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The authors congratulate Academician of the Russian Academy of Sciences I.L. Eremenko on his 70th jubilee

Mixed Amidohalotantalates $[Ta(NMe_2)_3X_3]^-$ (X = F, Cl)

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Abstract—The anionic tantalum complex $(I^tBuH)[Ta(NMe_2)_3Cl_3]$ (**I**) is synthesized by the reaction of $[Ta(NMe_2)_3Cl_2]_2$ with N-heterocyclic carbene I^tBu and is isolated as two crystalline modifications (**Ia** and **Ib**). Its fluoride analogue $(I^tBuH)[Ta(NMe_2)_3F_3]$ (**II**) is synthesized by the reaction of $Ta(NMe_2)_5$ with $(I^tBuH)BF_4$. The structures of the complexes are determined by X-ray diffraction analysis (CIF files CCDC nos. 1977540 (**Ia**), 1977541 (**Ib**), and 1977542 (**II**)).

Keywords: tantalum, amides, halogens, N-heterocyclic carbenes, X-ray diffraction analysis

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INTRODUCTION

Homoleptic metal dialkylamides are convenient precursors for many other classes of coordination compounds due to the pronounced basic and nucleophilic properties of the amide group [1]. Dialkylamides of early transition metals and their derivatives are used for the deposition of thin films of nitrides using the CVD method [2–5]. Mixed amidohalides of early transition metals are also known, although they are poorly studied. Interest in these compounds is related to the fact that the presence of ligands of various natures at the metal can be used for the target modification of the coordination mode. Binary amides $Ta(NMe_2)_5$ [6] and $Ta(NEt_2)_5$ [7] and also mixed neutral amidochlorides $[Ta(NMe_2)_4Cl]$ [8, 9], $[Ta(NMe_2)_3Cl_2]_2$ [10], and $[Ta(NEt_2)_3Cl_2]_2$ [11] are known among the tantalum dialkylamide derivatives. The complexes with silylated amides $[TaCl_3(N(SiMe_3)_2)_2]$ [12] and $[TaCl_2(N(SiMe_3)_2)_2]$ [11] were also described. As far as we can judge, similar compounds with other halides are unknown. Their niobium analogues are very few: binary amides $Nb(NMe_2)_5$ [13] and $Nb(NPh_2)_4$ [14] and mixed complexes $[NbX_2(N(SiMe_3)_2)_2]$ (X = Cl, Br) [14] are known. It is most likely that binary dialkylamides $Nb(NR_2)_4$ (R = Et, *n*-Pr, and *n*-Bu) are not individual compounds [4]. In addition, the anionic complexes *cis*-$[Ta(NMe_2)_4Cl_2]^-$ [15] and *fac*-$[Ta(NMe_2)_3Cl_3]^-$ [16] were structurally characterized. The latter was synthesized by the reaction of $Ta(NMe_2)_5$ with *N*,*N*′-dimesitylimidazolium chloride (IMesH)Cl. This salt is simultaneously a source of chloride ions and N-heterocyclic carbene IMes. The major reaction product of this reaction is the carbene complex $[(IMes)Ta(NMe_2)_3Cl_2]$, whereas the reaction of $Ta(NMe_2)_5$ with the tetrafluoroborate salt of the same cation affords $[(IMes)Ta(NMe_2)_2F_3]$ due to the exchange of halogen between Ta and B [16]. The reaction of $Nb(NMe_2)_5$ with $(IMesH)BF_4$ proceeds via a different route and affords $(IMes_2H)[NbF_6]$ [17].

This work is devoted to the study of the reactions of $Ta(NMe_2)_5$ with salts of *N*,*N*′-di(*tert*-butyl)-substituted imidazolium I^tBuH^+, which are precursors of N-heterocyclic carbene I^tBu.

