ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 7, pp. 505–509. © Pleiades Publishing, Ltd., 2013.
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Synthesis, Properties, and Crystal Structure of the Tin(IV) Complex with N-(2-Hydroxyethyl)ethylenediaminetriacetic Acid $[Sn(\mu\text{-Hedtra})(\mu\text{-OH})SnCl_3(H_2O)] \cdot 3H_2O$

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Received December 26, 2012

Abstract—The binuclear tin(IV) complex with N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (H_4Hedtra) is synthesized. The compound is characterized by elemental analysis, thermogravimetry, and IR spectroscopy. An X-ray diffraction analysis of complex $Sn(\mu\text{-Hedtra})(\mu\text{-OH})SnCl_3(H_2O)] \cdot 3H_2O$ (**I**) is carried out. Structure **I** is formed by the binuclear complexes and molecules of water of crystallization. One of the tin atoms coordinates six "active" sites $Hedtra^{4-}$ (the alcohol branch is deprotonated and forms a bridge between two tin atoms) and the bridging hydroxo group. The polyhedron is a pentagonal bipyramid. The octahedral environment of the second tin atom is formed by two bridging oxygen atoms, three chlorine atoms (*fac* isomer), and a coordination water molecule.

DOI: 10.1134/S1070328413070075

INTRODUCTION

N-(2-Hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (H_4Hedtra) is a complexone of the diaminocarboxylic series obtained by the replacement in an ethylenediamine-N,N,N',N'-tetraacetic acid of one acetate branch by the hydroxyethyl one. The participation of the latter in coordination depends on the metal nature. Monomeric $[Er(H_2O)_2(HHedtra)] \cdot 4H_2O$ and dimeric $[Ln_2(HHedtra)_2(H_2O)_4] \cdot 6H_2O$ (Ln = La, Ce) complexes with rare-earth metals were obtained in which the formation of the hydroxyethyl cycle is not accompanied by its deprotonation. In the binuclear complexes, one of the acetate groups is bridging and forms the four-membered "acetate" metallocycle with the second Ln atom of the dimer along with the formation of the glycinate cycle with "its" lanthanide atom [1].

This ligand with vanadium(III) forms both mononuclear $[V(HHedtra)(H_2O)] \cdot 2H_2O$ and $K[VO(HHedtra)] \cdot H_2O$ [2] and binuclear $(H_2En)[V(Hedtra)]_2 \cdot 2H_2O$ [3] complexes. The hydroxyethyl group in them is coordinated by vanadium. In the case of $(H_2En)[V(Hedtra)]_2 \cdot 2H_2O$, this group is deprotonated and performs the bridging function. In ruthenium hydroxyethylethylenediaminetriacetates, whose structure was determined from the spectral data, and in $[Ru^{II}(HHedtra)]^-$ [4], $[Ru^{II}(HHedtra)(Pyz)_n]^-$ (Pyz is pyridazine) [5], and $[Ru^{III}(HHedtra)(H_2O)]$ [6, 7], whose intensive study is due to their application as inhibitors of proteases, the $-CH_2CH_2OH$ group is not involved in coordination.

We have previously shown [8] that, regardless of the starting reactant (GeO_2, $GeCl_4$), complex $[Ge(HHedtra)(OH)] \cdot 1.5H_2O$ is formed with H_4Hedtra in which the hydroxyethyl branch is not bound with germanium.

A comparison of the compositions and structures of the above described complexes of various metals with H_4Hedtra showed that the dentate character, the mode and shape of the coordinated ligand, and the structural type of the formed compounds (mono- and binuclear) changed depending on the complexing agent.

The purpose of this work is the synthesis and determination of the composition and structure of the complex of H_4Hedtra with tin(IV), which is an electronic analog of germanium(IV).

