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Unusual Bridging Coordination Modes of THF and Piv Anions in the Hexanuclear Nickel(II) Carboxylate Complex

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Abstract—The recrystallization of complex $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ (Piv^- is anion of trimethylacetic acid) from a THF–MeCN (6 : 1) mixture gives a new hexanuclear compound of nickel(II): $[Ni_6(\mu_3\text{-}OH)_2(Piv)_{10}(THF)_4]$. Its structure (CIF file CCDC no. 1579976) exhibits rare examples of coordination of the μ_2-THF and μ_4-Piv ligands.

Keywords: nickel(II) carboxylate complexes, structure

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INTRODUCTION

It is known that the formation of the polynuclear carboxylate structures [1] in which the metal framework is formed due to various coordination modes of bridging carboxylate groups, as well as aqua, hydroxo, and oxo groups, is fairly typical of the synthesis of carboxylate complexes of 3*d* metals in the oxidation state +2, although the structures of these molecules substantially vary and the content of metal centers in them can range from two to very high values if speaking about the coordination carboxylate polymers [2–4]. Coordinated or solvate water molecules, as well as hydroxy or oxo groups strongly incorporated into the metal framework of carboxylates, are often met in these compounds. The origin of aqua, hydroxo, or oxo ligands is explained, as a rule, by the presence of water molecules in the starting salts of 3*d* metals and by the use of incompletely dehydrated organic solvents, although the application of similar solvents, in some cases, makes it possible to synthesize polynuclear carboxylates containing no coordinated or solvate molecules of water and its deprotonated forms [5–7].

As for the nickel(II) pivalate complexes, the simplest polynuclear structure formed by the reactions of nickel solvate salts with pivalates of alkaline metals is the binuclear complex $[(HPiv)_2Ni_2(Piv)_2(\mu\text{-}H_2O)(\mu\text{-}Piv)_2]$ containing the bridging water molecule along with the bridging anions of pivalic acid (Piv^-) [8]. However, in this case, water can easily be removed by boiling of the complex in decane, resulting in the extention of the metal framework and formation of the cyclic hexanuclear cluster $[Ni_6(\mu\text{-}Piv)_6(\mu_3\text{-}Piv)_6]$ [6]. Unlike the binuclear nickel complex, the nonanuclear hydroxopivalate complex $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ [9] does not lose the bridging OH groups during recrystallization from hexane but readily degrades to binuclear compounds under the action of organic N-donors, for example, pyridine [9, 10], or to clusters with 6–8 nickel(II) atoms under the action of pyrazolate-containing nitroxides [11].

The relative stability of particular fragments of the hydroxopivalate metal framework is also observed on reflux in ethanol of the nonanuclear complex $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$. In this case, the tetranuclear molecule $[Ni_4(OH)_2(Piv)_6(EtOH)_6]$ was obtained [12]. These processes show an evident transformation of the metal framework and also different coordination modes of some bridging carboxylate groups, which are likely "tuned" to the geometric characteristics of the metal hydroxide matrix formed under these or other reaction conditions.

In this work we present the results of studying the transformation of the metal framework of the nonanuclear hydroxide–pivalate compound $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ (**I**) in the course of standard recrystallization from a THF–MeCN (6 : 1) mixture to form a new hexanuclear nickel(II) complex $[Ni_6(\mu_3\text{-}OH)_2(Piv)_{10}(THF)_4]$ (**II**) containing THF and Piv^- manifesting rare types of bridging binding.

[†] Deceased.

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using commercially available tetrahydrofuran (reagent grade) and acetonitrile (reagent grade). The starting complex **I** was synthesized using a known procedure [11]. Elemental analysis was conducted on a Carlo Erba C,H,N analyzer.

The IR spectrum of the compound was recorded on a PerkinElmer Spectrum 65 FTIR spectrometer by the attenuated total internal reflection (ATR) method in a frequency range of 400–4000 cm^{-1}.

