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Synthesis and Structure of *catena*((μ_2-4,4,10,10-Tetramethyl-1,3,7,9-Tetraazaspiro[5.5]undecane-2,8-Dione-*O,O*')dichloro-Zinc)

E. E. Netreba[a, *] **and N. V. Somov**[b]

[a] *Taurida Academy, Vernadsky Federal University, Simferopol, Russia*
[b] *Lobachevsky National Research University, Nizhny Novgorod, Russia*
**e-mail: evgtnu@gmail.com*

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Abstract—The coordination polymer, *catena*-((μ_2-4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione-*O*,*O*')dichloro-zinc) $\{[Zn(C_{11}H_{20}N_4O_2)Cl_2]\}_n$ (**I**), is prepared for the first time from zinc chloride and bicyclic bis(urea), 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione, and investigated by X-ray diffraction (CIF file CCDC no. 877812). The crystals of **I** are monoclinic: space group $P2_1$, $a = 6.2121(17)$, $b = 11.276(3)$, $c = 11.387(3)$ Å, $\beta = 94.99(3)°$, $V = 794.6(3)$ Å^3, ρ(calcd.) = 1.574 g/cm^3, $Z = 2$. The singe-phase nature of the powder sample of **I** is confirmed by Rietveld refinement of the powder X-ray diffraction pattern; at 293 K, $a = 6.20369(11)$, $b = 11.23336(18)$, $c = 11.36013(16)$ Å, $\beta = 95.3001(11)°$, $V = 788.28(2)$ Å^3. The content of the major phase **I** in the sample is 100 ± 1%, no impurity lines are found. The zinc coordination polyhedron in the coordination polymer chain is a tetrahedron with vertices being occupied by two chlorine atoms and carbonyl O(1) and O(2) atoms of two TTSU molecules related by the symmetry code ($2 - x$, $1/2 + y$, $2 - z$). The zinc bond angles are 101.05(12)°–122.13(9)°. The Zn···Zn distance in the polymer is 9.480(2) Å. The chains in the coordination polymers are additionally combined by intermolecular hydrogen bonds, N(2)–H(2)···O(2)^{i} (^{i} $2 - x$, $1/2 + y$, $2 - z$) (H···O 2.17 Å, N–H···O 147°) and N(4)–H(4)···Cl(2)^{ii} (^{ii} $1 - x$, $-1/2 + y$, $2 - z$) (H···Cl 2.48 Å, N–H···Cl 159°). The chains are joined into layers along the (0 0 1) plane by intermolecular hydrogen bonds, N(1)–H(1)···Cl(1)^{iii} (^{iii} $1 - x$, $-1/2 + y$, $2 - z$) (H···Cl 2.78 Å, N–H···Cl 148°).

Keywords: bicyclic bis(urea), tetraazaspiro[5.5]undecane, zinc(II), coordination polymer, structure, single crystal X-ray diffraction, powder X-ray diffraction

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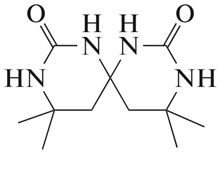
INTRODUCTION

Coordination polymers with symmetrical bridged ligands referring to the class of bicyclic bis(ureas) have been scarcely studied. One such ligand is a representative of bicyclic undecane spiro-bis(ureas), namely, 4,4,10,10-tetramethyl-1,3,7,9-tetraazaspiro[5.5]undecane-2,8-dione (C11H20N4O2, TTSU):



This compound, being an urea precursor, has a number of valuable biological properties: it is harmless and low-toxic [1], membranotropic [2], and capable of penetrating and accumulating in the cytoplasm of the mouse L1210 and human CEM-T4 leukemia cells [3]. It also increases the peptide level and decreases the polysaccharide level of oat grain [4]. TTSU has been proposed for stimulating callusogenesis and inducing rhizogenesis in various plants [5, 6] and as efficient growth and development stimulant in sheep breeding [7].

