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Adducts of Sterically Hindered Tellurium Catecholate with Ethers

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Abstract—Adducts of tellurium(IV) 3,6-di-*tert*-butyl catecholate ($Te(Cat^{36})_2$) with 1,2-dimethoxyethane (Dme), bis(2-methoxy)ethyl ether (diglyme), and crown ether 18-crown-6 (18c6) ($[Te(Cat^{36})_2(Dme)]_2$ (**I**), $[Te(Cat^{36})_2(diglyme)]$ (**II**), and $[Te_2(Cat^{36})_4(18c6)]$ (**III**), respectively) are synthesized and characterized by X-ray diffraction (XRD) (CIF files CCDC nos. 2208717 (**I**), 2208718 (**II**), and 2208719 (**III**)). The complexes are also characterized by NMR (^1H, ^{125}Te) and IR spectroscopy.

Keywords: tellurium, quinones, XRD, NMR
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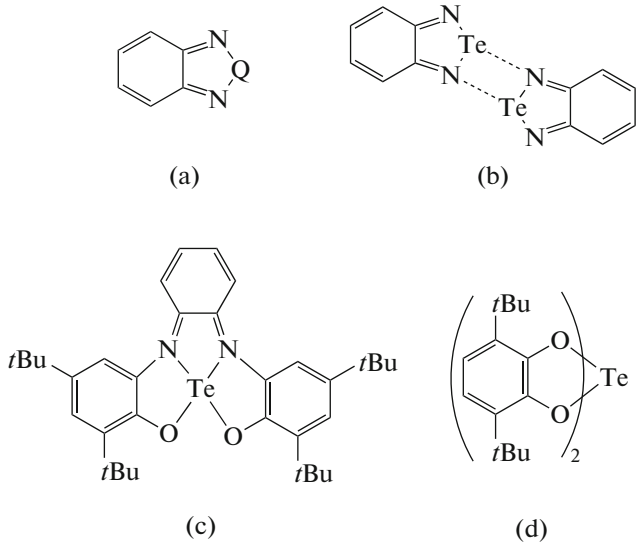
INTRODUCTION

Chalcogen–nitrogen heterocycles are considered as potential precursors of materials with interesting optical, electronic, and magnetic properties [1]. 2,1,3-Benzotellurodiazole and its analogs (Scheme 1a; Q = S, Se, Te) are characterized by the formation of stable radical anions, which were isolated, on the one hand, as salts with both diamagnetic and paramagnetic cations in the case of Q = S and Se [2]. On the other hand, the chemistry of 2,1,3-benzotellurodiazole is characterized by the formation of Te···N chalcogen bonds resulting in the oligomerization and complete coupling of the anion-radical fragments [3]. We showed that the structural analog of 2,1,3-benzotellurodiazole (Scheme 1c) can be synthesized from the redox-active ligand: the *o*-benzoquinone derivative [4]. The coordination of two phenoxy fragments to the Te atom and the presence of bulky *tert*-butyl groups in the complex prevent its oligomerization. We succeeded to isolate the radical anion by the reduction of the complex with cobaltocene. The radical anion is the first example of the structurally characterized paramagnetic derivative of the tellurium–nitrogen heterocycle. The obtained result impelled us to study tellurium complexes with other redox-active ligands. Tellurium(IV) catecholates have been known rather long ago [5–7], but their molecular and electronic structures were systematically studied only recently [8]. As turned out, tellurium catecholates are prone to the formation of adducts with diverse O- and N-donor ligands. Linear dependences of the Te···N bond length and $\delta(^{125}Te)$ chemical shift on pK_b of the ligand were found for the series of adducts with substituted pyridines [9]. The present work is devoted to the synthesis and characterization of the $Te(Cat^{36})_2$ complexes (Scheme 1d) with ethers: 1,2-dimethoxyethane (Dme), bis(2-methoxy)ethyl ether (diglyme), and crown ether 18-crown-6 (18c6).



Scheme 1.

