Synthesis and X-ray Structure of $[\{(Cp'_2Nb)_2WTe_4\}W(CO)_4]\cdot 1.5C_7H_8$, the First Organometallic Derivative of the WTe_4^{2-} Anion, and of $[Cp'_4Nb_2Te_2]$ ($Cp' = \eta^5\text{-}tBuC_5H_4$)

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Reaction of $[Cp'_2NbTe_2H]$ (**1**) ($Cp' = \eta^5\text{-}tBuC_5H_4$) with $[W(CO)_6]$ in decane at 140 °C gives red $[\{(Cp'_2Nb)_2WTe_4\}W(CO)_4]$ (**2**), whereas in the reaction of **1** with $[Cr(CO)_6]$ green-black $[Cp'_4Nb_2Te_2]$ (**3**) is formed. The crystal structures of **2** and **3** have been determined. The structure of **2** contains a slightly distorted WTe_4 tetrahedron to which two niobocene fragments and one $W(CO)_4$ group are coordinated. The crystal structure determination of **3** reveals the presence of two Cp'_2Nb units bridged by two Te atoms. Complex **2** represents the first example of an organometallic derivative of the unknown WTe_4^{2-} anion.

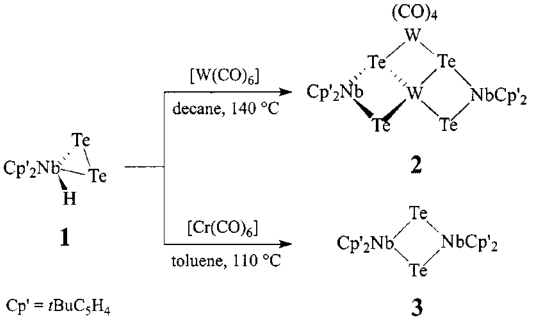
Introduction

Tetrathiometalates exhibit a rich structural chemistry upon coordination to inorganic and organometallic fragments.[1] The resulting heterometallic complexes possess more or less extended structures and they often show interesting electronic and optical properties.[1,2] Whereas an extension of this chemistry to MSe_4 compounds has been realized only very recently,[1,3] the corresponding tetratellurometalates are still unknown. This fact seems rather surprising if one takes into account the very varied coordination chemistry of Te-derived ligands.[4]

Recently, we have developed a synthetic method for the preparation of bimetallic tetrathio- and tetraselenometalates of the type $[(Cp^*_2Nb)_2ME_4]$ ($Cp^* = C_5Me_5$; M = Cr, Mo; E = S, Se). In these compounds the central "inorganic" core derives from a binary transition metal carbonyl, e.g. $[M(CO)_6]$, whereas the two peripheral niobocene units and the four chalcogen bridges are provided by $[Cp^*_2Nb(\eta^2\text{-}E_2)H]$, a niobocene(V) complex bearing a hydrido and a chalcogenido ligand.[5] In an extension of this work we now wish to report the synthesis of the first organometallic derivative of the still unknown WTe_4^{2-} salt from $[Cp'_2Nb(\eta^2\text{-}Te_2)H]$ (**1**; $Cp' = tBuC_5H_4$) and $[W(CO)_6]$. Complex **1** has been prepared from Cp'_2NbH_3 and elemental tellurium, and there is sufficient evidence that it bears an $\eta^2\text{-}Te_2$ ligand along with a hydride atom.[6]

Results and Discussion

The reaction of **1** with one equivalent of $[W(CO)_6]$ in decane (140 °C, 15 h) gives the red complex $[\{(Cp'_2Nb)_2WTe_4\}W(CO)_4]$ (**2**) in 54% yield [Equation (1)]. The composition of complex **2** follows from X-ray crystallography and elemental analyses. As a by-product, a dark green compound of composition $[Cp'_4Nb_2Te_2]$ (**3**) is formed in 6% yield. Compound **3** is formed in much better yield (64%) from the reaction of **1** with $[Cr(CO)_6]$ in boiling toluene along with traces of a red as-yet-unidentified compound [Equation (1)]. Complex **3** has been characterized by means of FD mass spectra and X-ray crystallography; the C value of elemental analyses of **3** differs by 1% for unknown reasons.