A TTSU molecule contains six heteroatoms and behaves as an ambidentate ligand. Previously, some coordination polymers with this molecule were prepared and described: $\{[UO_2(C_{11}H_{20}N_4O_2)(NO_3)_2] \cdot 2H_2O\}_n$ (CCDC 876539) [8], $\{[Mn(C_{11}H_{20}N_4O_2)_2(H_2O)_2]^{2+}2(NO_3)^-\}_n$ (CCDC 876570) [9], $\{[Cu(C_{11}H_{20}N_4O_2)_2(H_2O)]^{2+}\ 2(NO_3)^-\}_n$ (CCDC 903386) [10], and $\{[Sc_2(C_{11}H_{20}N_4O_2)_3(H_2O)_6]^{6+}6(NO_3)^-\}_n$ (CCDC 925791) [11].

Therefore, the synthesis and investigation of the coordination compounds formed by this ligand would help to elucidate more comprehensively the chemistry of its reaction with various metal ions and its coordi-

Table 1. Main crystallographic data and X-ray experiment details for compound **I**

Parameter	Value
M	376.58
System	Monoclinic
Space group	$P2_1$
Unit cell parameters	
a, Å	6.2121(17)
b, Å	11.276(3)
c, Å	11.387(3)
β, deg	94.99(3)
V, Å^3	794.6(3)
Z	2
ρ(calcd.), g/cm^3	1.574
μ(MoK_α), mm^{-1}	1.887
F(000)	388
Crystal size, mm	0.2 × 0.2 × 0.15
Range of θ, deg	3.29–28.79
Ranges of reflection indices	$-6 \le h \le 8$, $-13 \le k \le 15$, $-14 \le l \le 12$
Number of measured reflections	4950
Number of unique reflections (R_{int})	2859 (0.0575)
Number of reflections with $I > 2\sigma(I)$	2228
Number of refined parameters	185
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0531$, $wR_2 = 0.0859$
R-factor for all reflections	$R_1 = 0.0738$, $wR_2 = 0.1016$
GOOF on F^2	0.992
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.802/–0.771

nation behavior and to obtain compounds with new valuable properties for various applications.

The purpose of this study is to prepare the coordination polymer of zinc chloride with TTSU molecules, $[Zn(C_{11}H_{20}N_4O_2)Cl_2]_n$ (**I**), determine its molecular structure, and establish the single-phase nature of the obtained specimen.

EXPERIMENTAL

The synthesis was carried out using pharmacopoeia grade anhydrous $ZnCl_2$, TTSU prepared by reported procedures [12, 13], and high-purity grade acetone.

Synthesis of I. Zinc chloride (1.8 g, 13.25 mmol) was dissolved in 20 mL of acetone, TTSU (2.24 g, 8.68 mmol) was added, and the mixture was magnetically stirred for 5–10 min. The resulting solution was filtered and kept for several hours until 2/3 of the solvent was evaporated and crystals were formed. The white crystals were collected on a filter, washed with acetone, and dried in air. The yield was ~ 93% relative to the ligand. Complex **I** is air-stable.

For $C_{11}H_{20}N_4O_2Cl_2Zn$

anal. calcd., %:	C, 35.08;	H, 5.35;	N, 14.88.
Found, %:	C, 35.16;	H, 5.72;	N, 14.78.

The elemental analysis of **I** was performed on an EA-3000 Euro Vector analyzer. The IR spectra of the TTSU ligand and complex **I** were recorded on a Spectrum BX FT-IR spectrometer (Perkin Elmer) with an ATR attachment for a 2 × 2 mm crystal in a tungsten carbide disc in the 400–4000 cm^{-1}.

Single crystal X-ray diffraction study of **I** was performed on a Xcalibur 3 four-circle automated diffractometer. The structure was solved by the direct method using the SHELX-97 program package [14]. The hydrogen atom positions were calculated geometrically and refined by the riding model with $U_{iso} = nU_{equiv}$ of the bearing atom ($n = 1.5$ for water and methyl groups, $n = 1.2$ for other hydrogen atoms). The structure was solved by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms on F^2.

The main experiment details and unit cell parameters are summarized in Table 1 and selected bond lengths and angles are in Table 2.

The X-ray diffraction data for **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 877812; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Powder X-ray diffraction study of **I** was performed on a Siemens D500 diffractometer (Cu radiation, secondary beam graphite monochromator). The purity and single-phase composition of the sample were confirmed by the Rietveld refinement of the powder X-ray diffraction pattern using the results of single-crystal X-ray diffraction as the initial model for the FullProf program [15]. The sample of **I** after grinding was placed into a glass cell with the 2 × 1 × 0.1 cm^3 working volume for X-ray diffraction.