EXPERIMENTAL

All procedures on the synthesis, purification, and characterization of the complexes were carried out in an inert atmosphere using a standard Schlenk technique. Solvents for the syntheses were dehydrated and degassed by reflux and distillation in an inert gas atmosphere using the corresponding drying agents

[18]. Compounds $[Ta(NMe_2)_3Cl_2]_2$ [10], $(I^tBuH)BF_4$ [19], and I^tBu [20] were synthesized according to literature procedures. NMR spectra were recorded on a Bruker Avance III 500 spectrometer with the working frequency 500.03 MHz for ^1H and 125.73 MHz for ^{13}C. IR spectra in KBr pellets were recorded on a SCIMITAR FTS 2000 instrument.

Synthesis of complex I. A mixture of $[Ta(NMe_2)_3Cl_2]_2$ (102 mg, 0.13 mmol) and I^tBu (50 mg, 0.27 mmol) was placed in a Schlenk flask, cooled to −196°C, and evacuated, after which toluene (~30 mL) was condensed to the flask. The mixture was heated to room temperature, the formed lemon-yellow suspension was stirred for 14 days, and the resulting solution was filtered through a glass filter (G4) into a Γ-like ampule, which then was sealed. The slow evaporation of the solvent gave a mixture of yellow prismatic (**Ia**) and platy (**Ib**) crystals suitable for X-ray diffraction analysis. The yield was 15 mg (22%).

IR (KBr), ν, cm^{-1}: 3049 m, 3001 m, 1618 m, 1585 m, 1483 m, 1433 s, 1308 m, 1189 m, 1158 m, 1096 m, 1026 m, 998 m, 912 m, 839 m, 738 s, 691 s, 552 s, 516 s, 489 m, 442 w, 423 w. ^1H NMR: 9.55 (1H, NCHN), 6.89 (2H, −CH=CH−), 4.12 (18H, NMe_2), 1.36 (18H, $C(CH_3)_3$). ^{13}C NMR: 134.6 (C^2H), 119.5 (−CH=CH−), 60.6 ($\underline{C}(CH_3)_3$), 49.8 (NMe_2), 29.9 ($C(\underline{C}H_3)_3$).

For $C_{17}H_{39}N_5Cl_3Ta$

Anal. calcd., %	C, 33.98	H, 6.54	N, 11.66
Found, %	C, 33.8	H, 6.45	N, 11.5

Synthesis of complex II. A mixture of $Ta(NMe_2)_5$ (200 mg, 0.50 mmol) and $(I^tBuH)BF_4$ (130 mg, 0.49 mmol) was placed in a Schlenk flask, cooled to −196°C, and evacuated, and tetrahydrofuran (THF) (~25 mL) was condensed to the flask. The mixture was heated to room temperature, and the resulting suspension was stirred for 24 h and then refluxed with vigorous stirring for 24 h. The solution obtained after reflux was filtered through a glass filter (G4) in a Γ-like ampule, which was then sealed. The slow evaporation of the solvent gave a yellow oil and colorless crystals, which were washed with THF and dried. The yield was 45 mg (17%).

IR (KBr), ν, cm^{-1}: 3172 m, 3139 m, 3004 m, 2862 m, 2821 m, 2773 m, 1608 w, 1564 w, 1542 w, 1482 m, 1457 s, 1419 m, 1394 m, 1267 m, 1244 m, 1219 m, 1161 w, 1128 m, 1101 m, 1047 m, 978 s, 961 s, 930 m, 854 m, 736 s, 696 s, 587 m, 559 s.

