Synthesis and Structure of New Polymeric Lithium Pivalates

E. N. Zorina-Tikhonova^{*a*}, D. S. Yambulatov^{*a*}, M. A. Kiskin^{*a*}, E. S. Bazhina^{*a*}, S. A. Nikolaevskii^{*a*}, *, N. V. Gogoleva^{*a*}, I. A. Lutsenko^{*a*}, A. A. Sidorov^{*a*}, and I. L. Eremenko^{*a*}

^aKurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia *e-mail: sanikol@igic.ras.ru

Received September 27, 2019; revised September 29, 2019; accepted September 30, 2019

Abstract—Data on the synthesis and study of the crystal structure of $[Li_{10}(Piv)_{10}(MeCN)_2]_n$ (I) and $[Li_6(Piv)_6(MeCN)_2]_n$ (II) are presented. According to X-ray diffraction data (CIF files CCDC nos. 1957855 (I); 1955569 (II)), compounds I and II are 1D polymers composed of deca- and hexanuclear fragments, respectively, in which the lithium atoms are linked to one another by μ_3 - and μ_4 -bridging pivalate anions.

Keywords: lithium, trimethylacetate, carboxylate complexes, X-ray diffraction **DOI:** 10.1134/S1070328420020104

INTRODUCTION

Inorganic, organometallic, and coordination compounds of lithium occupy an important place in modern chemistry and materials sciences. They are valuable starting compounds for the synthesis of more complex molecules, key intermediates of various processes, and components of functional materials used in various fields of technology. Lithium carboxylates are used for the synthesis of heterometallic complexes in which they are linked to 3d metal atoms and to each other by bridging carboxylate groups [1-7]. By variation of additional ligands, it is possible to obtain both oligo- and polynuclear and polymeric heterometallic complexes, including metal-organic frameworks, possessing nontrivial redox [8], magnetic [9, 10], and sorption properties [11, 12] and functioning as precursors of complex oxides for the manufacture anode materials [13–15] and high-capacity storage batteries [16–18]. The formation of intramolecular ionic Li–O bonds can serve to fabricate heterometallic compounds, which are nonsensitive to excess chelating ligands, as opposed to accessibility of readily available starting compounds is a key issue both for fundamental research aimed at the synthesis of more complex molecules and for the manufacture of materials possessing valuable functional properties. It is paradoxical that the structure and properties of some valuable chemicals that have been routinely used in synthesis for several decades do not attract attention of scientific community and, therefore, remain unknown. As examples illustrating this statement, consider two cases belonging to the chemistry of redox active complexes. Data on the structure of crystalline phases of the sodium salts of bis(N-arylamino)acenaphthene ligands (Ar-bian) and preparative procedures for their synthesis were published only in 2003 [21]. By the time

75

of publication of these data, the Ar-bian sodium salts have been widely used as the starting reagents for more than 13 years. The crystal structure and magnetic behavior of sodium and potassium semiquinolates and sodium catecholate, which have a much longer history of laboratory use, were reported only in 2018 [22].

Here we report the procedure for the synthesis and data on the structure of lithium pivalate, which is a valuable initial reagent in the synthesis of heterometallic carboxylate architectures possessing broad structural diversity and nontrivial physicochemical properties.

EXPERIMENTAL

All operations on the synthesis of lithium pivalate were performed in air using commercially available LiOH \cdot H₂O, pivalic acid, hexane, acetonitrile, and THF.

The ATR IR spectra of the compound were measured in the 400–4000 cm⁻¹ range on a PerkinElmer Spectrum 65 spectrophotometer equipped with the Quest ATR Accessory attachment (Specac). Elemental analysis was carried out on a EuroEA-3000 C,H,N,S-analyzer (EuroVector).

Synthesis of Li(Piv). A weighed amount of LiOH \cdot H₂O (5.5 g, 0.13 mol) was dissolved in distilled water (20 mL) on boiling. An equimolar amount of crystalline pivalic acid was added to the obtained solution, the mixture was stirred and heated at 140°C until water completely evaporated. The product was cooled down to room temperature, washed with hexane, and dried in air to a constant weight. The yield was 12.4 g (88% based on LiOH \cdot H₂O).

For C ₅ H ₉ O ₂ Li		
Anal. calcld., %	C, 55.57	H, 8.39
Found, %	C, 55.29	H, 8.44

IR (ATR; v, cm⁻¹): 2963 m, 2933 w, 2903 w, 2874 w, 1675 m, 1578 s, 1558 vs, 1538 vs, 1477 vs, 1462 m, 1423 vs, 1407 vs, 1377 s, 1359 vs, 1224 s, 1032 vw, 938 vw, 895 m, 806 m, 795 m, 597 s, 547 s, 435 vs, 428 vs, 415 vs.