Synthesis of $[Ni_6(OH)_2(Piv)_{10}(THF)_4]$ (II). Tetrahydrofuran (5 mL) was added to a solution of complex **I** (0.5 g, 0.22 mol) in MeCN (30 mL). The obtained light green solution was concentrated to 7 mL on heating (40–50°C) and kept at 5°C. Green crystals suitable for X-ray diffraction analysis precipitated from the solution in 24 h. The crystals were washed with cold (–5°C) MeCN and dried in air. The yield of complex **II** was 0.15 g (26%) based on the initial amount of $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$).

For $C_{66}H_{124}O_{26}Ni_6$

Anal. calcd., %	C, 47.0	H, 7.4
Found, %	C, 47.1	H, 7.6

IR (ν, cm^{-1}): 3291 w, 2920 m, 2851 w, 1717 w, 1556 s, 1404 s, 1347 m, 1321 m, 1178 m, 1038 s, 918 m, 869 m, 794 m, 671 s, 633 s, 578 m, 561 m, 510 m, 490 w, 470 m, 440 w, 431 w, 422 w, 412 m.

The X-ray diffraction analysis of a crystal of compound **II** was carried out on a Bruker P4 diffractometer ($\lambda(MoK_\alpha) = 0.71073$ Å, graphite monochromator, ω scan mode, size of scan increment 0.3°, time of frame measurement 30 s). An absorption correction was applied semiempirically (T_{min}/T_{max} = 0.633/0.843) [13]. The structures of the synthesized compounds were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation using the SHELXL-2014/7 program package [14]. The hydrogen atoms in the ligands were calculated geometrically and refined by the riding model. The *tert*-butyl substituents at the carboxylate groups were determined with allowance for disordering. The positions of the methyl carbon atoms in the $\{CMe_3\}$ fragments were localized from the difference Fourier synthesis (the site occupancies of the atoms at C(2) were 0.63(2) and 0.37(2), and those at C(7) were 0.57(2) and 0.43(2)). The crystallographic parameters and details of structure refinement for complex **II** at $T = 293(2)$ K are the following: $C_{66}H_{124}O_{26}Ni_6$, M_w = 1685.90 g/mol, orthorhombic crystals (light green parallelepipeds), 0.37 × 0.24 × 0.17 mm, space group *Pbca*, $a = 19.047(4)$, $b = 20.174(5)$, $c = 22.267(4)$ Å, $V = 8557(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.309$ g cm^{-3}, μ = 1.360 mm^{-1}, $1.73° \le \theta \le 25.00°$, segment of sphere $0 \le h \le 21$, $0 \le k \le 23$, $-26 \le l \le 14$, 6988 measured reflections, 2911 reflections with $I > 2.0\sigma(I)$, $R_{int} = 0.023$, GOOF = 0.89, R_1 ($I > 2\sigma(I)$) = 0.082, wR_2 ($I > 2\sigma(I)$) = 0.226, R_1 (all data) = 0.200, wR_2 (all data) = 0.322.

The coordinates of atoms and other parameters for structure **II** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1579976; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The dissolution of $[Ni_9(OH)_6(Piv)_{12}(HPiv)_4]$ (**I**) in a THF–MeCN (6 : 1) mixture followed by heating to 40–50°C, concentrating, and crystallization at 5°C resulted in the isolation of new hexanuclear complex **II**.