EXPERIMENTAL

The synthesis of complex **I** was carried out in an inert atmosphere using the standard Schlenk technique. Solvents were dehydrated and degassed by reflux and distillation in an argon atmosphere using the corresponding drying agents [10]. Compound $Te(Cat^{36})_2$ was synthesized according to a published procedure [9]. NMR spectra were detected on a Bruker Avance III 500 spectrometer with a working frequency of 500.03 MHz (for ^1H) and 150.76 MHz (for ^{125}Te). IR spectra for samples in KBr pellets were

recorded on a SCIMITAR FTS 2000 instrument. Elemental analysis was carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

Synthesis of $[Te(Cat^{36})_2(Dme)]_2$ (I). Compound $Te(Cat^{36})_2$ (95 mg, 0.167 mmol) was placed in a Schlenk flask, and anhydrous 1,2-dimethoxyethane (Dme) (~5 mL) was condensed into the flask under reduced pressure on cooling. After the mixture was spontaneously warmed from −196°C to room temperature, a yellow solution was obtained and sealed into a Γ-like tube [11]. Yellow crystals of complex **I** suitable for XRD were formed after the slow evaporation of the solvent to the free branch of the tube. The yield was 75 mg (69%).

^{1}H NMR ($CDCl_3$; δ, ppm): 1.26 (s, 36H, CH_3 (Cat)), 3.41 (s, 6H, CH_3 (Dme)), 3.56 (s, 4H, CH_2), 6.68 (s, 4H, CH (Cat)). ^{125}Te NMR (CH_2Cl_2; δ, ppm): 1615.0.

IR (KBr; ν, cm^{-1}): 3096 w, 3083 w, 2949 s, 2907 s, 2867 s, 1601 w, 1546 w, 1491 w, 1467 w, 1456 w, 1398 s, 1384 s, 1357 m, 1306 w, 1272 m, 1232 s, 1202 w, 1145 s, 1087 s, 1029 w, 978 m, 938 m, 922 m, 857 m, 808 m, 801 m, 717 m, 686 s, 647 m, 602 m, 585 m.

For $C_{64}H_{100}O_{12}Te_2$		
Anal. calcd., %:	C, 58.38	H, 7.66
Found, %:	C, 58.65	H, 7.90

Synthesis of $[Te(Cat^{36})_2(diglyme)]$ (II). A weighed sample of $Te(Cat^{36})_2$ (58 mg, 0.102 mmol) was dissolved in a mixture of anhydrous CH_2Cl_2 (10 mL) and toluene (2 mL), and diglyme (2 droplets) was added to the solution. The slow evaporation of the solution in air resulted in the formation of yellow crystals of complex **II** suitable for XRD. The yield was 68 mg (95%).

^{1}H NMR ($CDCl_3$; δ, ppm): 1.26 (s, 36H, CH_3 (Cat)), 3.39 (s, 6H, CH_3 (diglyme)), 3.57 (m, 4H, CH_2), 3.62 (m, 4H, CH_2), 6.68 (s, 4H, CH (Cat)). ^{125}Te NMR (CH_2Cl_2; δ, ppm): 1618.6.

IR (KBr; ν, cm^{-1}): 3092 w, 2946 s, 2913 s, 2867 s, 1598 w, 1542 w, 1489 m, 1467 m, 1454 w, 1397 s, 1384 s, 1359 m, 1306 s, 1284 m, 1269 m, 1236 s, 1226 s, 1203 m, 1159 w, 1143 m, 1112 s, 1079 s, 1026 w, 1014 m, 970 m, 939 m, 921 m, 856 m, 808 m, 801 m, 707 m, 688 s, 647 m, 600 m, 587 w.

For $C_{34}H_{54}O_7Te$		
Anal. calcd., %:	C, 58.14	H, 7.75
Found, %:	C, 58.35	H, 7.60

Synthesis of $[Te_2(Cat^{36})_4(18c6)]$ (III). A mixture of $Te(Cat^{36})_2$ (52 mg, 0.092 mmol) and 18-crown-6 (18c6) (26 mg, 0.098 mmol) was dissolved in a mixture of anhydrous CH_2Cl_2 (10 mL) and toluene (2 mL). The slow evaporation of the solution in air resulted in the formation of yellow crystals of complex **III** suitable for XRD. The yield was 54 mg (84%).

^{1}H NMR ($CDCl_3$; δ, ppm): 1.26 (s, 36H, CH_3 (Cat)), 3.69 (s, 24H, CH_2), 6.68 (s, 4H, CH (Cat)). ^{125}Te NMR (CH_2Cl_2; δ, ppm): 1616.3.