The single crystals of $[Li_{10}(Piv)_{10}(MeCN)_2]_n$ (I) suitable for X-ray diffraction were grown by recrystallization of the product Li(Piv) from a THF–acetonitrile mixture at room temperature.

For $C_{54}H_{96}N_2O_{20}Li_{10}$			
Anal. calcld., %	C, 55.78	H, 8.32	N, 2.41
Found, %	C, 56.10	H, 8.51	N, 2.73

The single crystals of $[\text{Li}_6(\text{Piv})_6(\text{MeCN})_2]_n$ (II) suitable for X-ray diffraction were grown by recrystallization of the product Li(Piv) from acetonitrile under solvothermal conditions.

For C ₃₄ H ₆₀ N ₂ O ₁₂	2Li ₆		
Anal. calcld., %	C, 55.90	H, 8.28	N, 3.83
Found, %	C, 56.14	Н, 8.23	N, 3.87

IR (ATR; v, cm⁻¹): 2961 w, 2931 vw, 2905 vw, 2872 vw, 1675 w, 1578 m, 1557 s, 1538 s, 1478 s, 1462 w, 1422 m, 1408 m, 1377 m, 1360 s, 1224 m, 1031 vw, 939 vw, 895 w, 805 m, 795 m, 598 m, 550 m, 450 s, 435 s, 419 vs.

Single crystal X-ray diffraction study of complexes I and II was performed on a Bruker SMART Apex II diffractometer equipped with CCD detector (Mo K_{α} , $\lambda = 0.71073$ Å, graphite monochromator) [23]. Semiempirical absorption correction was applied [24]. The structures were solved by direct methods and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms at the carbon atoms of organic ligands were generated geometrically and refined using the riding model. The calculations were carried out by the SHELX-97 software package [25].

The crystallographic parameters of complexes I and II are summarized in Table 1. The full set of X-ray diffraction data is deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1957855 (I); 1955569 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Lithium pivalate is obtained by neutralization reaction between a solution of lithium hydroxide and trimethylacetic acid. The use of water as a solvent for LiOH enables uniform heating of the reaction mixture. Maintenance of the temperature at 140°C prevents removal of trimethylacetic acid from the reaction mixture, but allows efficient removal of surplus water after completion of the reaction. The single crystals of $[Li_{10}(Piv)_{10}(MeCN)_2]_n$ (I) suitable for X-ray diffraction were grown at room temperature from a THF– acetonitrile mixture. Crystallization from acetonitrile under solvothermal conditions in the absence of oxygen afforded single crystals of $[Li_6(Piv)_6(MeCN)_2]_n$ (II).

The infrared spectrum of compound II exhibits intense characteristic absorption bands in the 1578– 1538 and 1422–1408 cm⁻¹ ranges corresponding to antisymmetric v_{as} (COO) and symmetric v_s (COO) stretching vibrations of the coordinated carboxyl groups of the bridging pivalate anions, respectively. The bending vibrations δ (OCO) occur as two medium-intensity bands at 805 and 795 cm⁻¹. The spectrum of compound II also exhibits a group of bands at 1478, 1360, and 1224 cm⁻¹, corresponding to δ_{as} , δ_s , and γ modes of the geminal CH₃ groups.

According to X-ray diffraction data, compounds I and II are 1D coordination polymers formed by interconnected deca- and hexanuclear moieties, respectively. Compound I contains 10 non-equivalent lithium atoms (Fig. 1). Six atoms form three trinuclear moieties of similar structure (Li(1), Li(2), Li(5) and Li(4), Li(6), Li(10), which are connected to one another by four pivalate anions, two of which are coordinated in the μ_4 -bridging mode, while the other two anions show μ_3 -bridging coordination. One O atom of each anion is coordinated to one Li atom of the trinuclear moiety, whereas the other O atom is coordinated to all three lithium atoms of the second trinuclear moiety (in the case of μ_4 -bridging anions) and to two metal atoms (in the case of μ_3 -anions). The Li(3), Li(7), Li(8), and Li(9) atoms form a tetranuclear fragment. The Li(3) and Li(7) atoms have C.N. 5, whereas the other metal sites have C.N. 4. In the case of Li(8)and Li(9) atoms, one coordination site is occupied by the N atom of N-coordinated acetonitrile molecule. In the polymeric chain, a pair of trinuclear fragments alternates with one tetranuclear fragment being bound to it via three μ_4 -bridging pivalate anions (Fig. 2). The key bond lengths are as follows: Li-O, 1.837(7)-2.080(6) Å (for I) and 1.856(4)-2.064(4) Å (for II); Li-N, 2.090(7)-2.128(8) Å (for I) and 2.041(4)-2.057(4) Å (for II), and the Li…Li interatomic distances are 2.665(9)-2.943(8), 4.748(9)-4.924(9) Å (for I) and 1.952(4)–2.856(5) Å, 4.498(5) Å (for II).