According to the X-ray diffraction data, in the crystal of complex **II** the inversion center is arranged between the Ni(1), Ni(3) and Ni(1*A*), Ni(3*A*) atoms (Fig. 1a). The hexanuclear molecule of the complex represents two triangular $Ni_3(OH)$ fragments linked by two μ_4-O_2CR groups and two bridging THF molecules. In the central moiety of the molecule of the complex, Ni(1)Ni(3)Ni(1*A*)Ni(3*A*) in which the metal atoms are localized at the vertices of the rectangle (Ni(1)···Ni(3) 2.998(2), Ni(1)···Ni(3*A*) 3.522(2) Å), the μ_4-carboxylate groups are arranged from two sides of the plane. The bridging THF molecules bind the pairs of atoms Ni(1)Ni(3*A*) and Ni(3)Ni(1*A*), and the bridging OH groups link the pairs of atoms Ni(1)Ni(3) and Ni(1*A*)Ni(3*A*). The eight-atom cycle of nickel atoms and oxygen atoms of the OH groups and THF molecules is planar (Fig. 1b). The pairs of atoms Ni(1)Ni(3*A*) and Ni(3)Ni(1*A*) are bound by three bridging oxygen atoms. Their coordination polyhedra have the common face, which decreases the M···M distance compared to Ni(1)···Ni(3*A*) by more than 0.5 Å (Fig. 1c). In the triangular fragment, the pairs of metal atoms Ni(1)Ni(2) (3.363(2) Å) and Ni(2)Ni(3) (3.359(2) Å) are bound by the OH group and two μ_2-O_2CR groups. Thus, the polyhedra of the nickel(II) atoms in the triangular fragment Ni(1)Ni(2)Ni(3) are conjugated by the vertices only. The coordination of all metal atoms is octahedral (NiO_6). The coordination of the Ni(2) atom is built-up by the oxygen atom of the THF molecule bound via the monodentate mode. The bridging oxygen atom of the μ_3-OH group is arranged in the plane of the triangular Ni_3O fragment, but the thermal ellipsoid of the O(1M) atom is extended along the axis (Fig. 1b) perpendicular to the Ni_3O plane. This assumes that the atom of the OH group can shift from the Ni_3 plane at the both sides with close probabilities, and the absence of potential