(1)

Complex **2** shows in the IR spectrum (toluene) three strong CO absorptions at 2005, 1972, and 1904 cm^{-1}. This is one less than would be expected from the crystal structure (see below) so we presume that two of the bands are accidentally degenerate. The UV/Vis spectrum reveals one absorption band at $\lambda = 477$ nm. The ^1H NMR spectrum contains two singlets for the *t*Bu groups and eight multiplets of equal intensity between $\delta = 3.24$ and 6.05 for the C_5H_4 hydrogen atoms. Thus, the NMR pattern of **2** reflects two orientations of the Cp′ ligands with respect to the $W(CO)_4$ moiety as, due to the solid state structure, both W atoms are lying on a C_2 axis. The ^1H NMR spectrum of **3** shows two multiplets at 24 °C for the aromatic hydrogen atoms and one singlet for the *t*Bu groups.

The crystal structure of **2** reveals the presence of four independent molecules in the asymmetric unit, which are practically identical. The central feature of the structure of **2** is a WTe_4 tetrahedron to which two niobocene units are

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coordinated (Figure 1), giving rise to a nearly linear Nb−W−Nb arrangement. A $W(CO)_4$ fragment is inserted between two of the Te bridges of the central WTe_4 tetrahedron. The W−Te distances within the WTe_4 unit range from 2.540(2) to 2.604(2) Å, the μ_2-Te−W(1) distances being slightly shorter than those of μ_3-Te−W(1). Similar values have been found in $W(PMe_3)_4(Te)_2$ [2.596(1) Å][7] and in $[WOTe_3]^{2-}$ [2.530(1)−2.544(2) Å],[8] which have been attributed to W−Te double bonds. By contrast, the distances Te(2)−W(2) and Te(3)−W(2) [2.848(2) and 2.845(2) Å, respectively] are much longer, thus reflecting a formally lower oxidation state of the W(2) center.[9] In the central WTe_4 tetrahedron there is a slight distortion of the angle Te(3)−W(1)−Te(2), which is 119.30(6)°. Whereas the distances between opposite Te ligands seem to be far beyond direct bonding interactions, the Nb−W distances (3.333 Å mean) may be a borderline case for direct interactions between both metals.

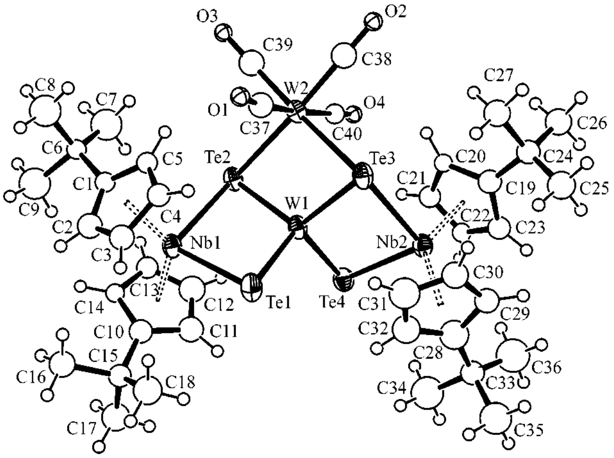
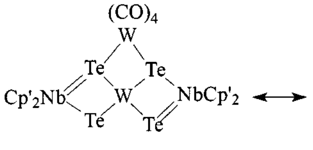
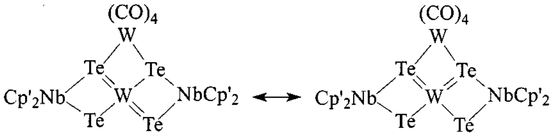