For $C_{17}H_{39}N_5F_3Ta$

Anal. calcd., %	C, 37.03	H, 7.13	N, 12.70
Found, %	C, 36.85	H, 7.4	N, 12.8

X-ray diffraction analysis (XRD). All measurements were conducted using a standard procedure on a Bruker-Nonius X8 APEX automated four-circle diffractometer (two-coordinate CCD detector, λ = 0.71073 Å, graphite monochromator). Reflection intensities were measured in the φ scan mode for narrow (0.5°) frames. An absorption correction was applied empirically (SADABS) [21]. The structures were solved using the SHELXT program [22] and refined using the SHELXL program [23] in the anisotropic approximation for non-hydrogen atoms using the Olex2 program shell [24]. Hydrogen atoms were localized geometrically and refined in the rigid body approximation. The crystallographic characteristics and XRD experimental details for complexes **Ia**, **Ib**, and **II** are presented in Table 1. The bond lengths and bond angles are given in Table 2.

The full sets of the XRD parameters for compounds **Ia**, **Ib**, and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1977540–1977542; http://www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

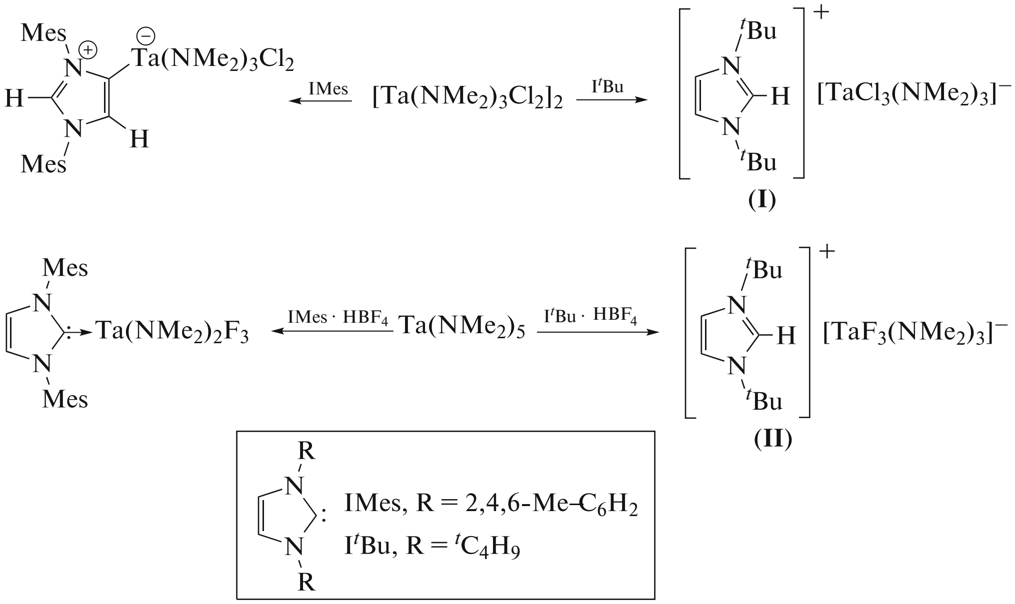
The complex with the abnormal (via the C(4) atom) coordination of the ligand to the Ta atom was previously synthesized by the reaction of $[Ta(NMe_2)_3Cl_2]_2$ and carbene IMes with mesityl substituents. It was assumed that a similar reaction with more bulky carbene I^tBu would also afford an abnormal complex. Contrary to expectations, the reaction of $[Ta(NMe_2)_3Cl_2]_2$ with I^tBu in toluene led only to the partial dissolution of the precipitate of the initial complex, and crystals of the ionic complex $(I^tBuH)[Ta(NMe_2)_3Cl_3]$ (**Ia**) were isolated from the solution in a low yield (Scheme 1). The formation of the same complex anion *fac*-$[Ta(NMe_2)_3Cl_3]^-$ was detected when we studied the products of the reaction of $[Ta(NMe_2)_5]$ with (IMesH)Cl. The formation of the ionic complex instead of the expected neutral complex $[(I^tBu)Ta(NMe_2)_3Cl_2]$ can be due to the hydrolysis of the product and/or initial carbene with water traces, which could exist in the solvent in spite of all precautions.

