



Mononuclear Mn(II), Co(II), and Cu(II) pivalates



Elena Fursova^a, Galina Romanenko^a, Renad Sagdeev^{a,b}, Victor Ovcharenko^{a,*}

^a International Tomography Center, Novosibirsk, Russia

^b Kazan Federal University, Volga Region, Russia

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ABSTRACT

Mononuclear Mn(II), Co(II), and Cu(II) pivalates were synthesized for the first time. They were isolated as salts with a composition $\text{NBu}_4[\text{MPiv}_3]$, where Piv is the pivalate anion. In the structure of the $[\text{MnPiv}_3]$ and $[\text{CoPiv}_3]$ coordination units, the environment of the central atom was found to be close to a trigonal prism. In $[\text{CuPiv}_3]$, the distorted square environment of Cu is formed by one bidentate O,O'-Piv and two monodentate Piv's; the second O atoms of monodentate Piv's tend to occupy the positions close to the apical positions of the elongated octahedron. An X-ray diffraction study of $\text{NBu}_4[\text{CoPiv}_3]$ and $\text{NBu}_4[\text{CuPiv}_3]$ crystals showed strong disordering of the O atoms of the coordinated carboxylate groups at room temperature, which was suppressed when $\text{NBu}_4[\text{CoPiv}_3]$ was cooled to 85 K and $\text{NBu}_4[\text{CuPiv}_3]$ to 30 K. In the synthesis of $\text{NBu}_4[\text{CoPiv}_3]$ and $\text{NBu}_4[\text{CuPiv}_3]$, new compounds, namely, tetranuclear $(\text{NBu}_4)_2[\text{Co}_4\text{Piv}_8(\text{AcO})_2(\text{H}_2\text{O})_4]$ and $(\text{NBu}_4)_2[\text{Cu}_4\text{Piv}_8(\text{AcO})_2(\text{H}_2\text{O})_2]$, respectively, formed along with the major product.

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1. Introduction

Mononuclear transition metal carboxylate complexes in which carboxylates perform an exceptionally chelate function that leads to the formation of four-membered chelate rings are very rare compounds. CCDC presents structural data for over 2000 various transition metal compounds containing coordinated pivalates [1]. Only two of these, namely, vanadyl *tris*-pivalate $[\text{VOPiv}_3]$ [2] and recently described $\text{NBu}_4[\text{NiPiv}_3]$ [3] have only cyclic bidentate pivalate anions in the coordination sphere of the transition metal. The synthetic approach used for the preparation of $\text{NBu}_4[\text{NiPiv}_3]$ was found to be also useful for the synthesis of $\text{NBu}_4[\text{MPiv}_3]$, where M = Mn, Co, and Cu. This allowed us to continue studies of this rare group of compounds.

The isolated complexes containing mononuclear $[\text{MPiv}_3]^-$ anions (M = Mn, Co, and Cu) were grown as single crystals and their structure was determined. As a result of the formation of four-membered metal-carboxylate rings with small $\angle\text{OMO}$ (chelate) angles in the $[\text{MnPiv}_3]$ and $[\text{CoPiv}_3]$ coordination anions, the environment of the central atom differs strongly from the octahedral environment that would be expected for c.n. = 6. The structure of MO_6 coordination units in $[\text{MnPiv}_3]$ and $[\text{CoPiv}_3]$ is more likely to be a distorted trigonal prism. This fact deserves

special attention because the strain of the four-membered metallocycles can be a reason for the increased reactivity of such mononuclear formations and hence for their absence among thousands of known transition metal pivalates.

Note that transition metal complexes with pivalates, which provide good solubility in organic solvents, are widely used for various purposes. These complexes are being actively studied, for example, as components of catalytic hydrocarbon-oxidizing systems [4], matrices for metal transport on the substrate surface [5], magnetically active units in the assembly of molecular magnets [6,7], and model objects of metal-containing enzymes [8]. For this reason, $\text{NBu}_4[\text{MPiv}_3]$ can serve as useful substrates instead of the widely used polynuclear pivalates, especially in those cases when the reaction is complicated by a destruction of the polynuclear complex. This paper reports on the synthesis and structure of the isolated compounds $\text{NBu}_4[\text{MPiv}_3]$, where M = Mn, Co, and Cu, and on the structure of two tetranuclear compounds, $(\text{NBu}_4)_2[\text{Co}_4\text{Piv}_8(\text{AcO})_2(\text{H}_2\text{O})_4]$ and $(\text{NBu}_4)_2[\text{Cu}_4\text{Piv}_8(\text{AcO})_2(\text{H}_2\text{O})_2]$, which occasionally formed in the syntheses of $\text{NBu}_4[\text{CoPiv}_3]$ and $\text{NBu}_4[\text{CuPiv}_3]$, respectively.

2. Experimental

2.1. Synthesis

The reagents and solvents were purchased from Merck and used without further purification.

* Corresponding author. Address: International Tomography Center, Russian Academy of Sciences, 3A Institut'skaya Street, 630090 Novosibirsk, Russia. Tel.: +7 383 333 1945; fax: +7 383 333 1399.

E-mail address: Victor.Ovcharenko@tomo.nsc.ru (V. Ovcharenko).