Each hexanuclear fragment of compound II contains three pairs of crystallographically nonequivalent lithium atoms (Fig. 3). In each of these fragments,

SYNTHESIS AND STRUCTURE

Table 1. Cryst	allographic dat	a and structure	refinement	details for]	and II
----------------	-----------------	-----------------	------------	---------------	--------

Demonster	Value		
Parameter	Ι	II	
Molecular formula	$C_{54}H_{96}N_2O_{20}Li_{10}$	C ₃₄ H ₆₀ N ₂ O ₁₂ Li ₆	
М	1162.73	730.48	
Т, К	150	296(2)	
System	Monoclinic	Triclinic	
Space group	$P2_{1}/n$	PĪ	
a, Å	11.6781(8)	12.1867(9)	
b, Å	21.9413(14)	12.2826(9)	
<i>c</i> , Å	26.8663(2)	16.0698(11)	
α, deg	90	107.760(2)	
β, deg	93.051(1)	90.193(2)	
γ, deg	90	103.271(2)	
$V, Å^3$	6874.3(8)	2222.6(3)	
Ζ	4	2	
ρ (calcd.), g/cm ³	1.123	1.092	
μ, mm ⁻¹	0.08	0.078	
θ, deg	2.2–28.3	2.26-26.37	
T_{\min}/T_{\max}	0.673/0.746	0.653/0.746	
Number of measured reflections	82590	22818	
Number of unique reflections	20985	9044	
Number of reflections with $I > 2\sigma(I)$	11189	4458	
<i>R</i> _{int}	0.068	0.0978	
Number of refined parameters	775	533	
GOOF	1.00	1.03	
$R_1 (I \ge 2\sigma(I))$	0.071	0.089	
$wR_2 (I > 2\sigma(I))$	0.218	0.190	
Residual electron density (min/max), e/Å ³	-0.76/1.37	-0.204/0.243	

four central lithium atoms (Li(1), Li(2) and Li(5), Li(6)) are linked by six bridging pivalate anions, four of which demonstrate μ_4 -bridging coordination (and bind four metal atoms each) and the other two show μ_3 -bridging coordination. Each anion of the first μ_4 bridging anion pair binds three central lithium atoms only via coordination of one carboxyl O atom, whereas the second carboxyl O atom links the central atoms to a peripheral lithium atom (Li(3) or Li(4)) within the hexanuclear fragment. Each of the two μ_3 -bridging pivalate anions binds two central lithium atoms to one peripheral atom. The second pair of μ_4 -bridging acid anions connects two central lithium atoms to two peripheral metal atoms, one of which belongs to the neighboring hexanuclear fragment; as a result, single fragments are connected into a polymeric chain (Fig. 4). Two of the four central lithium atoms (Li(1)

and Li(5)) additionally coordinate one acetonitrile molecule each.

It worth to note that the structures of both types of lithium pivalate we found considerably differ from the previously characterized potassium pivalate $[K(Piv)(HPiv)(MeCN)]_n$, which contains both pivalate anions and neutral trimethylacetic acid molecules [26].

Thus, we developed a reliable preparative procedure suitable for gram-scale synthesis of lithium pivalate, which is a valuable initial reagent for the preparation of heterometallic carboxylate complexes and Metal-Organic Frameworks. Variation of the crystallization conditions of the obtained product allowed us to isolate and structurally characterize two coordination polymers, $[Li_{10}(Piv)_{10}(MeCN)_2]_n$ and $[Li_6(Piv)_6(MeCN)_2]_n$.

No. 2

2020



Fig. 1. Structure of the decanuclear fragment forming the polymeric chain of compound I. The methyl groups of the pivalate anions and hydrogen atoms are omitted.



Fig. 2. Fragment of the polymeric chain of compound I. The methyl groups of the pivalate anions and hydrogen atoms are omitted.



Fig. 3. Structure of the two types of hexanuclear fragments forming the polymeric chain of compound II. The methyl groups of the pivalate anions and hydrogen atoms are omitted.





RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 46 No. 2 2020

ACKNOWLEDGMENTS

X-ray diffraction, IR spectroscopy, and elemental analysis were performed using Shared Experimental Facilities supported by IGIC RAS State Assignment.

