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Tantalum Dimethyldithiocarbamate Complexes

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Abstract—The reaction of $Ta(NMe_2)_5$ with CS_2 gave the tantalum(V) dimethyldithiocarbamate complex $[Ta(^{Me}Dtc)_4](^{Me}Dtc)$ (**I**). An ionic structure of the complex with a dodecahedral coordination of the tantalum atom was determined for toluene (**I** · Tol) and THF (**I** · THF) solvates by X-ray diffraction (CCDC no. 1544283 and no. 1544284, respectively). The reaction of **I** with CH_2Cl_2 leads to exchange of the outer-sphere anion to give the known complex $[Ta(^{Me}Dtc)_4]Cl$ (**II**). The cyclic voltammogram of **II** in CH_3CN exhibits a quasi-reversible transition at $E_{1/2} = -0.735$ V corresponding to the Ta^V/Ta^{IV} pair.

Keywords: tantalum, amides, dithiocarbamates, X-ray diffraction analysis, cyclic voltammetry
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Metal amides are important for the modern coordination chemistry and serve as precursors of many other ligands [1]. Indeed, the insertion of CS_2 into the M–N bond of early transition metal amides is a general method for the synthesis of metal dithiocarbamates [2, 3]. This reaction was described for the first time in the 1960s, but the products were studied by X-ray diffraction more recently. As assumed by Bradley and co-workers [2, 3] relying on analytical and spectroscopic data, reactions of the tetramides $[M(NR_2)_4]$ (M = Ti, Zr, Hf, V) with CS_2 afford neutral tetrakis(dithiocarbamate) complexes $[M(^{R}Dtc)_4]$ with a stoichiometry corresponding to both the oxidation number of 4+ and C.N. of 8, which is preferred for these central atoms. Later, this assumption was confirmed by X-ray diffraction [4, 5]. However, in the case of Group V metal amides, the reactions with CS_2 follow a different route. The reaction of $[Nb(NMe_2)_5]$ with CS_2 gives rise to a tetravalent niobium complex $[Nb^{IV}(^{Me}Dtc)_4]$ and 0.5 equivalents of thiuram disulfide $(^{Me}Dtc)_2$ [3]. A similar reaction of $Ta(NMe_2)_5$ results in the product described as $Ta(^{Me}Dtc)_5$; provided that the bidentate (κ^2-S,S') coordination usual for ^{R}Dtc is retained, the Ta coordination number in this compound should have been ten, which is abnormally high. Therefore, it was assumed that the tantalum atom has C.N. of 8, with three dithiocarbamate ligands being coordinated in the bidentate mode and the other two dithiocarbamate ligands being monodentate. Particularly this structure of the coordination unit is observed for Nb and Ta carbamates described as $[M(O_2CNR_2)_5]$ [6–8] and also, for example, for $[Ta(Me_2Pz)_5]$ (Me_2Pz = 3,5-dimethylpyrazolate) [9]. Despite the lack of X-ray diffraction data for $[Ta(^{R}Dtc)_5]$, this somewhat speculative assumption about the structure of the coordination unit of these complexes has even been included in inorganic chemistry textbooks (see, for example, [10]).

An alternative way to prepare dithiocarbamate complexes is the reaction of a transition metal halide with sodium or potassium dithiocarbamate. However, the reactions of $TaHal_5$ with $^{R}Dtc^-$ give mixed-ligand complexes, $Ta(^{R}Dtc)_xHal_{5-x}$ (x = 2–4), in which the ^{R}Dtc : halogen ratio is not more than four [11]. As expected, the central atom environment in $[Ta(^{Me}Dtc)_4]Cl$ has a dodecahedral geometry and the C.N. is 8 [12]. The cationic moieties of $[Ta(^{Me}Dtc)_4][TaCl_6]$ [12], $[Nb(^{Et}Dtc)_4]Br$ [13], and $[Nb(^{Et}Dtc)_4]_2[NbSCl_5]$ [14] have a similar geometry. The present study addresses the reaction of $Ta(NMe_2)_5$ with CS_2, which is dictated by the lack of structural data for the homoleptic $[Ta(^{R}Dtc)_5]$ complexes.