Table 1. Crystallographic data and structure refinement parameters for compounds **Ia**, **Ib**, and **II**

Parameter	Value		
	Ia	**Ib**	**II**
FW	600.83	600.83	551.48
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group; *Z*	$P2_1/c$; 4	$P2_1/c$; 16	$P2_1/c$; 4
a, Å	15.0188(9)	14.7545(9)	13.9032(5)
b, Å	9.5763(5)	14.7189(10)	10.5711(4)
c, Å	16.9822(10)	46.432(3)	17.1947(5)
β, deg	91.152(2)	94.397(2)	112.4830(10)
V, $Å^3$	2442.0(2)	10053.9(12)	2335.06(14)
F(000)	1200	4800	1104
μ_{Mo}, mm^{-1}	4.841	4.703	4.740
Crystal size, mm	0.31 × 0.16 × 0.12	0.19 × 0.19 × 0.07	0.31 × 0.23 × 0.1
Range of data collection over θ, deg	4.798–59.356	1.76–48.814	3.17–51.566
Ranges of *h*, *k*, *l*	$-20 \le h \le 20$, $-13 \le k \le 12$, $-23 \le l \le 23$	$-17 \le h \le 17$, $-17 \le k \le 14$, $-53 \le l \le 53$	$-16 \le h \le 16$, $-12 \le k \le 9$, $-20 \le l \le 15$
Number of measured, independent, and observed ($I > 2\sigma(I)$) reflections	41310, 6897, 6531	67628, 16534, 12231	11295, 4428, 3953
R_{int}	0.0238	0.1036	0.0174
Number of refined parameters and restraints	247.0	984.18	247.0
GOOF for F^2	1.059	1.177	0.978
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0117$, $wR_2 = 0.0282$	$R_1 = 0.0763$, $wR_2 = 0.1469$	$R_1 = 0.0171$, $wR_2 = 0.0425$
R_1, wR_2 (all reflections)	$R_1 = 0.0133$, $wR_2 = 0.0288$	$R_1 = 0.1083$, $wR_2 = 0.1566$	$R_1 = 0.0216$, $wR_2 = 0.0445$
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	0.71/–0.44	1.73/–2.33	0.82/–0.58

Table 2. Selected bond lengths (Å) and angles (deg) in complexes **Ia**, **Ib**, and **II**

Bond	**Ia**	**Ib**	**II**
	d, Å		
Ta–N	1.9772(11)–2.0001(11)	1.952(14)–2.014(12)	2.007(2)–2.016(3)
Ta–X	2.5035(4)–2.5295(3)	2.487(4)–2.531(4)	1.9821(17)–1.9987(16)
Angle	ω, deg		
NTaN	90.67(5)–102.51(5)	88.8(5)–102.2(5)	93.14(11)–94.41(11)
XTaX	82.553(11)–88.271(11)	83.33(14)–88.84(14)	83.03(7)–85.02(7)
XTaN	169.28(3)–175.13(3)	169.0(4)–176.2(4)	167.34(9)–169.21(10)



Scheme 1.

The structure of complex **I** is presented in Fig. 1. The anionic complex $[Ta(NMe_2)_3Cl_3]^-$ in compound **Ia** is a *fac*-isomer. The geometry of the coordination mode deviates from the ideal octahedral geometry because of the bulky dimethylamide ligands. As a consequence, the *trans* angles ClTaN differ noticeably from 180° (Table 2). The N(1)C(1)N(2) angle (108.59(11)°) is characteristic of the imidazolium cations. The I^tBuH^+ cation is linked with the complex anion by the hydrogen bond (C(1)···Cl(1), 3.6142(13) Å, ∠C(1)H(1)Cl(1) 172.0°). This bond along with one more hydrogen bond (C(3)···Cl(3), 3.6334(14) Å, ∠C(3)H(3)Cl(3) 159.4°) forms zigzag chains of alternating cations and anions along the *b* direction. In addition to XRD, complex **Ia** was characterized by the results of ^1H and ^{13}C NMR spectroscopy and elemental analysis data.

