ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 10, pp. 635–637. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © P.A. Petrov, A.V. Rogachev, N.B. Kompan'kov, P.A. Abramov, M.N. Sokolov, 2017, published in Koordinatsionnaya Khimiya, 2017, Vol. 43, No. 10, pp. 598–601.

Tantalum Complex with 2-(2-Pyridine)Benzimidazolate

P. A. Petrov[a, b, *], **A. V. Rogachev**[a], **N. B. Kompan'kov**[a], **P. A. Abramov**[a], **and M. N. Sokolov**[a, b]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
**e-mail: panah@niic.nsc.ru*

Received February 14, 2017

Abstract—The reaction of $Ta(NMe_2)_5$ with 2-(2-pyridine)benzimidazole (HBzImPy) gave the molecular complex $[Ta(NMe_2)_4(BzImPy)]$, which was characterized by X-ray diffraction (CIF file CCDC no. 1531835). Data of ^1H and ^{13}C NMR spectroscopy in solution confirmed the structure detected in the crystalline phase.

Keywords: tantalum, amides, X-ray diffraction analysis

DOI: 10.1134/S1070328417100062

Tantalum nitride (TaN) films are widely used in microelectronics owing to combination of chemical, mechanical, and thermal stability and electrical conductivity [1, 2]. The TaN coating is deposited most often by chemical vapor deposition (CVD) or atomic layer deposition (ALD) technique. The requirements to compounds that serve as precursors for these methods include sufficient volatility, thermal stability, and stability against oxygen and moisture. Most often, the amides $[Ta(NR_2)_5]$ or amidoimides $[Ta(NR)(NR'_2)_3]$ are used for this purpose; they, however, have a relatively low thermal stability and are highly sensitive to moisture. In addition, deposition may result in the formation of Ta_3N_5, which is a dielectric unlike TaN. The variation of ligands in the precursor complex makes it possible to stabilize the complex by means of combination of steric and electronic factors and to affect the phase and elemental (N/C/Hal) composition of the obtained film. In addition, by replacement of aliphatic amides by heterocyclic ones, it is possible to vary the effective charge on the central atom due to the difference between their π-donor properties [3]. Apart from the theoretical interest, this variability can affect the catalytic properties of the resulting early transition metal complexes, for example, towards hydroaminoalkylation of alkenes [4, 5]. In this connection, it is important to search for new tantalum complexes with purely nitrogen environment of the central atom. Previously, mixed-ligand Ta complexes containing, apart from amides, amidinates or guanidinates [6–11], hydrazides [12, 13], amidopyridines [14, 15], or other N,N-donor ligands have been studied as complexes of this type.

This study is devoted to the synthesis of the different-ligand tantalum complex of dimethylamide and 2-(2-pyridin)benzimidazolate, $[Ta(NMe_2)_4(BzImPy)]$ (**I**).

EXPERIMENTAL

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 inert gas atmosphere using appropriate drying agents [16]. NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^1H nuclei and 125.76 MHz for ^{13}C nuclei. The C_6D_6 solvent signals served as the standard. The IR spectrum of the product was recorded on a SCIMITAR FTS 2000 instrument using KBr pellets. Elemental analysis was performed at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences.

Synthesis of complex I. A mixture of solid $Ta(NMe_2)_5$ (330 mg, 0.822 mmol) and HBzImPy (160 mg, 0.820 mmol) was placed into a Schlenk vessel and evacuated, and ~25 mL of toluene was condensed on cooling. The flask was heated at 70°C for 24 h and the content was evaporated to dryness. The lemon-yellow residue was washed with pentane and dissolved in 15 mL of toluene, and the solution was filtered through a glass filter (G4) into a L-shaped tube, which was then sealed. Slow evaporation of the solution resulted in the formation of dark yellow crystals of **I** suitable for X-ray diffraction. Yield 325 mg (70%).