EXPERIMENTAL

All of the syntheses were carried out in an inert atmosphere using the standard Schlenk techniques. The solvents were dehydrated and degassed by refluxing and distillation under argon using appropriate drying agents [15]. CS_2 (Acros) was dried over 3A molecular sieves and then degassed.

NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^1H

nuclei; the solvent signals were used as the standards [16]. IR spectra were recorded on a SCIMITAR FTS 2000 instrument for KBr pellets. Elemental analysis was performed at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences. Cyclic voltammograms were measured on a Metrohm 797 VA Computrace electrochemical analyzer at the test complex concentration of ~1 mmol/L. All measurements were carried out in a three-electrode cell consisting of a glass carbon working electrode, a platinum auxiliary electrode, and a silver chloride (Ag/AgCl) reference electrode filled with a 3 M solution of KCl. Prior to each measurement, the test solution was purged with argon for 5–10 min for the removal of gases. A solution of Bu_4NPF_6 in CH_3CN (0.05 M) was used as the electrolyte. The potentials ($E_{1/2}$) were found as (E_a + E_c)/2, where E_a and E_c are the anode and cathode potentials, respectively.

Synthesis of [Ta(^{Me}Dtc)$_4$](^{Me}Dtc) (I · Tol). $Ta(NMe_2)_5$ (403 mg, 1.00 mmol) was placed into a Schlenk vessel and dissolved in toluene (8 mL). Toluene (2 mL) and then a solution of CS_2 (500 μL, 400 mg, 5.21 mmol) in toluene (2 mL) were layered onto the surface of the orange solution using PTFE capillary. Within several minutes, a light brown flaky precipitate started to form. The vessel was allowed to stand until the liquids were completely mixed. After 7 days, a small amount of yellow crystals of **I** · Tol suitable for X-ray diffraction was selected from the precipitate. The remaining light brown precipitate was collected on a filter and dried *in vacuo*. Yield 630 mg (80%).

IR (KBr; ν, cm^{-1}): 3002 w, 2956 m, 2925 m, 2854 m, 1550 vs, 1458 m, 1399 vs, 1338 m, 1245 s, 1148 s, 1106 m, 1051 m, 1031 m, 1000 w, 977 s, 903 w, 895 m, 881 w, 860 w, 785 w, 743 m, 700 w, 576 m.

Synthesis of [Ta(^{Me}Dtc)$_4$](^{Me}Dtc) · C_4H_8O (I · THF). A solution of $Ta(NMe_2)_5$ (400 mg, 1.00 mmol) in THF (10 mL) was placed into one knee of an H-shaped Schlenk vessel. The other knee was filled with CS_2 (500 μL, 400 mg, 5.21 mmol) in THF (2 mL). The vessel was allowed to stand until the liquids were completely mixed via diffusion through the gas phase. After several days, a light brown precipitate, together with a minor amount of colorless crystals, was formed on the vessel bottom. After 7 more days, coarse dark brown crystals appeared in the upper part of the solution. The mother liquor with the voluminous light brown precipitate was removed with a capillary. The dark brown crystals were collected and dried in vacuo. Yield 150 mg (18%).

For $C_{19}H_{38}N_5OS_{10}Ta$

anal. calcd., %:	C, 26.72;	H, 4.48;	N, 8.20.
Found, %:	C, 26.35;	H, 4.75;	N, 8.45.

^1H NMR (CD_3COCD_3; δ, ppm): 3.62 (m, 8H, THF-(C2,5)), 3.51 (s, 6H, ^{Me}Dtc), 3.49 (s, 24H, [Ta(^{Me}Dtc)$_4$]$^+$), 1.81 (m, 8H, THF-(C3,4)).

