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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 Łyszczyk, 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>

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

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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 $[Li_2(\mu-L)(\mu-H_2O)_2(H_2O)_2]$ (**1**) and $[Na_2(\mu_4-L)(\mu-H_2O)_2(H_2O)_2]$ (**2**) to 3D metal-organic frameworks $[Na_2(\mu_6-L)(\mu-H_2O)_2]$ (**3**) and $[K_2(\mu_{10}-L)]$ (**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 μ_2-L^{2-} (**1**) and μ_4-L^{2-} (**2**) to μ_5-L^{2-} (**3**) and $\mu_{10}-L^{2-}$ (**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

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