EXPERIMENTAL

Synthesis. Since in all complexes with H_4Hedtra studied to presently [1–8] the molar ratio metal : ligand = 1 : 1 is observed regardless of the electronic structure of the metal, an equimolar amount of $SnCl_4$ (0.5 mL) was added to a solution containing H_4Hedtra (1.19 g, 0.0043 mol) in hot water (20 mL) in the synthesis of a coordination compound with tin(IV). In order to shift the equilibrium towards complex formation, pH 2 was created with ammonium hydroxide. The resulting transparent solution was heated for 10 min. In 2 days, a precipitate containing single crys-

Table 1. Main crystallographic data and refinement results for structure **I**

Parameter	Value
Temperature, K	153
Radiation; λ, Å	MoK_α; 0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a, Å	8.6760(6)
b, Å	13.4653(9)
c, Å	10.0549(7)
β, deg	111.8580(10)
V, Å^3	1090.22(13)
Z	2
ρ_{calcd}, g/cm^3	2.154
μ, mm^{-1}	2.717
Crystal size, mm	0.35 × 0.28 × 0.25
θ Range, deg	2.53–28.32
Range of h, k, l	$-11 \le h \le 11$, $-17 \le k \le 17$, $-13 \le l \le 8$
Collected reflections	9137
Independent reflections	5110
R_{int}	0.0200
Reflections with $I > 2\sigma(I)$	5110
Number of refined parameters	262
Flack parameter	−0.020(16)
Goodness-of-fit (F^2)	1.026
R_1, wR_2 ($I > 2\sigma(I)$)	0.0225, 0.0456
R_1, wR_2 (all reflections)	0.0262, 0.0469
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.725, −0.469

tals suitable for X-ray diffraction analysis was formed. A similar synthesis at the reactant ratio $SnCl_4$: H_4Hedtra = 2 : 1 gave the same product.

An analysis to tin was carried out using atomic emission spectroscopy with inductively coupled plasma on an Optima 2000 DV instrument (Perkin-Elmer). Carbon, nitrogen, and hydrogen were analyzed on a hemi-automated C,N,H-analyzer. The chlorine content was measured mercurimetrically [9]. The elemental analysis data for the products obtained at different molar ratios are identical.

For $C_{10}H_{23}Cl_3N_2O_{12}Sn_2$ (M = 707.07)
anal. calcd., %: C, 16.99; H, 3.28; N, 3.96; Cl, 15.04; Sn, 33.58.
Found, %: C, 17.00; H, 3.19; N, 3.95; Cl, 15.00; Sn, 33.60.

Thermogravimetric analysis was carried out on a Q-1500D derivatograph (air atmosphere, temperature range 20–1000°C, heating rate 10 deg/min). The IR absorption spectra (400–4000 cm^{-1}) of the ligand and complex were recorded on a Frontier spectrophotometer (PerkinElmer).