Crystals of compound **Ib** of the same composition are formed as an impurity to the crystals of compound

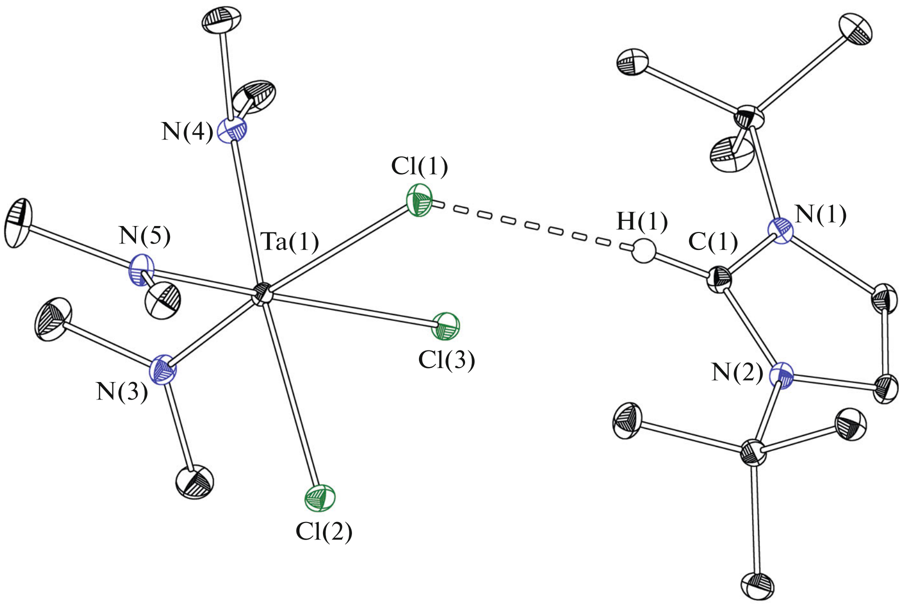
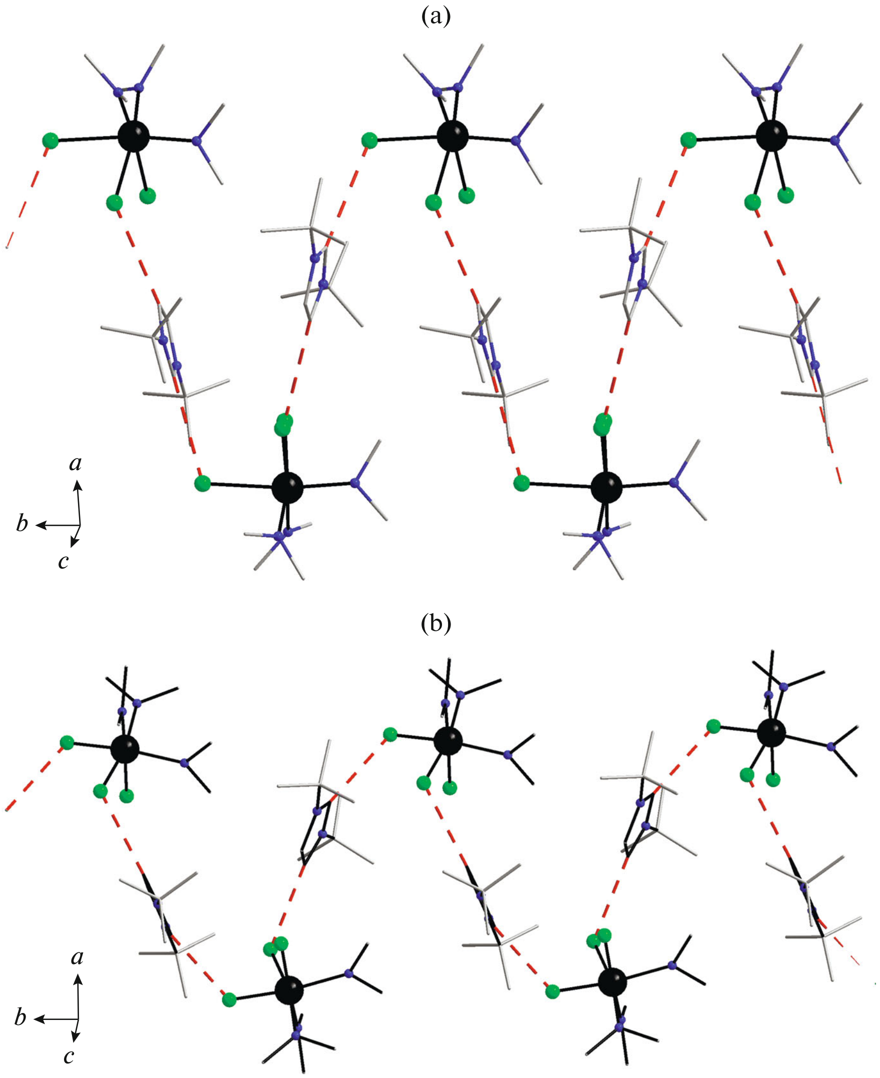