IR (KBr; ν, cm^{-1}): 2954 m, 2922 m, 2856 m, 1554 vs, 1458 m, 1399 vs, 1366 m, 1247 m, 1155 s, 1099 m, 1061 m, 997 w, 975 s, 907 m, 576 m.

Synthesis of [Ta(^{Me}Dtc)$_4$]Cl) · CH_2Cl_2 (II · CH_2Cl_2). Carbon disulfide (500 μL, 400 mg, 5.21 mmol) was added to a solution of $Ta(NMe_2)_5$ (400 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). As this took place, the solution darkened and slightly warmed up. After several minutes, a yellow precipitate was formed, which was collected on a filter and dried in vacuo. Yield 375 mg (55%). Alternatively, complex **II** · CH_2Cl_2 can be prepared by recrystallizing the precipitate of **I**, resulting from the reaction of $Ta(NMe_2)_5$ with CS_2 in toluene, from CH_2Cl_2. The crystals of **II** · CH_2Cl_2 suitable for X-ray diffraction were obtained by slow diffusion of toluene into a solution of **II** in CH_2Cl_2.

For $C_{13}H_{26}N_4S_8Cl_3Ta$

anal. calcd., %:	C, 19.97;	H, 3.35;	N, 7.16.
Found, %:	C, 19.90;	H, 3.85;	N, 7.30.

IR (KBr; ν, cm^{-1}): 3002 w, 2956 w, 2924 w, 2860 w, 1560 vs, 1396 vs, 1319 m, 1246 s, 1148 s, 1050 m, 996 m, 980 m, 905 w, 890 w, 873 w, 806 w, 732 m, 696 m, 576 m. ESI(+)-MS (CH_3CN, *m/z*): 661 ([Ta(^{Me}Dtc)$_4$]$^+$).

X-Ray Diffraction. The crystallographic and X-ray diffraction data for **I** · Tol and **I** · THF were collected on a Bruker Duo automated diffractometer (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å). The absorption corrections were applied empirically (SADABS) [17]. The structure was solved by direct methods and refined by least squares methods in the anisotropic approximation (SHELXTL) [18]. The hydrogen atom positions were calculated geometrically and refined in the rigid body approximation. Selected crystal data and structure refinement parameters are summarized in Table 1. The full tables of interatomic distances and bond angles, atom coordinates, and displacement parameters are deposited with the Cambridge Crystallographic Data Centre (CCDC nos 1544283 (**I** · Tol), 1544284 (**I** · THF); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

The reaction of $Ta(NMe_2)_5$ with 5 equiv. of CS_2 in toluene affords a voluminous precipitate of unknown structure. By slow mixing of the reactants, we were able to isolate some yellow crystals of [Ta(^{Me}Dtc)$_4$](^{Me}Dtc) · C_7H_8 (**I** · Tol). The same reaction in THF also produces a voluminous light brown

Table 1. Crystallographic data and structure refinement parameters for **I** · Tol and **I** · THF

Parameter	Value	
	I · Tol	**I** · THF
Molecular formula	$C_{22}H_{38}N_5S_{10}Ta$	$C_{19}H_{38}N_5OS_{10}Ta$
M	874.12	854.09
System, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
Temperature, K	150	150
a, Å	11.6132(7)	11.1766(4)
b, Å	14.3171(7)	13.6020(5)
c, Å	20.8495(11)	13.8040(5)
α, deg.	90	77.758(2)
β, deg.	101.171(2)	70.901(1)
γ, deg.	90	71.612(2)
V, Å^3	3400.9(3)	1867.87(12)
Z	4	2
μ, mm^{-1}	3.87	3.52
Crystal size, mm	0.25 × 0.25 × 0.05	0.45 × 0.22 × 0.12
F(000)	1752	856
Data collection range of θ, deg	1.736–26.372	1.589–26.372
Ranges of reflection indices h, k, l	$-14 \le h \le 14$, $-13 \le k \le 17$, $-26 \le l \le 24$	$-13 \le h \le 13$, $-16 \le k \le 15$, $-17 \le l \le 17$
Number of measured, unique, and observable ($I > 2\sigma(I)$) reflections	23961, 6946, 5361	18267, 7593, 7259
R_{int}	0.0565	0.0280
R_1, wR_2 ($I > 2\sigma(I)$)	0.0289, 0.0540	0.0270, 0.0798
R_1, wR_2 (all reflections)	0.0486, 0.0577	0.0285, 0.0813
GOOF	0.982	1.112
Number of refined parameters	354	426
Number of restraints	0	39
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.65/–0.77	1.20/–0.86