Figure 1. Molecular structure of $[\{(Cp'_2Nb)_2WTe_4\}W(CO)_4]$ (**2**); selected distances [Å] and angles [°]: W(1)−Te(1) 2.539(2), W(1)−Te(2) 2.600(2), W(1)−Te(3) 2.604(2), W(1)−Te(4) 2.553(2), W(2)−Te(2) 2.845(2), W(2)−Te(3) 2.841(2), Nb(1)−Te(1) 2.823(3), Nb(1)−Te(2) 2.827(2), Nb(2)−Te(3) 2.844(3), Nb(2)−Te(4) 2.834(3), Te(1)···Te(2) 4.22(3), Te(3)···Te(4) 4.25(2), Nb(1)···W(1) 3.35(1), Nb(2)···W(1) 3.33(2); Te(1)−W(1)−Te(2) 109.9(1), Te(1)−W(1)−Te(3) 103.5(1), Te(1)−W(1)−Te(4) 108.4(1), Te(2)−W(1)−Te(3) 119.3(1), Te(2)−W(1)−Te(4) 104.8(1), Te(3)−W(1)−Te(4) 110.6(1), Te(2)−W(2)−Te(3) 104.2(1), Nb(1)−Te(1)−W(1) 77.2(1), Nb(1)−Te(2)−W(1) 76.2(1), Nb(2)−Te(3)−W(1) 75.3(1), Nb(2)−Te(4)−W(1) 76.3(1), Te(1)−Nb(1)−Te(2) 96.2(1), Te(3)−Nb(2)−Te(4) 96.6(1), W(1)−Te(2)−W(2) 68.3(1), W(1)−Te(3)−W(2) 68.1(1), Nb(1)−W(1)−Nb(2) 163.8(1)

On the basis of these results a formal description of the bonding system in **2** either includes a W^{II} center, which is chelated by two $[Cp'_2NbTe_2]^-$ anions (structure type **A**), or a derivative of a tetratellurotungstate(VI) with two coordinated niobocene(III) ligands (structure type **B**). Taking into account the relatively short W−Te bonds in the central WTe_4 unit, it seems likely that the canonical forms **B** contribute more to the overall bonding system than **A**. In this sense **2** may be assumed to be the missing link in the series of bis(niobocene)tetrachalcogenido metalates $[(Cp^*_2Nb)_2ME_4]$ (M = Cr, Mo, W; E = S, Se, Te). These compounds are characterized by a delocalized bonding system including the whole metal-ligand system, as has been established by means of spectroscopic and theoretical investigations.[5]



A



B

The crystal structure of **3** contains a planar rhombohedral Nb_2Te_2 core to which four Cp′ ligands are coordinated. Additionally, the molecule has a crystallographic inversion center and the conformation of the Cp′ ligands corresponds to that of the *meso* diastereomer (Figure 2). A similar conformation has been found in the related compound $[Cp'_4Zr_2(\mu\text{-}Te)_2]$.[10] From the distances (>3.6 Å) one can exclude direct bonding interactions between opposite atoms of the core. The Nb−Te distances (2.80 Å) are only slightly shorter than those in **2** and they are in the range of Nb−Te single bonds.[11] As a consequence, compound **3** should formally contain two Nb^{IV} centers which is in obvious contrast to the observed diamagnetism of the molecule. For these reasons considerable through-space metal−metal coupling must be considered, as has been recently established for $[(C_5H_5)_4Zr_2(\mu\text{-}I)_2]$.[12] This point, as well as studies of the chemical behavior, are currently under investigation.

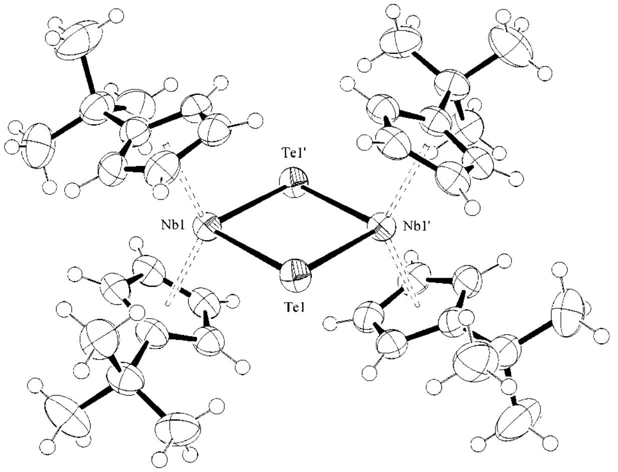


Figure 2. Molecular structure of $[Cp'_4Nb_2Te_2]$ (**3**); selected distances [Å] and angles [°]: Nb(1)−Te(1) 2.7969(4), Nb(1′)−Te(1) 2.8127(4), Nb(1)···Nb(1′) 3.647(1), Te(1)···Te(1′) 4.262(1); Nb(1)−Te(1)−Nb(1′) 81.12(1), Te(1)−Nb(1)−Te(1′) 98.88(1)

