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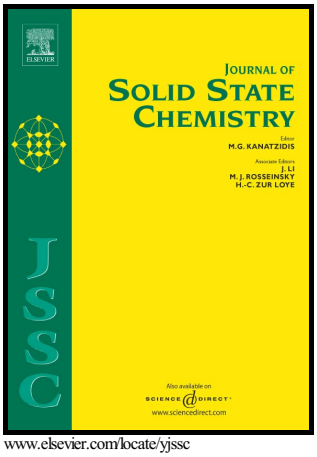

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PII: S0022-4596(18)30211-1
DOI: https://doi.org/10.1016/j.jssc.2018.05.022
Reference: YJSSC20228

To appear in: *Journal of Solid State Chemistry*

Received date: 16 March 2018
Revised date: 9 May 2018
Accepted date: 15 May 2018

Cite this article as: Renata Łyszczek, Halina Głuchowska, Liliana Mazur, Bogdan Tarasiuk, Vasyl Kinzhybalo and Alexander M. Kirillov, Structural diversity of alkali metal coordination polymers driven by flexible biphenyl-4,4'-dioxydiacetic acid, *Journal of Solid State Chemistry,* https://doi.org/10.1016/j.jssc.2018.05.022

Structural diversity of alkali metal coordination polymers driven by flexible biphenyl-4,4'-dioxydiacetic acid

Renata Łyszczek[a]*, Halina Głuchowska[a], Liliana Mazur[a], Bogdan Tarasiuk[b], Vasyl Kinzhybalo[c], Alexander M. Kirillov[d]

[a]Department of General and Coordination Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, M.C. Skłodowskiej Sq. 2, 20-031 Lublin, Poland

[b]Faculty of Chemistry, Maria Curie-Skłodowska University, M.C. Skłodowskiej Sq. 2, 20-031 Lublin, Poland

[c]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland

[d]Technical University of Lisbon, Rovisco Pais, 1049-001 Lisbon, Portugal

*Corresponding author. renata.lyszczek@poczta.umcs.lublin.pl

Abstract

A new series of four coordination polymers of alkali metals (Li, Na, and K) was assembled from a poorly explored building block, biphenyl-4,4'-dioxydiacetic acid (H_2L), and characterized by FTIR-ATR, TG-DSC, elemental analysis, and single crystal X-ray diffraction methods. The obtained structures range from 2D coordination polymers $[Li_2(\mu\text{-}L)(\mu\text{-}H_2O)_2(H_2O)_2]$ (1) and $[Na_2(\mu_4\text{-}L)(\mu\text{-}H_2O)_2(H_2O)_2]$ (2) to 3D metal-organic frameworks $[Na_2(\mu_6\text{-}L)(\mu\text{-}H_2O)_2]$ (3) and $[K_2(\mu_{10}\text{-}L)]$ (4). The influence of metal ionic radii on the crystal structures of the coordination polymers and conformation of the flexible biphenyl-4,4'-dioxydiacetate ligand was analyzed. Structural complexity increases within the series of products **1**-**4** following the Li < Na < K trend, accompanied by the evolution of the coordination modes of biphenyl-4,4'-dioxydiacetate ligand from the $\mu_2\text{-}L^{2-}$ (**1**) and $\mu_4\text{-}L^{2-}$ (**2**) to $\mu_5\text{-}L^{2-}$ (**3**) and $\mu_{10}\text{-}L^{2-}$ (**4**). Topological classification of the simplified underlying metal-organic networks in **1**-**4** was performed, disclosing the hcb (**1**), 3,4L13 (**2**), and fit (**4**) topological networks, whereas a topologically unique framework was identified in 3. The obtained coordination polymers are thermally stable and decompose in one (**4**) or several stages (**1**-3) forming metal carbonates and/or oxides as final decomposition products. The obtained products **1**-**4** represent the first