precipitate. Later, dark brown crystals of $[Ta(^{Me}Dtc)_4](^{Me}Dtc) \cdot THF$ (**I** · THF) precipitate from the mother liquor. The single crystals of both solvates were studied by X-ray diffraction.

The complex cations $[Ta(^{Me}Dtc)_4]^+$ in both solvates have similar geometry, which also resembles the geometry of previously described [12] complexes, $[Ta(^{Me}Dtc)_4][TaCl_6]$ and $[Ta(^{Me}Dtc)_4]Cl$ (Table 2). The coordination unit is formed by the sulfur atoms of four dithiocarbamate ligands coordinated in the bidentate fashion; one more dithiocarbamate anion is not coordinated. This structure of the coordination unit differs from the above-mentioned Ta and Nb pentacarbamate structures, which comprise three bidentate and two monodentate ligands. Note that uncoordinated dithiocarbamate anions (Cambridge Crystallographic Data Centre [19, 20]) are more rarely encountered than monocoordinated ones (75 and 195 examples, respectively).

The coordination polyhedron geometry is close to dodecahedral in all $[Ta(^{Me}Dtc)_4]^+$ cations (Fig. 1). The dihedral angles ω between the planes of body-diagonal trapezoids, S(11)S(12)S(31)S(32) and S(21)S(22)S(41)S(42), are 89.9° and 89.2° for toluene and THF solvates, respectively. For an ideal Hoard dodecahedron, this angle is 90° [21]. According to criteria proposed by Porai-Koshits and Aslanov, the cations in both solvates are also dodecahedral [22]. Indeed, in the solvate **I** · Tol, the solid angles δ between pairs of triangular faces that intersect at type *b* edges (see explanations in [22]) occur in the range of 29.4°–35.6° (29.5° for an ideal dodecahedron). The φ angles (0.2° and 0.8°), which are the measure of

Table 2. Selected geometric parameters of complexes **I** · Tol and **I** · THF

Parameter	**I** · Tol	**I** · THF	$[Ta(^{Me}Dtc)_4]Cl \cdot CH_2Cl_2$	$[Ta(^{Me}Dtc)_4][TaCl_6] \cdot 0.5CH_2Cl_2$
Ta–S (short), Å	2.5068(9)–2.5241(10) (aver. 2.515 [8])	2.5137(9)–2.5191(9) (aver. 2.516 [3])	2.513(3)–2.528(3) (aver. 2.521 [3])	2.505(6)–2.523(7) (aver. 2.515 [7])
Ta–S (long), Å	2.5858(9)–2.6002(9) (aver. 2.592 [6])	2.5855(9)–2.5964(9) (aver. 2.592 [5])	2.589(3)–2.591(3) (aver. 2.521 [3])	2.559(6)–2.617(7) (aver. 2.591 [6])
∠STaS, deg	67.58(3)–68.12(3) (aver. 67.8 [3])	67.78(3)–68.02(3) (aver. 67.86 [11])	67.38(8)–67.78(8) (aver. 67.6 [2])	67.3(2)–68.0(2) (aver. 67.7 [3])
∠SCS (coord.), deg	111.1(2)–112.4(2)	111.5(2)–112.5(2)	110.8(6)–111.7(6)	109(1)–113(1)
∠SCS (uncoord.), deg	121.6(2)	122.3(2)		
ω, deg.	89.9	89.2	89.4	89.1
δ, deg.	29.4, 29.8, 34.8, 35.6	26.9, 32.0, 32.7, 37.0	29.9, 31.5, 34.9, 34.9	23.8, 33.9, 34.1, 35.7
φ, deg.	0.2, 0.8	2.7, 3.6	2.9	2.8, 4.8
Ref.	This work	This work	[12]	[12]