FUNDING

This work was supported by the Russian Foundation for Basic Research (project no. 18-29-04043).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Sidorov, A.A., Kiskin, M.A., Aleksandrov, G.G., et al., *Russ. J. Coord. Chem.*, 2016, vol. 42, p. 621. https://doi.org/10.1134/S1070328416100031
- Bazhina, E.S., Aleksandrov, G.G., Efimov, N.N., et al., *Russ. Chem. Bull., Int. Ed.*, 2013, vol. 62, no. 4, p. 962.
- Bazhina, E.S., Aleksandrov, G.G., Kiskin, M.A., et al., Russ. Chem. Bull., Int. Ed., 2016, vol. 65, no. 1, p. 249.
- 4. Zorina-Tikhonova, E., Gogoleva, N., Sidorov, A., et al., *Eur. J. Inorg. Chem.*, 2017, p. 1396.
- 5. Gogoleva, N.V., Zorina-Tikhonova, E.N., Bogomyakov, A.S., et al., *Eur. J. Inorg. Chem.*, 2017, p. 547.
- Zauzolkova, N.V., Nikiforova, M.E., Kiskin, M.A., et al., *Russ. Chem. Bull. Int. Ed.*, 2011, vol. 60, no. 2, p. 273.
- Gogoleva, N.V., Zorina-Tikhonova, E.N., Kiskin, M.A., et al., *Russ. Chem. Bull. Int. Ed.*, 2014, vol. 63, no. 12, p. 2741.
- 8. Ferey, G., Millange, F., Morcrette, M., et al., *Angew. Chem.*, *Int. Ed.*, 2007, vol. 46, p. 3259.
- 9. Aromi, G., Bell, A.R., Helliwell, M., et al., *Chem.-Eur. J.*, 2003, vol. 9, p. 3024.
- Bazhina, E.S., Aleksandrov, G.G., Kiskin, M.A., et al., *Polyhedron*, 2017, vol. 137, p. 246.

- 11. Sapianik, A.A., Zorina-Tikhonova, E.N., Kiskin, M.A., et al., *Inorg. Chem.*, 2017, vol. 56, p. 1599.
- 12. Sapianik, A.A., Kiskin, M.A., Kovalenko, K.A., et al., *Dalton Trans.*, 2019, vol. 48, p. 3676.
- 13. Dobrokhotova, Zh., Emelina, A., Sidorov, A., et al., *Polyhedron*, 2011, vol. 30, p. 132.
- 14. Burkhardt, S.E., Bois, J., Tarascon, J.-M., et al., *Chem. Mater.*, 2013, vol. 25, p. 132.
- 15. Lutsenko, I.A., Kiskin, M.A., Aleksandrov, G.G., et al., *Russ. Chem. Bull., Int. Ed.* 2018, vol. 67, no. 3, p. 449.
- Bykov, M., Emelina, A., Kiskin, M., et al., *Polyhedron*, 2009, vol. 28, no. 16, p. 3628.
- Dobrohotova, Zh.V., Sidorov, A.A., Kiskin, M.A., et al., *J. Solid State Chem.*, 2010, vol. 183, no. 10, p. 2475.
- Hong, M., Choi, H.C., and Byon, H.R., *Chem. Mater.*, 2015, vol. 27, p. 2234.
- 19. Cheprakova, E.M., Verbitskiy, E.V., Kiskin, M.A., et al., *Polyhedron*, 2015, vol. 100, p. 89.
- Sidorov, A.A., Kiskin, M.A., Aleksandrov, G.G., and Eremenko, I.L., *Russ. Chem. Bull., Int. Ed.*, 2016, vol. 65, no. 11, p. 2754.
- 21. Fedushkin, I.L., Skatova, A.A., Chudakova, V.A., and Fukin, G.K., *Angew. Chem., Int. Ed.*, 2003, vol. 42, p. 3294.
- 22. Fokin, S.V., Letyagin, G.A., Romanenko, G.V., et al., *Russ. Chem. Bull.*, *Int. Ed.*, 2018, vol. 67, no. 1, p. 61.
- SMART (control) and SAINT (integration) Software. Version 5.0. Madison (WI, USA): Bruker AXS, Inc., 1, p. 997.
- 24. Sheldrick, G.M., *SADABS. Program for Scanning and Correction of Area Detector Data*, Göttinngen (Germany): Univ. of Göttingen, 2004.
- 25. Sheldrick, G.M., Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, vol. 64, no. 1, p. 112.
- 26. Kiskin, M.A., Fomina, I.G., Aleksandrov, G.G., et al., *Inorg. Chem. Commun.*, 2004, vol. 7, p. 734.

Translated by Z. Svitanko