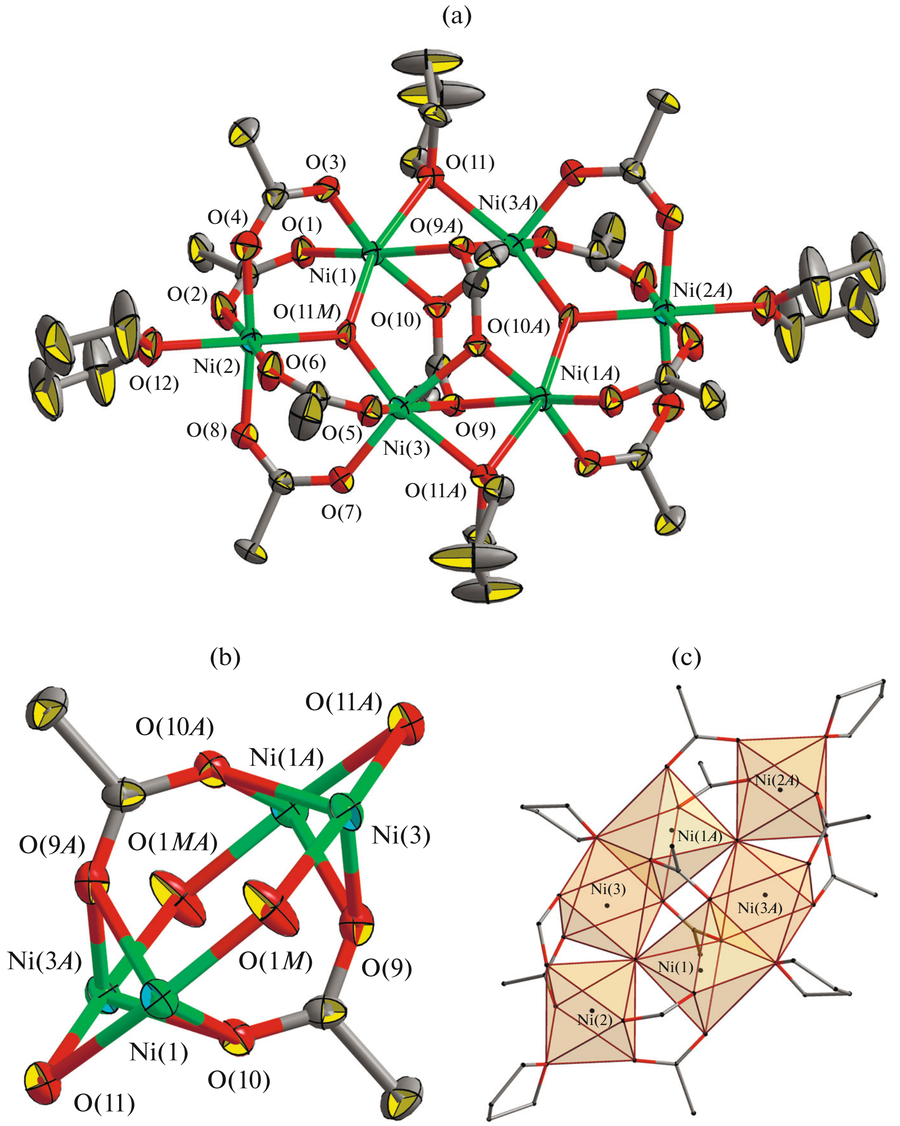

Fig. 1. (a) Molecular structure, (b) central fragment Ni_4, and (c) representation in polyhedra of complex **II**. For (a) and (b), thermal ellipsoids with 30% probability (hydrogen atoms and methyl groups are omitted).

acceptors of the hydrogen atom of the OH group does not stabilize one of two positions.

The μ_4-bridging coordination mode is observed for two carboxylate groups in compound **II** as well as in the starting complex **I**. The μ_4-bridging function of the carboxylate anion in the complexes of 3*d* transition metals is fairly rare, for example, in the polynuclear carboxylate structures with Fe [15], Mn [16, 17], Co [18, 19], Ni [11, 20], Cu [21, 22], and Zn [23] atoms. About 100 examples of 3*d*-metal complexes with this coordination mode of the carboxylate group are known. In addition, another rare bridging ligand is involved in the formation of the metal framework of compound **II**: THF molecule. A few structures with the bridging coordination of a THF molecule are known for polynuclear 3*d*-metal complexes: the complexes of Ti [24], Fe [25], Co [26–29], Cu [30–32], and Zn [33–35]. This coordination mode of THF is most probable under the conditions of deficient of other donor ligands in the composition of the complexes.

To conclude, when using a THF–MeCN (6 : 1) system in the syntheses of numerous carboxylate complexes, we observed the incorporation of molecules of these solvents into the compounds if any and, as a rule, in the form of solvate molecules. Water or its deprotonated forms and/or oxygen atoms of carboxylic acid or its anion usually acted as a bridging or terminal O-donor ligand. The preparation of the above considered compound illustrates the following: if a stable polynuclear complex exists, its composition can be rather unexpected upon the formation from a multicomponent system.