Fig. 1. Structure of complex **Ia**. Thermal ellipsoids of 30% probability are presented. Hydrogen atoms (except for H(1)) are omitted.


(a)

(b)

Fig. 2. Structures of the cationic and anionic chains in compounds (a) **Ia** and (b) **II** linked by hydrogen bonds (shown by dash).

Ia. Each crystal of this modification contains four crystallographically independent anions and cations, whose bond lengths and angles are close to those in compound **Ia** (Table 2). The difference between the crystal packings of compounds **Ia** and **Ib** is that each cation in the latter participates in the formation of only one hydrogen bond with the chloride ligand. This implies that only individual pairs of cations and anions can be distinguished in the case of compound **Ib**.

The reaction of $\mathrm{Ta(NMe_2)_5}$ with $(\mathrm{I}^t\mathrm{BuH})\mathrm{BF_4}$ in THF affords the ionic complex *fac*-$[\mathrm{Ta(NMe_2)_3F_3}]^-$ in the composition of $(\mathrm{I}^t\mathrm{BuH})[\mathrm{Ta(NMe_2)_3F_3}]$ (**II**). A smaller ionic radius of the fluoride ion compared to that of the chloride ion is a reason for shorter tantalum–halogen distances, which, in turn, leads to a stronger distortion of the coordination polyhedron (Table 2). This complex is not isostructural to chloride analogue **Ia** but has a similar crystalline packing. The chains of alternating cations and anions linked by the hydrogen bonds (C(1)···F(1), 3.048(3) Å, ∠C(1)H(1)F(1) 158.7°, C(3)···F(3)', 3.082(3) Å, ∠C(3)H(3)F(3)' 172.6°) are also observed along the *b* direction in the structure of complex **II**. Differences in the structures of the chains of complexes **Ia** and **II** are observed: for example, in complex **Ia** the equivalent C(3) atoms are remote at a longer distance from the 2_1 axis (0.82 Å) than in complex **II** (0.09 Å, Figs. 2, 3). The arrangement of one of the $\mathrm{NMe_2}$ ligands (including the N(5) atom) also differs: in compound **Ia** the angle between the normal to the plane passing through three ligand atoms and the *b* axis is 42.1°, whereas in complex **II** the angle is increased to 87.5°. In the structure of compound **Ia**, the shortest Ta···Ta distances between the chains of cations and anions and six adjacent chains are approximately equal and range from 8.26 to 8.76 Å. Similar distances

