6(1)
N(3)	47(2)	21(1)	43(1)	5(1)	-2(1)	-9(1)
N(4)	34(1)	23(1)	37(1)	11(1)	-18(1)	-15(1)
N(5)	26(1)	16(1)	26(1)	1(1)	-2(1)	-10(1)
N(6)	31(1)	29(1)	37(1)	2(1)	-10(1)	-17(1)
N(7)	18(1)	22(1)	21(1)	3(1)	-3(1)	-9(1)
N(8)	24(1)	22(1)	21(1)	1(1)	-8(1)	-8(1)
N(9)	36(1)	41(1)	28(1)	7(1)	-3(1)	-25(1)
N(10)	19(1)	21(1)	22(1)	2(1)	-2(1)	-8(1)
N(11)	27(1)	16(1)	19(1)	4(1)	-4(1)	-9(1)
N(12)	22(1)	26(1)	37(1)	4(1)	3(1)	-7(1)
N(13)	21(1)	22(1)	24(1)	4(1)	-6(1)	-9(1)
N(14)	19(1)	14(1)	28(1)	1(1)	-7(1)	-5(1)
N(15)	38(1)	28(1)	28(1)	6(1)	-13(1)	-10(1)
N(16)	24(1)	28(1)	24(1)	0(1)	-1(1)	-2(1)
N(17)	19(1)	24(1)	28(1)	0(1)	2(1)	-4(1)
N(18)	31(1)	37(1)	21(1)	-1(1)	2(1)	-3(1)
N(19)	31(1)	29(1)	20(1)	-2(1)	-2(1)	-19(1)
N(20)	24(1)	26(1)	29(1)	-5(1)	1(1)	-12(1)
N(21)	43(2)	47(2)	33(1)	-14(1)	-4(1)	-21(1)
N(22)	69(2)	73(2)	41(2)	8(2)	-17(1)	-49(2)
C(1)	16(1)	18(1)	15(1)	-3(1)	-2(1)	-6(1)
C(2)	21(1)	17(1)	21(1)	0(1)	-4(1)	-8(1)
C(3)	21(1)	20(1)	26(1)	-6(1)	-2(1)	-6(1)
C(4)	21(1)	28(1)	23(1)	-8(1)	2(1)	-12(1)
C(5)	24(1)	25(1)	22(1)	0(1)	-2(1)	-13(1)
C(6)	20(1)	15(1)	22(1)	-1(1)	-5(1)	-6(1)
C(7)	18(1)	18(1)	14(1)	-2(1)	0(1)	-9(1)

C(8)	19(1)	20(1)	18(1)	-1(1)	-2(1)	-8(1)
C(9)	24(1)	29(1)	19(1)	-4(1)	-4(1)	-14(1)
C(10)	28(1)	24(1)	22(1)	-7(1)	3(1)	-16(1)
C(11)	23(1)	19(1)	25(1)	-2(1)	1(1)	-8(1)
C(12)	21(1)	19(1)	21(1)	1(1)	-2(1)	-8(1)
C(13)	18(1)	19(1)	15(1)	-3(1)	-3(1)	-6(1)
C(14)	25(1)	24(1)	24(1)	4(1)	-8(1)	-14(1)
C(15)	31(1)	24(1)	28(1)	6(1)	-13(1)	-11(1)
C(16)	22(1)	27(1)	23(1)	-4(1)	-7(1)	-5(1)
C(17)	21(1)	34(1)	24(1)	-2(1)	-3(1)	-14(1)
C(18)	22(1)	24(1)	21(1)	1(1)	-4(1)	-11(1)
C(19)	18(1)	16(1)	21(1)	1(1)	-2(1)	-8(1)
C(20)	19(1)	23(1)	22(1)	1(1)	-3(1)	-10(1)
C(21)	26(1)	27(1)	26(1)	9(1)	-7(1)	-13(1)
C(22)	25(1)	19(1)	38(2)	8(1)	-4(1)	-9(1)
C(23)	24(1)	19(1)	36(1)	-5(1)	0(1)	-9(1)
C(24)	23(1)	22(1)	22(1)	-3(1)	0(1)	-10(1)
C(25)	21(1)	21(1)	22(1)	0(1)	-6(1)	-8(1)
C(26)	24(1)	30(1)	23(1)	0(1)	-3(1)	-13(1)
C(27)	36(2)	43(2)	26(1)	2(1)	-5(1)	-27(1)
C(28)	43(2)	31(1)	29(1)	-2(1)	-10(1)	-19(1)
C(29)	27(1)	29(1)	28(1)	-8(1)	-6(1)	-7(1)
C(30)	19(1)	30(1)	29(1)	-6(1)	-4(1)	-9(1)
C(31)	16(1)	25(1)	20(1)	0(1)	-1(1)	-8(1)
C(32)	24(1)	26(1)	21(1)	-4(1)	-2(1)	-11(1)
C(33)	24(1)	37(2)	20(1)	-5(1)	-1(1)	-11(1)
C(34)	22(1)	37(2)	22(1)	2(1)	-4(1)	-6(1)
C(35)	24(1)	25(1)	30(1)	0(1)	1(1)	-4(1)
C(36)	22(1)	24(1)	27(1)	-3(1)	0(1)	-8(1)
C(37)	18(1)	22(1)	21(1)	-3(1)	-1(1)	-8(1)
C(38)	25(1)	26(1)	21(1)	-1(1)	-5(1)	-7(1)
C(39)	26(1)	28(1)	28(1)	-3(1)	-7(1)	-1(1)
C(40)	21(1)	31(1)	30(1)	-10(1)	0(1)	-9(1)
C(41)	31(1)	34(2)	27(1)	-2(1)	5(1)	-16(1)
C(42)	26(1)	20(1)	29(1)	2(1)	1(1)	-7(1)
C(43)	18(1)	21(1)	21(1)	-2(1)	1(1)	-6(1)

C(44)	27(1)	32(1)	27(1)	-3(1)	-5(1)	-13(1)
C(45)	33(2)	35(2)	39(2)	-3(1)	3(1)	-20(1)
C(46)	32(1)	30(1)	31(1)	3(1)	6(1)	-13(1)
C(47)	25(1)	29(1)	23(1)	1(1)	0(1)	-5(1)
C(48)	18(1)	30(1)	23(1)	-3(1)	0(1)	-7(1)
C(49)	46(2)	36(2)	23(1)	0(1)	-12(1)	-20(1)
C(50)	66(2)	54(2)	35(2)	-3(1)	-4(2)	-41(2)