RESULTS AND DISCUSSION

The IR spectra of complex **I** and free TTSU molecule exhibit the following characteristic bands (ν, cm^{-1}): 3486 (HOH); 3338, 3290, 3213, (NH); 3074, 2974, 2933, 2883 (CH_3, CH_2); 1655 (C=O, amide-I); 1460, 1421 (C–N) for TTSU; and 3377, 3332,

Table 2. Selected bond lengths (Å) and bond angles (deg) in structure I*

Bond	*d*, Å	Angle	ω, deg
Zn(1)–Cl(1)	2.2165(18)	Cl(1)Zn(1)Cl(2)	122.13(9)
Zn(1)–Cl(2)	2.223(2)	O(1)Zn(1)Cl(1)	105.20(15)
Zn(1)–O(1)	1.979(5)	O(1)Zn(1)Cl(2)	112.42(15)
Zn(1)–O(2)^{i}	2.028(4)	O(1)Zn(1)O(2)^{i}	103.52(19)
O(1)–C(1)	1.273(8)	O(2)^{i}Zn(1)Cl(1)	101.05(12)
O(2)–Zn(1)^{ii}	2.028(4)	O(2)^{i}Zn(1)Cl(2)	110.50(13)
O(2)–C(7)	1.273(7)	C(1)O(1)Zn(1)	126.0(4)
		C(7)O(2)Zn(1)^{ii}	130.9(4)

* Symmetry code: ^{i} $2 - x$, $1/2 + y$, $2 - z$; ^{ii} $2 - x$, $-1/2 + y$, $2 - z$.

3304 (NH); 3062, 2975, 2940, 2877 (CH_3, CH_2); 1642 (C=O, amide-**I**); 1511, 1445 (C–N) for **I**.

A comparison of the ν(C=O, amide-**I**) stretching bands for TTSU and **I** shows a 13 cm^{-1} shift to longer wavelengths upon coordination of the bicyclic urea to zinc via the carbide oxygen atoms and a shift of the ν_s(NH) and ν_{as}(NH) modes to shorter wavelengths, which is typical of coordinated carbonyl group [16, 17]. The spectrum of **I** does not show a band for water molecule, which is present in the spectrum of the free ligand; this indicates the absence of water in **I**.

According to X-ray diffraction data, compound **I** is the coordination polymer $\{[Zn(C_{11}H_{20}N_4O_2)Cl_2]\}_n$. The coordination polyhedron of zinc is a tetrahedron with vertices occupied by two chlorine atoms and O(1) and O(2) carbonyl atoms of two organic ligand molecules related by the symmetry code ($2 - x$, $1/2 + y$, $2 - z$). The bond angles at the zinc atom are 101.05(12)°–122.13(9)°. The Zn···Zn distance in the polymer is 9.480(2) Å (Fig. 1). The six-membered heterocycles occur in the asymmetrical half-chair conformation with noticeably twisted N(2)–C(1)–N(1)–C(4) and N(4)–C(7)–N(3)–C(4) moieties (the torsion angles are 21.4(10)° and 22.4(10)°) and C(2), C(3) and C(8),