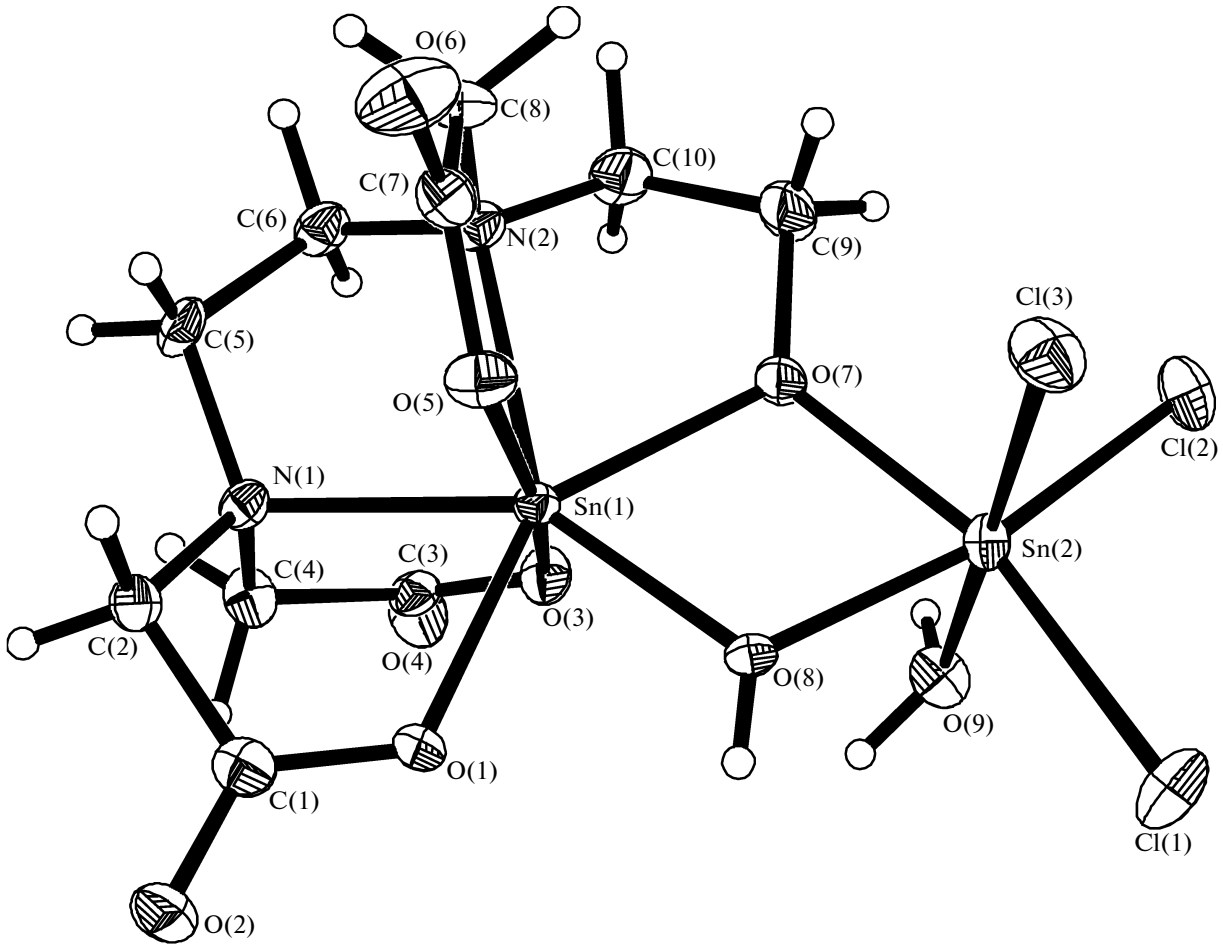
X-ray diffraction analysis. The crystals of complex **I** decompose (become turbid) at ambient temperature within 1 h. At 153 K no crystal degradation was observed in N_2 vapors within 4 h.

The experimental data for complex **I** were obtained on a Bruker SMART APEX II diffractometer [10] (TsKP of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences), and an absorption correction was applied by the semiempirical method (SADABS) [11]. The structure was determined by a combination of a direct method and Fourier syntheses. The absence of an inversion center in structure **I** was confirmed using the PLATON program [12]. The hydrogen atoms of the water molecules and hydroxo group were localized from the difference Fourier syntheses, and the aliphatic hydrogen atoms were calculated from geometric concepts. The structure was refined by full-matrix anisotropic least squares with allowance for hydrogen atoms. All calculations were performed using the SHELXS-97 and SHELXL-97 programs [13].

The main structural data are given in Table 1. The experimental data for compound **I** were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 915906; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Structure **I** is formed by the binuclear complex and molecules of water of crystallization. The Hedtra^{4-} ligand in the complex is coordinated through the hexadentate mode by one of the tin atoms (Sn(1)), whose coordination is supplemented to a coordination number of 7 by the bridging hydroxo group (the polyhedron of Sn(1) is a pentagonal bipyramid). The octa-



Structure of complex **I**.

hedral environment of the Sn(2) atom is formed by three chlorine atoms (*fac* isomer) and three oxygen atoms (figure).

The structure of complex **I** is well consistent with the data of IR spectroscopy and thermogravimetry. Four water molecules are removed with a heat uptake (mass loss 10.2%) on heating complex **I** in the temperature range from 100 to 180°C. The broad temperature range of this process is due to the removal of both water of crystallization and coordination water. The complex is stable up to 330°C. The endothermic processes of dehydrochlorination and decarboxylation (removal of 3HCl and $3CO_2$, mass loss 34.1%) occur at 330–360°C. The organic moiety of the molecule of the complex begins to burn out at 360°C with a sharp mass loss. The final thermal decomposition product at 680°C is SnO_2 (total mass loss 57.4%).