In conclusion the reaction of $[Cp'_2NbTe_2H]$ with $[Cr(CO)_6]$ or $[W(CO)_6]$ provides access to new polymetallic telluride complexes. Complex **2** is the first organometallic derivative of the still unknown WTe_4^{2-} anion, whereas the analogous $CrTe_4$ derivative does not form under comparable conditions. Instead, formation of the dinuclear chromium-free complex **3** has been observed.

Experimental Section

General Methods. Experimental and spectroscopic techniques are reported in ref.[13] [$Cp'_2Nb(Te_2)H$] (**1**) was prepared from [Cp'_2NbH_3] and Te powder in THF.[6]

Synthesis of 2: A solution of [Cp'_2NbTe_2H] (**1**) (560 mg, 0.946 mmol) and [W(CO)$_6$] (330 mg, 0.938 mmol) in 140 mL of decane was stirred for 12 h at 140 °C in the dark. The color turned from dark orange to red during the reaction. After evaporation of the solvent the residue was dissolved in 12 mL of toluene and transferred to a column containing SiO_2 (15 × 3 cm). A red band was eluted with toluene containing [{(Cp'_2Nb)$_2$$WTe_4$}W(CO)$_4$] (**2**) (420 mg, 0.252 mmol, 54%). A following dark green band contained [$Cp'_4Nb_2Te_2$] (**3**) (25 mg, 0.027 mmol, 6%). Recrystallization of **2** from toluene gave red needles. − IR (toluene): ν(CO) = 2005 (s), 1972 (vs), 1904 (s) cm^{-1}. − ^{1}H NMR (400 MHz, CD_2Cl_2, 24 °C): δ = 6.05 (m, 2 H, C_5H_4), 5.87 (m, 2 H, C_5H_4), 5.59 (m, 2 H, C_5H_4), 5.56 (m, 2 H, C_5H_4), 5.48 (m, 2 H, C_5H_4), 4.78 (m, 2 H, C_5H_4), 4.01 (m, 2 H, C_5H_4), 3.24 (m, 2 H, C_5H_4), 1.53 (s, 18 H, *t*Bu), 1.43 (s, 18 H, *t*Bu). − UV/Vis (THF): λ (ε) (Lmol^{-1}cm^{-1}) = 477 nm (3208). − $C_{40}H_{52}Nb_2O_4Te_4W_2C_7H_8$ (1752.87): calcd. C 32.20, H 3.45; found C 32.38, H 3.49.

Synthesis of 3: Compound **1** (560 mg, 0.946 mmol) and [Cr(CO)$_6$] (200 mg, 0.909 mmol) were dissolved in 140 mL of toluene and stirred for 12 h at 110 °C in the dark. The color turned from dark orange to green-black during the reaction. The mixture was cooled to room temperature and the solvent evaporated. The residue was dissolved in 12 mL of toluene and chromatographed on SiO_2 (column 15 × 3 cm). Elution with toluene first gave a red band containing 20 mg of a still unidentified compound and then a green-black band containing [$Cp'_4Nb_2Te_2$] (**3**) (280 mg, 0.302 mmol, 64%). Complex **3** was recrystallized from toluene/pentane (1:2). − ^{1}H NMR (400 MHz, CD_2Cl_2, 24 °C): δ = 5.05 (m, 8 H, C_5H_4), 4.46 (m, 8 H, C_5H_4), 1.44 (s, 36 H, *t*Bu). − FD-MS (toluene): *m*/*z* = 925.6 [M$^+$]. − $C_{36}H_{52}Nb_2Te_2$ (925.81): calcd. C 46.70, H 5.66; found C 45.78, H 5.69.