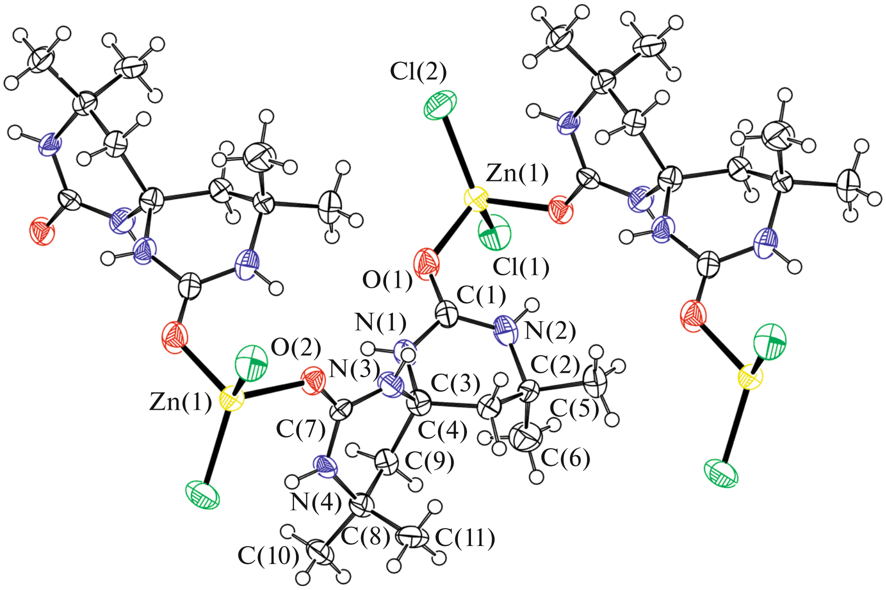


Fig. 1. Fragment of the molecular structure of **I**. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level.

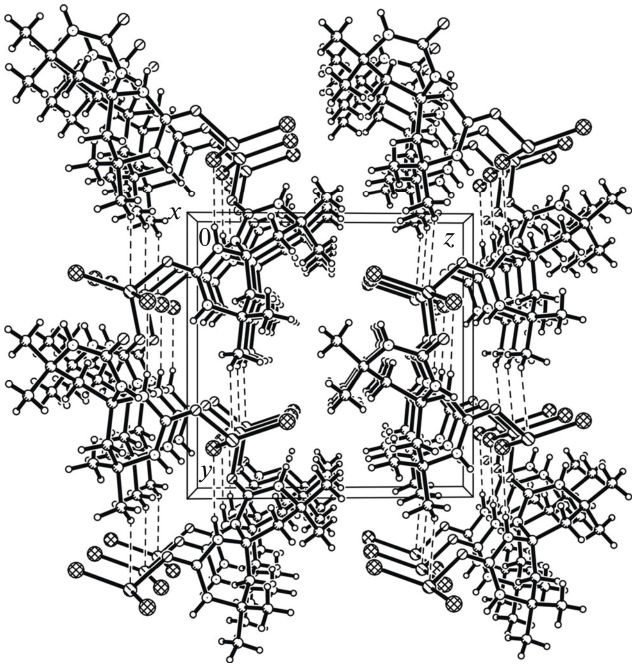


Fig. 2. Fragment of the crystal packing of **I** along the [001] direction.

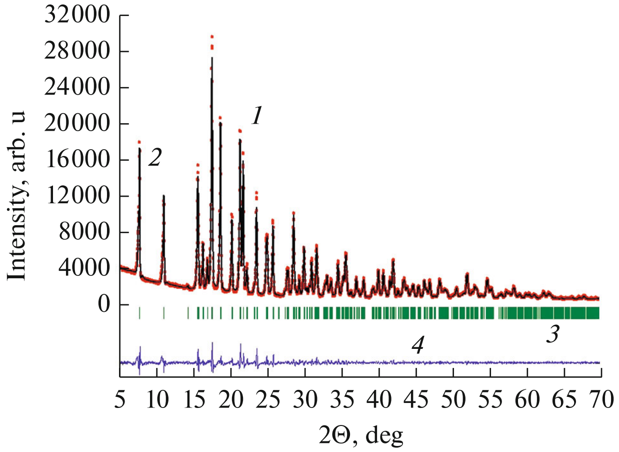


Fig. 3. Results of Rietveld refinement of the X-ray diffraction pattern of **I**: experimental X-ray diffraction pattern (*1*); simulated X-ray diffraction pattern (*2*); positions of lines (*3*); differential curve $I_{\text{exp}} - I_{\text{calcd}}$ (*4*).

C(9) atoms being displaced from the mean planes of these moieties by –0.41(1), 0.26(1), 0.45(1), and –0.22(1) Å, respectively. No shortening of intramolecular contacts between the methylene and methyl groups of the two rings is observed. The C=O bonds are markedly elongated (to 1.27 Å) with respect to the average value for ureas (1.24 Å [18]) upon the coordination to zinc. There is no stronger conjugation between the carbonyl group and one of the urea nitrogen atoms, as indicated by the similarity of the N–C(=O) bond lengths (1.328(8)–1.344(8) Å).