IR (KBr; ν, cm^{-1}): 3093 w, 2948 s, 2907 s, 2876 s, 1638 w, 1598 w, 1489 m, 1467 m, 1399 s, 1384 s, 1355 s, 1307 w, 1270 m, 1235 s, 1202 w, 1144 s, 1111 s, 1028 w, 971 s, 922 m, 845 m, 807 m, 686 m, 647 m, 598 m.

For $C_{68}H_{104}O_{14}Te_2$		
Anal. calcd., %:	C, 58.30	H, 7.48
Found, %:	C, 58.15	H, 7.30

XRD. All measurements were carried out using a standard procedure on a Bruker-Nonius X8 APEX automated four-circle diffractometer (two-coordinate CCD detector, λ = 0.71073 Å, graphite monochromator) at T = 150 K. Reflection intensities were measured in the φ scan mode for narrow (0.5°) frames. An absorption correction was applied empirically (SADABS) [12]. The structures were solved using the SHELXT program [13] and refined using the SHELXL program [14] in the anisotropic approximation for non-hydrogen atoms in Olex2 [15]. Hydrogen atoms were localized geometrically and refined in the rigid body approximation. The crystallographic characteristics of the complexes and experimental XRD details are given in Table 1.

The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2208717 (**I**), 2208718 (**II**), and 2208719 (**III**)) and can be received at request: http://www.ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

The attempts of synthesizing $Te(Cat^{36})_2$ adducts with THF and diethyl ether were unsuccessful. However, the crystallization from 1,2-dimethoxyethane gave crystals of $[Te(Cat^{36})_2(Dme)]_2$ (**I**) suitable for XRD. The crystal structure of compound **I** is formed by the $\{Te(Cat^{36})_2\}$ fragments linked via two Dme molecules into a centrosymmetric dimer. The $Te\cdots O_{Dme}$ distances (3.002(2)–3.554(3) Å) are substantially longer than those in the dicatecholate fragment $\{Te(Cat^{36})_2\}$ (Table 2). It is known that shorter and longer $Te-O_{cat}$ bonds differed by 0.05–0.10 Å are always observed in tellurium(IV) catecholates and their adducts. As in the previously described $Te(Cat^{36})_2$ derivatives, the shorter $Te\cdots O_{Dme}$ distances in complex **I** are in the *trans* position toward the shorter $Te-O_{cat}$ bonds (1.9377(17) and 1.9449(17) Å).

Table 1. Crystallographic data and structure refinement parameters for compounds **I**–**III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{64}H_{100}O_{12}Te_2$	$C_{34}H_{54}O_7Te$	$C_{68}H_{104}O_{14}Te_2$
FW	1316.63	702.37	1400.71
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic $P2_1/n$
a, Å	10.3536(4)	10.9930(4)	16.6233(5)
b, Å	10.8293(4)	28.9366(10)	19.5644(5)
c, Å	15.9290(6)	11.7287(4)	42.6515(12)
α, deg	71.4380(10)	90	90
β, deg	73.5960(10)	114.5880(10)	95.5130(10)
γ, deg	83.1050(10)	90	90
V, Å^3	1623.28(11)	3392.6(2)	13 807.2(7)
Z	1	4	8
μ, mm^{-1}	0.955	0.921	0.905
F(000)	684.0	1464.0	5824.0
Crystal size, mm	0.2 × 0.06 × 0.04	0.16 × 0.15 × 0.14	0.14 × 0.11 × 0.09
Range of data collection over 2θ, deg	4.104–54.298	4.744–55.866	2.554–55.778
Range of indices *h*, *k*, *l*	$-13 \le h \le 13$, $-13 \le k \le 13$, $-20 \le l \le 20$	$-14 \le h \le 12$, $-38 \le k \le 34$, $-15 \le l \le 14$	$-21 \le h \le 17$, $-25 \le k \le 25$, $-56 \le l \le 50$
Number of measured, independent, and observed ($I > 2\sigma(I)$) reflections	28804, 7182, 6370	28869, 8091, 7298	140961, 32861, 27594
R_{int}	0.0495	0.0294	0.0542
Number of refined parameters	366	393	1571
Number of restraints	0	0	51
GOOF	0.956	1.130	1.194
R_1, wR_2 ($I > 2\sigma(I)$)	0.0320, 0.0801	0.0316, 0.0776	0.0945, 0.2007
R_1, wR_2 (all reflections)	0.0385, 0.0849	0.0363, 0.0801	0.1086, 0.2064
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.65/–0.49	0.55/–0.56	2.43/–1.82