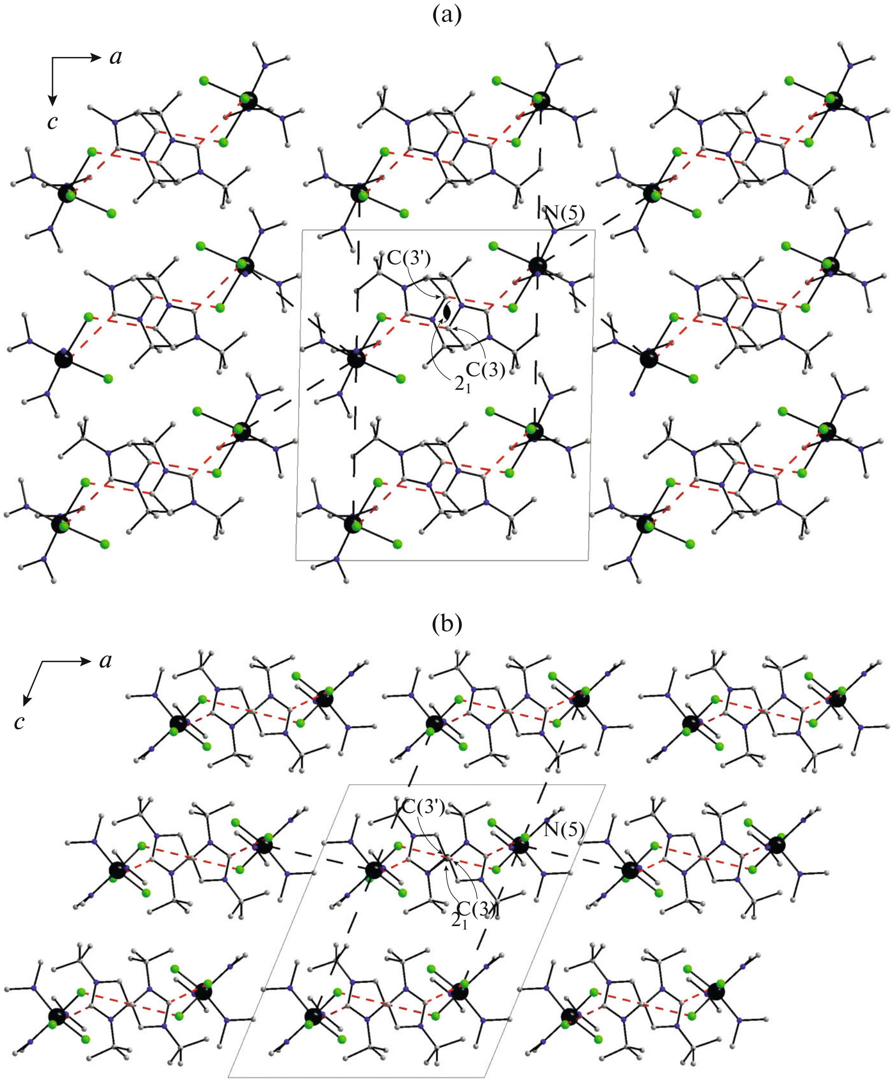


Fig. 3. Packing of the cationic and anionic chains in compounds (a) **Ia** and (b) **II**. Hydrogen bonds and shortest Ta···Ta distances are shown by dash.

in the structure of complex **II** (8.08–8.76 Å) are observed only for four adjacent chains.

Thus, mixed amidohalide tantalum complexes containing anions *fac*-$[\mathrm{Ta(NMe_2)_3X_3}]^-$ (X = F, Cl) were synthesized. The complexes were characterized by XRD, IR spectroscopy, and NMR spectroscopy. Two crystalline modifications differed in cationic and anionic packings were isolated for the chloride complex $(\mathrm{I}^t\mathrm{BuH})[\mathrm{Ta(NMe_2)_3Cl_3}]$. It should be mentioned that the formation of facial isomers is consistent with the situation typical of the presence in the coordination sphere of transition metal ions with the d^0 electronic configuration of three π-donor ligands. In this case, dimethylamide ligands act as π-donor ligands [25, 26].

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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