X-ray Structure Determination: For the crystals of both compounds **2** and **3** the shape and the size were determined for numerical absorption correction. The structures of **2** and **3** were solved by direct methods (Table 1). For **3**, subsequent difference Fourier syntheses revealed the position of the non-hydrogen atoms and all these atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included on idealized positions and refined using a riding model.

Table 1. Crystallographic data for compounds **2** and **3**

	2·1.5C_7H_8	**3**
Formula	$C_{50.5}H_{64}Nb_2O_4Te_4W_2$	$C_{36}H_{52}Nb_2Te_2$
MW	1798.9	925.8
Cryst syst	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	17.927(1)	8.6683(8)
b, Å	23.664(1)	13.336(1)
c, Å	28.799(2)	15.408(1)
α, deg	79.017(8)	
β, deg	76.486(8)	93.691(9)
γ, deg	71.949(8)	
V, Å^3	11202.0(14)	1777.5(3)
Z	8	2
d_{calc}, g/cm^3	2.130	1.730
F(000)	6684	908
Cryst size, mm^3	0.16×0.04×0.04	0.22×0.18×0.14
Diffractometer	STOE-IPDS	STOE-IPDS
Temp, K	173	297
θ, deg	1.82−25.19	2.65−25.95
No. of reflns collected	76102	24820
No. of indep reflns	37186	3418
R_{int}	0.1090	0.0488
No. obsd reflns [$I > 2\sigma(I)$]	12089	2769
μ, mm^{-1}	6.574	2.28
No. of data/restraints/params.	37186/0/1070	3418/0/181
GOF on F^2	0.617	0.988
T_{max}, T_{min}	0.7781, 0.5146	0.7467, 0.6201
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0527, 0.0792	0.0234, 0.0557
$R1$, $wR2$ (all data)	0.1789, 0.1102	0.0297, 0.0567

The structure refinement of **2** was handicapped by two problems: i) For data collection only thin needles were available giving rise to very weak intensities mainly at higher reflection angles. Only one third of the measured reflections were observed with an intensity greater than 2σ(*I*). This causes some peculiarities concerning the results of the refinement. Internal *R* values, especially $R(\sigma)$ = 0.3451, are high and are mainly influenced by the large number of weak reflections. The same is true for the low value of GOF. The unexpectedly high $R1$ for all data can be explained by the fact that too many very weak or even negative intensities are setting a wrong bias, when transformed to *F* values. The "normal" behavior of $R1$ and $wR2$ for the observed data [$I > 2\sigma(I)$] supports this point of view. Also, due to the large number of weak reflections no weighting factor could be refined and so unit weights were applied. Finally, only the heavy atoms could be refined with anisotropic thermal parameters. ii) Five toluene solvent molecules could be located by difference Fourier syntheses but there was still a solvent accessible void present. Since from the remaining difference Fourier peaks no reasonable molecule could be built all these maxima were erased and the size and electron content of this void was determined by the program SQUEEZE.[14] The center of the void was located at (0.5, 0, 0.5), the size and electron content was refined to 766 Å^3 with 65 e$^-$. For one more toluene molecule, the size of the void and the electron number are too high. The possibility that one decane molecule (reaction medium) was still present after chromatography and recrystallisation seemed unlikely. Nevertheless, for the calculation of molecular weight, *F*(000) and density one more toluene molecule was included, because no chance was seen to find the proper molecule from a data set with so many weak reflections at high reflection angles. The final refinement, leading to the given results, was carried out after back-Fourier transformation of all density found in the disordered solvent area.

The unusual result that four symmetry independent molecules were found in the elementary cell was checked and proved to be right by programs implemented in the PLATON package: a) No different cell choice was suggested by LEPAGE, therefore only an anorthic cell and space group is possible. The highest possible, $P\bar{1}$ was chosen; b) Even if only the heavy atoms were included in the file for calculations, PLATON could not find additional symmetry elements nor did it suggest a higher symmetry than applied. Obviously a denser packing of **2** with higher symmetry of cell and structure is not possible.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148287 (**2**) and -148288 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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