Although the structure of binary catecholate [Te(Cat^{36})$_2$] is unknown, a comparison of the geometric characteristics of isomeric 3,5-di-*tert*-butyl catecholate [Te(Cat^{35})$_2$]$_2$ indicates a weak influence of the coordination of the ether on the Te–O bond lengths and chelate angles (Table 2). The known adducts of tin(IV) catecholates [Sn(Cat^{36})$_2$L$_2$] (L = Et$_2$O, Thf) have a different structure: the ether molecules are in the *trans* position relative to each other [16]. Unlike the Sn–O$_{cat}$ distances in the tellurium analogs, those in tin(IV) catecholates are nearly identical. The C–O and C–C bond lengths in the chelate cycles of complex **I** and other Te(Cat^{36})$_2$ adducts unambiguously indicate the dianionic nature of the dioxolene ligand.

In spite of long Te···O$_{Dme}$ distances in complex **I**, the Dme ligand can be considered as that coordinated via the bridging μ-κ^{2}O,O':κ^{2}O,O' type, which was earlier unknown for this ligand (Fig. 1, **I**). A similar coordination mode of the 2,2'-bipyridyl ligand (Bipy) was detected earlier in the [Te(Cat^{36})$_2$(Bipy)]$_2$ adduct in which the Te···N distances range from 2.9463(19) to 3.582(2) Å [9]. It is most likely that the long Te···O and Te···N distances favor this coordination mode. The

Table 2. Selected geometric characteristics of adducts **I**–**III**

Bond, Å and angle, deg	**I***	**II***	**III***		$[Te(Cat^{35})_2]_2$**
			molecule 1	molecule 2	
d(Te–O_{cat}), Å	1.9377(17), 2.0246(17), 1.9449(17), 2.0172(17)	1.9595(15), 2.0190(15), 1.9606(14), 2.0286(15)	1.957(5), 2.032(5), 1.950(5), 2.037(5), 1.946(5), 2.038(5), 1.958(5), 2.008(5)	1.941(6), 2.027(6), 1.962(5), 2.030(5), 1.951(6), 2.025(6), 1.943(6), 2.044(6)	1.952(1), 2.008(1), 1.952(1), 2.042(1)
d(Te···O_L), Å	3.002(2), 3.114(2), 3.392(2), 3.554(3)	2.9184(16), 3.1338(17), 2.8434(16)	2.800(6), 3.086(6), 2.873(6), 3.091(7)	2.890(11), 2.940(13), 2.944(11)	
Angle ($O_{cat}TeO_{cat}$), deg	81.09(6), 80.80(6)	80.32(6), 80.40(6)	80.7(2), 80.1(2), 80.2(2), 81.4(2)	80.9(2), 80.8(2), 80.3(2), 80.5(2)	80.96(5), 81.84(5)

* This work.
** [8].

average Te···O distances in the known adducts $[TeCl_4(Dme)_2]$ (2.777 Å), $[TeF_4(Dme)_2]$ (2.859 Å), and $[TeF_2(CN)_2(Dme)_2]$ (2.806 Å) are substantially shorter than those in compound **I**, which indicates an appreciably higher Lewis acidity of tellurium(IV) halides and pseudohalides compared to that of catecholates [17, 18].

The crystallization of $Te(Cat^{36})_2$ from a CH_2Cl_2–toluene mixture in the presence of diglyme gave crystals of molecular complex $[Te(Cat^{36})_2(diglyme)]$ (**II**) (Fig. 1, **II**). This complex is a very rare example of the coordination of diglyme to the nonmetal (complexes $[Te(CN)_4(diglyme)_2]$ and $[Te(CN)_4(diglyme)]_\infty$ were described earlier [19]). In the structure of complex **II**, the dihedral angle between the planes of the catecholate ligands is rather small (65.4°), which can be explained by the presence of the bulky diglyme molecule. The latter is coordinated to the Te atom via three oxygen atoms. The corresponding distances are 2.8434(16), 2.9184(16), and 3.1338(17) Å, and the longest distance corresponds to the bond with the central oxygen atom. The Te···O distances in the aforementioned complex $[Te(CN)_4(diglyme)]_\infty$ (2.621(7)–2.821(7) Å) are substantially shorter than those in complex **II** even in spite of the higher coordination number of the Te atom.