^1H NMR (C_6D_6; δ, ppm): 8.69 (d, $J = 7.8$ Hz, 1H), 8.32 (d, $J = 8$ Hz, 1H), 8.24 (d, $J = 5$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.44 (td, $J_1 = 7$ Hz, $J_2 = 1.1$ Hz, 1H),

Table 1. Crystallographic data and structure refinement parameters for compound I

Parameter	Value
M	551.47
System, space group	Monoclinic, $P2_1/c$
Temperature, K	296
a, Å	14.3215(8)
b, Å	9.1407(5)
c, Å	17.2268(8)
β, deg	96.569(2)
V, Å^3	2240.3(2)
Z	4
F(000)	1096
μ, mm^{-1}	4.926
Crystal size, mm	0.20 × 0.20 × 0.12
Data collection range of θ, deg	2.380–27.503
Ranges of reflection indices h, k, l	$-18 \le h \le 18$, $-11 \le k \le 11$, $-22 \le l \le 22$
Number of measured, unique, and observable ($I > 2\sigma(I)$) reflections	17742, 5138, 4518
R_{int}	0.0253
R_1, wR_2 ($I > 2\sigma(I)$)	0.0206, 0.0434
R_1, wR_2 (all reflections)	0.0268, 0.0450
GOOF	1.035
Number of refined parameters	253
Number of restraints	0
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e Å^{-3}	0.61, –0.76

7.36 (td, J_1 = 8.1 Hz, J_2 = 1.1 Hz, 1H), 7.03 (td, J_1 = 7.7 Hz, J_2 = 1.5 Hz, 1H), 6.58 (m, 1H), 3.80 (6H, NMe_2), 3.30 (6H, NMe_2), 2.85 (12H, 2× NMe_2). ^{13}C NMR (C_6D_6; δ, ppm): 158.1 (C_{arom}), 152.7 (C_{arom}), 149.1 (C_{arom}), 147.2 (CH_{arom}), 145.0 (C_{arom}), 138.2 (CH_{arom}), 122.6 (CH_{arom}), 122.4 (CH_{arom}), 122.3 (CH_{arom}), 122.0 (CH_{arom}), 120.8 (CH_{arom}), 116.1 (CH_{arom}), 50.3 (NMe_2), 46.3 (NMe_2), 46.0 (2× NMe_2). IR (KBr; ν, cm^{-1}): 2980 w, 2851 m, 2812 m, 2768 m, 1610 m, 1563 m, 1519 m, 1444 s, 1374 m, 1330 m, 1270 m, 1237 m, 1158 w, 1131 m, 1046 m, 985 w, 970 s, 947 s, 818 w, 793 m, 746 s, 645 m.

For $C_{20}H_{32}N_7Ta$

Anal. calcd., %	C, 43.56;	H, 5.85;	N, 17.78.
Found, %:	C, 43.85;	H, 5.50;	N 17.50.

X-ray Diffraction study of I. The crystallographic and X-ray diffraction data were collected on a Bruker X8 Apex CCD automated diffractometer (graphite monochromator, λ(MoK_α) = 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 atom coordinates are deposited with the Cambridge Crystallographic Data Centre (no. 15318354; 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 HL affords a lemon-yellow solution, from which the crystals of complex **I** were isolated. The structure of the complex was determined by X-ray diffraction (Fig. 1). Compound **I** crystallizes from toluene. The tantalum atom coordination geometry is a distorted octahedron. One of the octahedron edges is occupied by the nitrogen atoms of deprotonated 2-(2-pyridine)benzimidazole (L). The N(1)TaN(2) chelate angle of 70.29(7)° virtu-

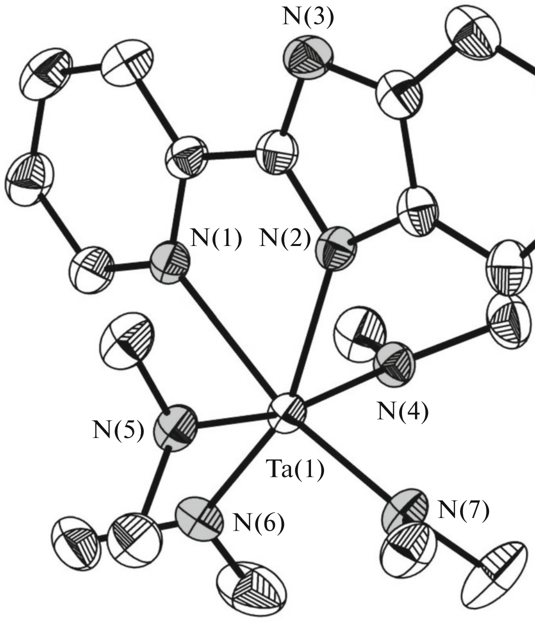

Fig. 1. Structure of complex **I** (thermal ellipsoids at 30% probability; H atoms are not shown). Selected bond lengths (Å): Ta(1)–N(1), 2.383(2); Ta(1)–N(2), 2.230(2); Ta(1)–N(4), 2.0289(19); Ta(1)–N(5), 2.023(2); Ta(1)–N(6), 2.002(2); Ta(1)–N(7), 1.995(2).