The absence of the ν(C=O) band in the IR spectrum of complex **I** compared to the spectrum of the ligand and the appearance of stretching vibration bands ν_{as}(COO) (1689 cm^{-1}) and ν_s(COO) (1360 cm^{-1}) characteristic of carboxylate ions indicate that all carboxy groups are bound with tin(IV). The hydroxy group of the ligand is deprotonated and coordinated by the complexing agent, which is confirmed by the presence of a band at 1081 cm^{-1} caused by ν(C–O) of the alcoholate type [14]. The spectrum also exhibits a band at 520 cm^{-1} corresponding to the ν(Sn–O) stretching vibrations.

The coordination of the nitrogen atoms of the ligand by tin(IV) results in the appearance in the IR spectrum of complex **I** of a band at 659 cm^{-1} corresponding to the ν(Sn–N) vibrations and agrees with the shift to the low-frequency region by 27 cm^{-1} of the band characteristic of the ν(CH) vibrations (2977 and 3004 cm^{-1} for **I** and H_4Hedtra, respectively) [1].

The environment of the Sn(1) atom in structure **I** is similar to that found in the dimeric complex $(H_2En)[V(Hedtra)]_2 \cdot 2H_2O$ [3], and that of Sn(2) is similar to the environment in $[Sn(\mu\text{-}OH)Cl_3(H_2O)]_2 \cdot 2Et_2O$ [15]. The formation of the binuclear tin complexes with different environments of the metal atoms has previously been observed in compounds $[SnCl_2\{\mu\text{-}O(CH_2CH_2O)_4\}SnCl_4] \cdot MeCN$ [16] and $[Sn(\mu\text{-}OCPhCMeNMeCH_2CMe_2O)SnBr_4] \cdot PhMe$ [17]. The structure of the Sn(Hedtra)(OH) fragment

Table 2. Bond lengths Sn–L in structure **I**

Bond	*d*, Å	Bond	*d*, Å
Sn(1)–O(1)	2.121(2)	Sn(2)–Cl(1)	2.3689(9)
Sn(1)–O(3)	2.041(2)	Sn(2)–Cl(2)	2.3631(9)
Sn(1)–O(5)	2.045(2)	Sn(2)–Cl(3)	2.4108(9)
Sn(1)–O(8)	2.072(2)	Sn(2)–O(7)	2.066(2)
Sn(1)–O(7)	2.161(2)	Sn(2)–O(8)	2.057(2)
Sn(1)–N(1)	2.337(3)	Sn(2)–O(9)	2.093(2)
Sn(1)–N(2)	2.319(3)		

in complex **I** is usual for similar compounds [18]. The octahedral fragment $Sn(OH)(O_{Hedtra})Cl_3(H_2O)$ can exist as different isomers: *fac* and *mer* (in the latter case, there are two isomers: a water molecule in the *trans* position to Hedtra or OH). The *fac* isomer found in complex **I** is usual for the octahedral tin(IV) complexes containing three chlorine and/or bromine atoms in the coordination sphere. The CCDC (version 5.33, August 2012) [19] contains 76 similar compounds, and *mer* isomers are observed in 16 of them. However, in all these compounds, stereochemistry is determined by the tridentate ligands with the rigid planar structure. Other 60 compounds, as six complexes from the ICSD (version 2012-1) [20], have the *fac* structure.

The bond lengths in complex **I** are usual for similar compounds (Table 2), for example, [16]. All nine hydrogen atoms of the hydroxy group and water molecules are involved in hydrogen bonding (Table 3), and their combined action joins the structural units into a framework.