The reaction of $Te(Cat^{36})_2$ with cyclic ether 18-crown-6 afforded crystals of adduct $[\{Te(Cat^{36})_2\}_2$-(18c6)] (**III**) (Fig. 1, **III**). Its crystal structure contains two independent molecules. In each molecule, two $\{Te(Cat^{36})_2\}$ fragments are linked to the crown ether molecule via weak Te···O_{18c6} contacts (Table 2). The shortest contacts for each Te atom are close to 2.80–2.98 Å, which are somewhat shorter than the contacts in complexes **I** and **II** and are close to that in the $Te(Cat^{36})_2$ adduct with acetone (2.7997(13) Å). The next in length Te···O_{18c6} contacts increase to 2.94–3.09 Å. This tendency is also observed for the earlier described adduct of tellurium(IV) tetrachlorocatecholate $[Te(CatCl4)_2(18c6)]$, whose shortest contacts Te···O_{18c6} are 2.983(7), 3.104(7), and 3.117(7) Å [7].

The data of ^1H NMR spectroscopy confirm the compositions of adducts **I**–**III**. The ^{125}Te NMR chemical shifts of the synthesized adducts lie in a range of 1615.0–1618.6 ppm, which is close to the $Te(Cat^{36})_2$ chemical shift in Thf (1617.9 ppm) [9].

Thus, the adducts of tellurium(IV) 3,6-di-*tert*-butyl catecholate ($Te(Cat^{36})_2$) with 1,2-dimethoxyethane, bis(2-methoxy)ethyl ether, and crown ether 18-crown-6 were synthesized. According to the XRD data, the complex with diglyme is mononuclear. Two other complexes are binuclear with the bridging ether molecules, and the earlier unknown coordination type μ-κ^2O,O':κ^2O,O' was detected for Dme.