The polymer chains are additionally linked by intermolecular hydrogen bonds: N(2)–H(2)···O(2)^{i} (^{i} $2 - x$, $1/2 + y$, $2 - z$) (H···O 2.17Å, N–H···O 147°) and N(4)–H(4)···Cl(2)^{ii} (^{ii} $1 - x$, $-1/2 + y$, $2 - z$) (H···Cl 2.48 Å, N–H···Cl 159°). They are also connected into layers along the (0 0 1) plane by intermolecular hydrogen bonds: N(1)–H(1)···Cl(1)^{iii} (^{iii} $1 - x$, $-1/2 + y$, $2 - z$) (H···Cl 2.78 Å, N–H···Cl 148°) (Fig. 2).

The results of powder X-ray diffraction refinement of the composition of **I** attest to the absence of impurities. The following unit cell parameters were found: (T = 293 K): a = 6.20369(11), b = 11.23336(18), c = 11.36013(16) Å, β = 95.3001(11)°, V = 788.28(2) Å^3. The average crystallite size in the powder sample was 76 nm, and microstresses were virtually absent. All the lines present in the powder X-ray diffraction pattern correspond to the major phase, no impurity lines being observed (Fig. 3). The content of the major phase in the sample was 100 ± 1%.

REFERENCES

1. Mahbub, A. and Fazal Khalid, L., *Indian J. Experim. Biol.*, 1992, vol. 30, p. 1181.
2. Starikovich, L.S., Dudok, E.P., Sibirnaya, N.A., et al., *Med. Khim.*, 2009, vol. 11, no. 1, p. 57.
3. Starikovich, L.S., Starikovich, M.A., Rechitskii, A.N., et. al., *Biologichni Studii—Studia biologica*, 2009, vol. 3, no. 2, p. 93.
4. Musatov, A.G., Semyashkina, A.A., and Dashevskii, R.F., *Khranenie i Pererabotka Zerna*, 2007, no. 7, p. 38.
5. Gurevich, A.S., Titov, V.A., Babaeva, E.V., et al., *Introduktsiya, akklimatizatsiya i kul'tivatsiya rastenii: Sb. nauch. tr.* (Introduction, Acclimatization, and Cultivation of Plants: Collection of Scientific Papers), Kaliningrad: Kaliningrad Univ., 1998, p. 30.
6. Netreba, E.E., *Chornomorskii Botanichnii Zh.*, 2013, vol. 9, no. 2, p. 203.
7. Kozichar, M.V., Methods for increasing the wool output of askania fine-wool sheep, *Candidate (Agriculture) Dissertation*, Kherson, 1998.
8. Netreba, E.E. and Fedorenko A.M., *Russ. J. Coord. Chem.*, 2013, vol. 39, no. 2, p. 214.
9. Netreba, E.E. and Fedorenko, A.M., *J. Struct. Chem.*, 2013, vol. 54, no. 2, p. 373.
10. Netreba, E.E. *J. Struct. Chem.,* 2013, vol. 54, no. 5, p. 944.
11. Netreba, E.E., *Russ. J. Inorg. Chem.*, 2014, vol. 59, no. 4, p. 315.
12. Netreba, E.E., Fedorenko, A.M., and Pavlov, A.A., *Nauch. Visnik Uzhgorod. Un-tu. Ser. Khim.*, 2011, no. 1(25), p. 107.
13. 15. Netreba, E.E. and Papayanina, E.S., *J. Struct. Chem.*, 2014, vol. 55, no. 4, p. 722.
14. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.

15. Rodriguez-Carvajal, J. and Roisnel, T., *FullProf 98 and WinPLOTR: New Windows 95/NT Applications for Diffraction,* Commission for Powder Diffraction, International Union of Crystallography, Newsletter no. 20, 1998.
16. Grigor'ev, A.I., *Vvedenie v kolebatel'nuyu spektroskopiyu neorganicheskikh soedinenii* (Introduction to Vibrational Spectroscopy of Inorganic Compounds), Moscow: MGU*,* 1977.
17. Nakamoto, K., *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
18. Burgi, H.-B. and Dunitz, J.D., *Structure Correlation*, Weinheim: VCH, 1994, vol. 2.

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