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REFERENCES

1. Kiskin, M.A. and Eremenko, I.L., *Usp. Khim.*, 2006, vol. 75, p. 627.
2. Lin, Z., Wragg, D.S., Warren, J.E., and Morris, R.E., *J. Am. Chem. Soc.*, 2007, vol. 129, p. 10334.
3. Forster, P.M., Yang, Z., and Cheetham, A.K., *Solid State Sci.*, 2003, vol. 5, p. 635.
4. Weber, B., Betz, R., Bauer, W., and Schlamp, S., *Z. Anorg. Allg. Chem.*, 2011, vol. 637, p. 102.
5. Kiskin, M.A., Fomina, I.G., Aleksandrov, G.G., et al., *Inorg. Chem. Commun.*, 2004, vol. 8, p. 89.
6. Fomina, I.G., Aleksandrov, G.G., Dobrokhotova, Zh.V., et al., *Izv. Akad. Nauk, Ser. Khim.*, 2006, no. 11, p. 1841.
7. Eremenko, I.L., Kiskin, M.A., Fomina, I.G., et al., *J. Cluster Sci.*, 2005, vol. 16, p. 331.
8. Eremenko, I.L., Nefedov, S.E., Sidorov, A.A., et al., *Inorg. Chem.*, 1999, vol. 38, p. 3764.
9. Eremenko, I.L., Golubnichaya, M.A., Nefedov, S.E., et al., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 4, p. 725.
10. Eremenko, I.L., Nefedov, S.E., Sidorov, A.A., and Moiseev, I.I., *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 2, p. 409.
11. Ovcharenko, V., Fursova, E., Romanenko, G., et al., *Inorg. Chem.*, 2006, vol. 45, p. 5338.
12. Sidorov, A.A., Fomina, I.G., Talismanov, S.S., et al., *Russ. J. Coord. Chem.*, 2001, vol. 27, no. 8, p. 548.
13. Sheldrick, G.M., *SADABS. Program for Scanning and Correction of Area Detector Data*, Göttinngen: Univ. of Göttingen, 2004.
14. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
15. Weber, B., Betz, R., Bauer, W., and Schlamp, S., *Z. Anorg. Allg. Chem.*, 2011, vol. 637, p. 102.
16. Déniz, M., Hernández-Rodríguez, I., Pasán, J., et al., *CrystEngComm*, 2014, vol. 16, p. 2766.
17. Chen, Z., Quan, L., Liu, L., et al., *Eur. J. Inorg. Chem.*, 2015, p. 1463.
18. Kuhlman, R., Schimek, G.L., and Kolis, J.W., *Inorg. Chem.*, 1999, vol. 38, p. 194.
19. Fursova, E., Kuznetsova, O., Ovcharenko, V., et al., *Polyhedron*, 2007, vol. 26, p. 2079.
20. Kuznetsova, O.V., Fursova, E.Yu., and Ovcharenko, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 2008, no. 10, p. 2156.
21. Mikuriya, M., Azuma, H., and Handa, M., *Mol. Cryst. Liq. Cryst.*, 2002, vol. 379, p. 205.
22. Wenga, C.-H., Chenga, S.-C., Wei, H.-M., et al., *Inorg. Chim. Acta*, 2006, vol. 359, p. 2029.
23. Pang, Y. and Zheng, Y., *Chin. J. Chem.*, 2015, vol. 33, p. 1347.
24. Herzog, A., Liu, F.-Q., Roesky, H.W., et al., *Organometallics*, 1994, vol. 13, p. 1251.
25. Duan, X.E., Yuan, S.F., Tong, H.B., et al., *Dalton Trans.*, 2012, vol. 21, p. 9460.
26. Burkovskaya, N.P., Nikiforova, M.E., Kiskin, M.A., et al., *Polyhedron*, 2011, vol. 30, p. 2941.
27. Crescenzi, R., Solari, E., Floriani, C., et al., *Inorg. Chem.*, 1996, vol. 35, p. 2413.
28. Snyder, C.J., Heeg, M.J., and Winter, C.H., *Inorg. Chem.*, 2011, vol. 50, p. 9210.
29. Duan, X.-E., Yuan, S.-F., Tong, H.-B., et al., *Dalton Trans.*, 2012, vol. 41, p. 9460.
30. Baxter, C.W., Higgs, T.C., Bailey, P.J., et al., *Chem.-Eur. J.*, 2006, vol. 12, p. 6166.
31. Anson, C.E., Langer, R., Ponikiewski, L., and Rothenberger, A., *Inorg. Chim. Acta*, 2005, vol. 358, p. 3967.
32. Koerner, R., Olmstead, M.M., Ozarowski, A., and Balch, A.L., *Inorg. Chem.*, 1999, vol. 38, p. 3262.
33. Komorski, S., Leszczyński, M.K., Justyniak, I., and Lewiński, J., *Inorg. Chem.*, 2016, vol. 55, p. 5104.
34. Anantharaman, G., Chandrasekhar, V., Walawalkar, M.G., et al., *Dalton Trans.*, 2004, p. 1271.
35. Bury, W., Justyniak, I., Prochowicz, D., et al., *Chem. Commun.*, 2012, vol. 48, p. 7362.

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