non-planarity of the diagonal trapezoids [22], are also close to the value of 0° expected of an ideal dodecahedron. The corresponding angles are summarized in Table 2. The dihedral angles between the Ta(1)S(*n*1)S(*n*2)C(*n*1) planes of neighboring dithiocarbamate ligands are close to 90° (86.9°–93.3° for **I** · Tol and 86.8°–95.8° for **I** · THF).

The SCS angles in uncoordinated $^{Me}Dtc^-$ anions are 121.6(2)° and 122.3(2)° for **I** · Tol and **I** · THF, respectively; this is ~10° greater than the same values in the coordinated anions. The difference between the shortest and longest C–S bond lengths in the uncoordinated anion is also greater than that in the coordinated one.

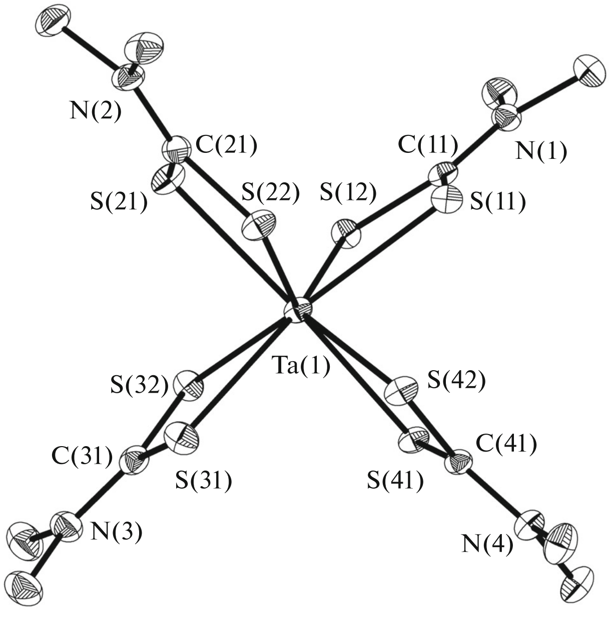

Fig. 1. Structure of the $[Ta(^{Me}Dtc)_4]^+$ cation in complex **I** (thermal ellipsoids at 30% probability, H atoms are not shown).

The known complex $[Ta(^{Me}Dtc)_4]Cl$ (**II**) was prepared by two methods, namely, the reaction of $Ta(NMe_2)_5$ with CS_2 in CH_2Cl_2 or in a CH_2Cl_2–toluene mixture and recrystallization from CH_2Cl_2 of the product formed in the reaction of $Ta(NMe_2)_5$ with CS_2 in toluene. The identity of **II** and the previously described [12] complex was confirmed by measurements of the single crystal unit cell parameters and by IR spectroscopy and mass spectrometry data. The IR spectrum of **II**, as compared with **I**, does not exhibit bands at 1458 and 1338 cm^{-1} corresponding to the uncoordinated anions $(^{Me}Dtc)^-$. The C–N absorption bands in coordinated ^{Me}Dtc occur at 1550 and 1554 cm^{-1} for solvates **I** · Tol and **I** · THF, respectively, which is close to published data for **II** (1557 cm^{-1}) [12]. The similarity of the IR spectra of two solvates of **I** and the light brown precipitate formed by the reaction of $Ta(NMe_2)_5$ with CS_2 in toluene suggests that this precipitate also has the ionic structure $[Ta(^{Me}Dtc)_4](^{Me}Dtc)$.