ally coincides with these angles in the tantalum complexes with the N,N'-coordinated 4,4-dimethyl-2-pyrrole-2-oxazoline anion [19]. The Ta–N distances in **I** are 2.383(2) and 2.230(2) Å for the pyridine and amide nitrogen atoms, respectively. The ligand L is nearly planar; the dihedral angle between the pyridyl and benzimidazole planes is 7.9°. The distances between the Ta and dimethylamide N atoms vary in the range of 1.995(2)–2.0289(19) Å; the shortest of them correspond to the groups located in the *trans*-positions relative to each other. The NC_2 planes of the dimethylamide groups are nearly perpendicular to each other, the angle between the N(4)C(41)C(42) and N(5)C(51)C(52) planes being 79.5°. The N(4)TaN(5) angle is 168.72(9)°. The above-described arrangement of the amide groups is encountered in many $[Ta(NR_2)_4L]$ complexes. The authors of [6] assume that this is caused by maximization of the π-bonding of the amide ligands to metal *d*-orbitals.

In conformity with the X-ray diffraction data, the ^1H NMR spectrum contains multiplet signals for eight non-equivalent protons at 6.5–8.7 ppm and three singlets with 1 : 1 : 2 ratio, corresponding to the dimethylamide groups. The more intense high-field signal (δ 2.84 ppm) can be assigned to two NMe_2 groups located in *trans*-positions to each other. Similarly, the signals at 3.30 and 3.80 ppm correspond apparently to dimethylamide groups in *trans* position to the benzimidazolide group and the pyridine ring, respectively. The JMOD ^{13}C NMR spectra also attest to the presence of eight aromatic CH groups and three non-equivalent NMe_2 groups in 1 : 1 : 2 ratio.

Thus, a new pseudo-octahedral Ta complex with deprotonated 2-(2-pyridine)-benzimidazole was synthesized and characterized by X-ray diffraction. The NMR spectra of complex **I** in solution are in agreement with the X-ray diffraction data, indicating that the molecular structure is stereochemically rigid.

REFERENCES

1. Sun, X., Kolawa, E., Chen, J.-S., et al., *Thin Solid Films*, 1993, vol. 236, p. 347.
2. Winter, C.H., *Aldrichimica Acta*, 2000, vol. 33, p. 3.
3. Tanski, J.M. and Parkin, G., *Inorg. Chem.*, 2003, vol. 42, p. 264.
4. Roesky, P.W., *Angew. Chem., Int. Ed. Engl.*, 2009, vol. 48, p. 4892.
5. Garcia, P., Payne, P.R., Chong, E., et al., *Tetrahedron*, 2013, vol. 69, p. 5737.
6. Tin, M.K.T., Yap, G.P.A., and Richeson, D.S., *Inorg. Chem.*, 1999, vol. 38, p. 998.
7. Thirupathi, N., Yap, G.P.A., and Richeson, D.S., *Organometallics*, 2000, vol. 19, p. 2573.
8. Baunemann, A., Winter, M., Csapek, K., et al., *Eur. J. Inorg. Chem.*, 2006, p. 4665.
9. Baunemann, A., Rische, D., Milanov, A., et al., *Dalton Trans.*, 2005, p. 3051.
10. Rische, D., Parala, H., Baunemann, A., et al., *Surf. Coat. Technol.*, 2007, vol. 201, p. 9125.
11. Chen, T., Xu, C., Baum, T.H., et al., *Chem. Mater.*, 2010, vol. 22, p. 27.
12. Baunemann, A., Kim, Y., Winter, M., and Fischer, R.A., *Dalton Trans.*, 2006, p. 121.
13. Gaess, D., Harms, K., Pokoj, M., et al., *Inorg. Chem.*, 2007, vol. 46, p. 6688.
14. Pugh, S.M., Trosch, D.J.M., Skinner, M.E.G., et al., *Organometallics*, 2001, vol. 20, p. 3531.
15. Gade, L.H. and Mountford, P., *Coord. Chem. Rev.*, 2001, vols 216-217, p. 65.
16. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
17. Sheldrick, G.M., *SADABS. Program for Empirical X-ray Absorption Correction*, Bruker, 1990–2010.
18. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, vol. 71, p. 3.
19. Mohebbi, S. and Assoud, A., *Polyhedron*, 2008, vol. 27, p. 2127.

Translated by Z. Svitanko