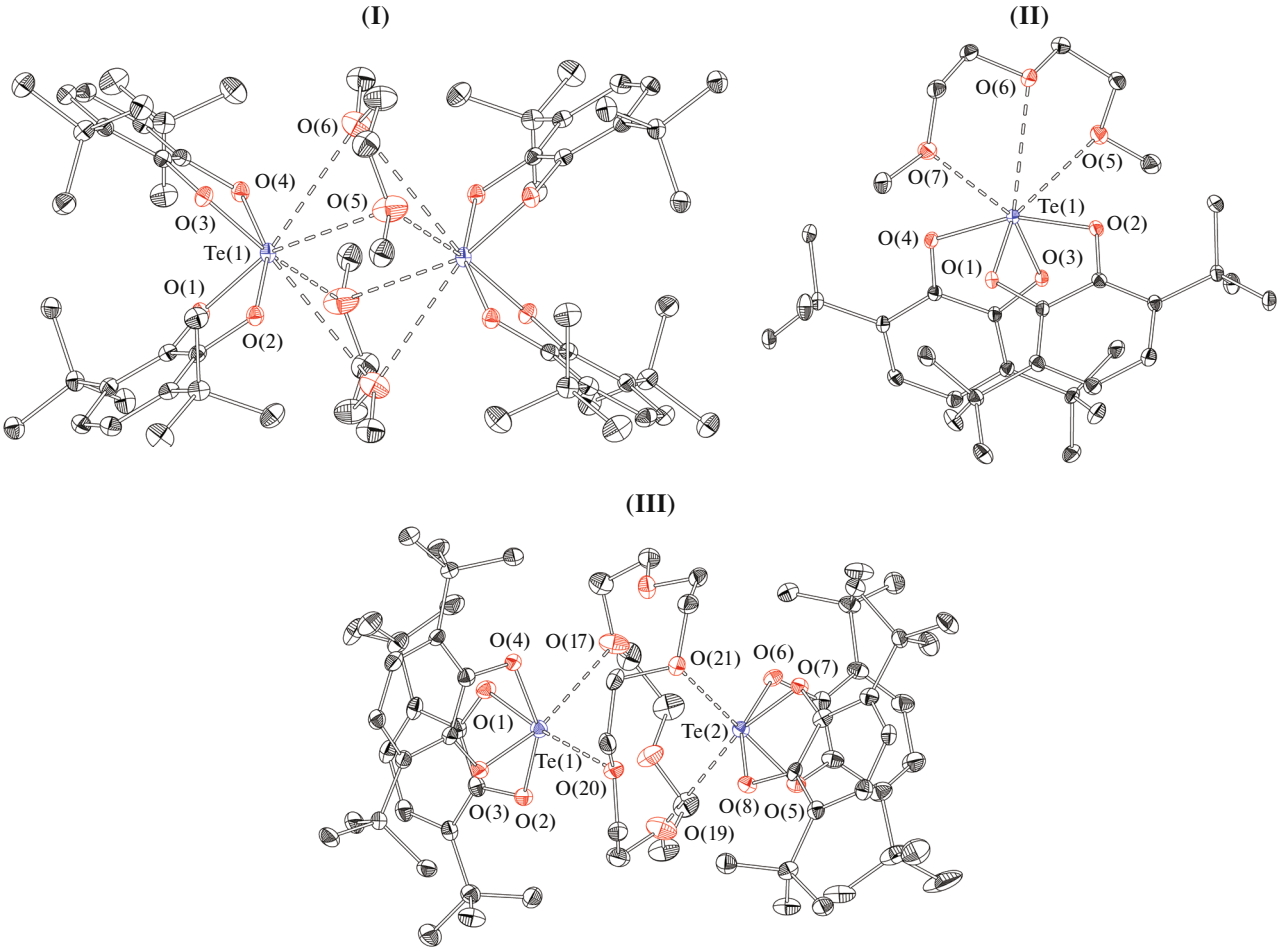


Fig. 1. Molecular structures of complexes **I**–**III** (thermal ellipsoids of 30% probability; hydrogen atoms are omitted; one independent molecule and the shortest Te···O_{18c6} contacts are shown for complex **III**).

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CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

ADDITIONAL INFORMATION

This article is prepared for the memorial issue in tribute to the Corresponding Member of the Russian Academy of Sciences K.Yu. Zhizhin on his 50th birthday.

REFERENCES

1. Chivers, T., *A Guide to Chalcogen-Nitrogen Chemistry*, London: World Scientific, 2005.
2. Gritsan, N.P. and Zibarev, A.V., *Russ. Chem. Bull.*, 2011, vol. 60, p. 2131. https://doi.org/10.1007/s11172-011-0331-4
3. Puskarevsky, N.A., Smolentsev, A.I., Dmitriev, A.A., et al., *Chem. Commun.*, 2020, vol. 56, p. 1113.
4. Petrov, P.A., Kadilenko, E.M., Sukhikh, T.S., et al., *Chem.-Eur. J.*, 2020, vol. 26, p. 14688.
5. Antikainen, P.J. and Mälkönen, P.J., *Z. Anorg. Allg. Chem.*, 1959, vol. 299, p. 292.
6. Lindqvist, O., Jerslev, B., Cyvin, S.J., et al., *Acta Chem. Scand.*, 1967, vol. 21, p. 1473.
7. Annan, T.A., Ozarowski, A., Tian, Z., and Tuck, D.G., *Dalton Trans.*, 1992, p. 2931.
8. Kieser, J.M., Jones, L.O., Lin, N.J., et al., *Inorg. Chem.*, 2021, vol. 60, p. 3460.
9. Petrov, P.A., Filippova, E.A., Sukhikh, T.S., et al., *Inorg. Chem.*, 2022, vol. 61, p. 9184.

10. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.

11. Petrov, P.A., Smolentsev, A.I., Bogomyakov, A.S., and Konchenko, S.N., *Polyhedron*, 2017, vol. 129, p. 60.

12. *APEX2 (version 1.08), SAINT (version 7.03), SADABS (version 2.11), SHELXTL (version 6.12)*, Madison: Bruker AXS Inc., 2004.

13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, vol. 71, p. 3.

14. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.

15. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.

16. Piskunov, A.V., Lado, A.V., Fukin, G.K., et al., *Heteroatom. Chem.*, 2006, vol. 17, p. 481.

17. Fritz, S., Lentz, D., and Szwaka, M., *Eur. J. Inorg. Chem.*, 2008, p. 4683.

18. Shlykov, S.A., Giricheva, N.I., Titov, A.V., et al., *Dalton Trans.*, 2010, vol. 39, p. 3245.

19. Lentz, D. and Szwaka, M., *Dalton Trans.*, 2008, p. 1289.

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