The ^{1}H NMR spectrum of **I** in CD_3COCD_3 exhibits singlets for the protons of coordinated and uncoordinated dithiocarbamates in 4 : 1 ratio and signals for THF molecules. As the temperature increases from 278 to 318 K, both dithiocarbamate signals slightly (by ~0.03 ppm) shift downfield, with the difference between the chemical shifts remaining virtually the same (0.02 ppm). This behavior indicates that no exchange between the coordinated and outer-sphere ^{Me}Dtc ligands takes place in this temperature range.

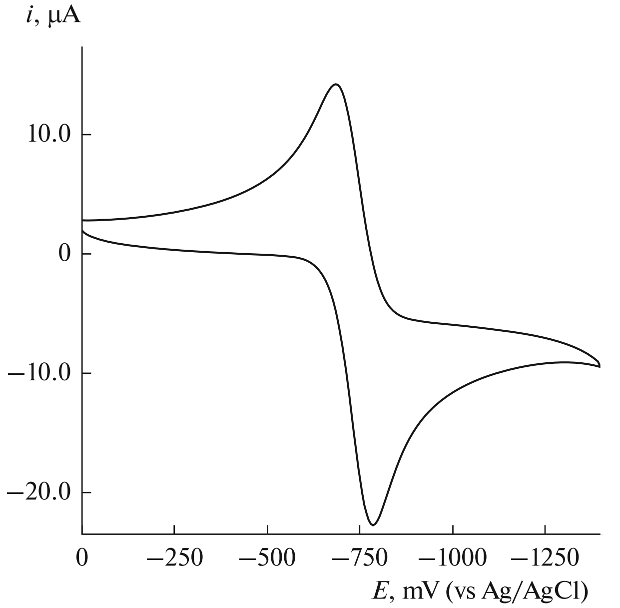

Fig. 2. Cyclic voltammogram of a 1.0 mM solution of $[Ta(^{Me}Dtc)_4]Cl$ (**II**) in CH_3CN in the presence of a 0.05 M solution of Bu_4NPF_6 in the range from 0 to −1.4 V. The scanning speed is 100 mV/s.

The cyclic voltammogram of the complex $[Ta(^{Me}Dtc)_4]Cl$ in CH_3CN (Fig. 2) attests to chemically reversible single-electron reduction at the potential $E_{1/2} = -0.735$ V vs. Ag/AgCl, which corresponds to the Ta^V/Ta^{IV} pair. This reversible redox behavior is rarely encountered for tantalum, which is known for its electrochemical inertness. One of the few examples is represented by Ta^V complexes with thiolate-substituted phthalocyanines (Pc) reported in [23]. They also show reversible reduction in the range from −0.67 to −0.74 V, which corresponds to the $Ta^VPc^{2-}/Ta^{IV}Pc^{2-}$ pair. Redox processes related to the reduction of the phthalocyanine ligand occur at higher potentials.

The redox process found for complex **II** is not fully electrochemically reversible. This is indicated by quite a large difference between the potentials ($\Delta E = |E_c - E_a|$), which is 102 mV at the scanning speed $v = 100$ mV/s; this markedly differs from the theoretical value for a fully reversible single-electron process (60 mV). This value slightly decreases with decreasing scanning speed to become 90 mV at 25 mV/s. Meanwhile, the i_c/i_a ratio is only slightly greater than unity and varies in the range of 1.1–1.2 depending on the scanning speed. The product $i_p v^{-1/2}$ ($i_p = i_c$ or i_a) is a constant. This means that the electrochemical process is rate-limited by diffusion of the complex toward the working electrode [24].

Thus, it was shown that, as opposed to the accepted opinion [10], the structure of tantalum pentakis(dimethyldithiocarbamate) corresponds to the ionic compound $[Ta(\eta^2\text{-}S_2CNMe_2)_4](S_2CNMe_2)$ rather than to the molecular compound $[Ta(\eta^2\text{-}S_2CNMe_2)_3(\eta^1\text{-}S_2CNMe_2)_2]$.

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