Complex **I** substantially differs in composition and structure from hydroxylethylenediamine triacetates of other metals. In their series, complex **I** is the first binuclear complex with the molar ratio metal : ligand = 2 : 1. This determines specific features of its structure: two coordination sites Sn(1) and Sn(2) with different coordination numbers and ligand environments and with the bridging function of the deprotonated hydroxyethyl and hydroxy groups. Moreover, the structures of the complexes of electronic analogs of Sn(IV) and Ge(IV) are basically different: $[Ge(HHedtra)(OH)] \cdot 1.5H_2O$ is the mononuclear complex with the pentadentate-chelating coordination mode of the ligand involving no $-CH_2CH_2OH$ group and the polyhedron of germanium that is built up to an octahedron by the hydroxo ligand.

REFERENCES

1. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksony i kompleksonaty metallov* (Complexones and Metal Complexonates), Moscow: Khimiya, 1988.
2. Ogino, H., Shimoi, M., and Saito, Y., *Inorg. Chem.,* 1989, vol. 28, no. 18, p. 3596.
3. Shepherd, R.E., Hatfield, W.E., Debashis, G., et al., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 18, p. 5511.
4. Chen, Ya., Lin, F.-T., and Shepherd, R.E., *Inorg. Chem.*, 1997, vol. 36, no. 5, p. 818.

Table 3. Geometric parameters of hydrogen bonds in structure **I**

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of A atom
	D–H	H···A	D···A		
O(8)–H(1)···O(12)	0.80	1.84	2.634(4)	174	x, y, z
O(9)–H(3)···O(10)	0.97	1.60	2.534(3)	160	$-x+1, y-1/2, -z$
O(9)–H(2)···O(11)	0.90	1.69	2.568(4)	166	x, y, z
O(10)–H(4)···O(2)	0.77	1.96	2.720(4)	168	x, y, z
O(10)–H(5)···O(6)	0.77	1.99	2.705(4)	154	$x+1, y, z$
O(11)–H(6)···Cl(3)	0.89	2.36	3.195(3)	157	$x+1, y, z$
O(11)–H(7)···O(6)	0.79	2.28	3.048(4)	165	$x+1, y, z$
O(12)–H(9)···O(10)	0.89	1.93	2.800(4)	164	x, y, z
O(12)–H(8)···O(4)	0.76	2.01	2.752(4)	165	$-x+1, y+1/2, -z$

5. Chen, Ya. and Shepherd, R.E., *Inorg. Chim. Acta*, 1998, vol. 279, no. 1, p. 85.
6. Chatterjee, D., Sengupta, A., Mirta, A., et al., *J. Coord. Chem.*, 2005, vol. 58, no. 18, p. 1703.
7. Chatterjee, D., Sengupta, A., Mirta, A., et al., *Inorg. Chim. Acta*, 2005, vol. 358, no. 10, p. 2960.
8. Martsinko, E.E., Seifullina, I.I., Minacheva, L.Kh., et al., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 10, p. 1519.
9. Klyuchnikov, N.G., *Rukovodstvo po neorganicheskomu sintezu* (Guide on Inorganic Synthesis), Moscow: Khimiya, 1965.
10. *APEX II and SAINT,* Madison (WI, USA): Bruker AXS Inc., 2007.
11. Sheldrick, G.M., *SADABS*, Göttingen (Germany): Univ. of Göttingen, 1997.
12. Spek, A.L.J., *Appl. Crystallogr.*, 2003, vol. 36, no. 1, p. 7.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
14. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
15. Yang, M., Yin, H., Quan, L., et al., *Acta Crystallogr., Secr. E: Structure Reports Online*, 2008, vol. 64, no. 11, p. m1430.
16. Bel'skii, V.K., Bulychev, B.M., Strel'tsova, N.R., et al., *Dokl. Akad. Nauk SSSR*, 1988, vol. 303, no. 5, p. 1137.
17. Iovkova-Berends, L., Berends, T., Dietz, C., et al., *Eur. J. Inorg. Chem.,* 2011, no. 24, p. 3632.
18. Porai-Koshits, M.A., *Sov. Sci. Rev., B.*, 1987, vol. 10, p. 91.
19. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, no. 3, p. 380.
20. Bergerhoff, G. and Brown, I.D., *Crystallographic Databases*, Allen F.H., et al., Eds., Chester: International Union of Crystallography, 1987.

Translated by E. Yablonskaya