ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2024, Vol. 50, No. 7, pp. 485–491. © Pleiades Publishing, Ltd., 2024.

# The First Example of Dicubane Nickel(II) Complex in the Series of Unsymmetrically Substituted Diketones

**L. A. Khamidullina[a, b], I. S. Puzyrev[a, *], P. V. Dorovatovskii[c], V. N. Khrustalev[d, e], and A. V. Pestov[a, b]**

[a] *Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

[b] *Ural Federal University named after the First President of Russia B.N. Yeltsin, Yekaterinburg, Russia*

[c] *National Research Center, Kurchatov Institute, Moscow, Russia*

[d] *Peoples' Friendship University of Russia, Moscow, Russia*

[e] *Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia*

**e-mail: puzyrev@ios.uran.ru*

Received February 20, 2024; revised April 2, 2024; accepted April 3, 2024

**Abstract**—The first homometal dicubane nickel(II) complex based on unsymmetrically substituted 1,3-diketone (1,1,1-trifluoro-4-(2-methoxyphenyl)butan-2,4-dione) was synthesized and studied by X-ray diffraction using synchrotron radiation (CCDC no. 861889). In the crystal of the complex, nickel atoms are joined into tetrahedra sharing a common vertex with Ni...Ni distances of 3.026–3.127 Å; the geometry is completed to a distorted dicubane by $\mu_3$-bridging oxygen atoms of the hydroxyl groups. The coordination environment of each metal center is a distorted octahedron, the ligand is deprotonated and performs a bidentate function, forming six-membered chelate rings.

**Key words:** cubane nickel(II) complex, diketones, complex formation

**DOI:** 10.1134/S1070328424600499

## INTRODUCTION

The polynuclear transition metal complexes attract a lot of attention [1], owing to their potential use as functional molecular materials for future technologies, e.g., as molecular catalysts [2] single-molecule magnets [3], biomimetic catalysts [4], and promising anticancer drug candidates [5] in medicine. Polydentate ligands can form a series of polynuclear complexes with metal ions such as cubanes, helices, spheres [6], polyhedra [7], cages [8], wires [9], rings [10], discs [11], and grids [12]. Unlike low-nuclearity systems, giant superstructures are usually synthesized by self-assembly with a high degree of randomness [1].

The coordination compounds of nickel play an important role in the chemistry of polynuclear metal complexes. In combination with various ligands, nickel can form single-molecule magnets of various structures such as planar polycubane [13], Ni(7) and Ni(21) chain complexes [14], disc-shaped decametallic complex [15], etc. Among them, worthy of note are several examples of dicubane Ni complexes with the $\{Ni_7O_8\}$ metal–oxygen core [16–20], which tend to exhibit single-molecule magnet behavior [16, 17, 19]. The first homometallic dicubane Ni complex $[Ni_7(OH)_8(Ox)_3(Pip)_3]$ (Ox = oxalate, Pip = piperazine) was obtained in 2004 via autoclave synthesis (180°C, 72 h) [16]. In most cases, the possibility of obtaining a polynuclear complex with a dicubane structure and the choice of organic ligands are unpredictable. The arising dicubanes are often random. In [19], a complex was synthesized using an aroylhydrazone ligand; however, the complex $[Ni_7(\mu_3\text{-}OH)_8(DMF)_{18}](ClO_4)_6\cdot 2DMF$ contained no organic ligand molecules. Among the complexes reported in the literature, one dicubane with the $\{Ni_7Cl_2O_6\}$ metal–oxygen core was obtained using 2-methyl-1-(pyridyl-2-yl)propan-2-ol as an organic ligand [21]. As noted by the authors, who carried out coupling of two chemically different nickel cubanes to obtain an octanuclear complex, they isolated the dicubane complex $[Ni_7(\mu_3\text{-}Cl)_2(\mu_3\text{-}OH)_6Cl_4(H_2O)_2(HL)_6]Cl_2$ in one of the experiments. The presence of the heptanuclear dicubane nickel core in the octanuclear $[Ni_8(\mu_3\text{-}Cl)_3(\mu_3\text{-}OH)_5(\mu\text{-}Cl)_2Cl_6(HL)_7]$ complex deserves attention.

Although β-diketones are widely used in the synthesis of metal complexes, only two compositionally similar dicubane nickel complexes with a β-diketone, namely, hexafluoroacetylacetone ($H_2Hfac$), have been reported. First, the heptanuclear dicubane $[Ni_7(OH)_8(Hfac)_6(Py)_6]\cdot Py$ (Py = pyridyl) was prepared by condensation of the tetranuclear cubane $[Ni_4(Hfac)_4(MeO)_4(MeOH)_4]$ in pyridine [17]. Then other authors demonstrated that the tetranuclear

compound can be converted to $[Ni_7(OH)_8(Hfac)_6(H_2O)_6]\cdot 2H_2O$ on refluxing in toluene [20].

Previously, we investigated the complex-forming properties of 1,1,1-trifluoro-4-(2-methoxyphenyl)butane-2,4-dione (HL) towards copper(II) [22]. The compound HL is unsymmetrically substituted β-diketone, which effectively chelates the metal center. In the present work, the dicubane complex $[Ni_7(L\text{-}\kappa^2\text{-}O,O')_6(\mu_3\text{-}OH)_8(EtOH)_6]\cdot H_2O$ (**I**) was prepared by the reaction of HL with nickel acetate and studied by X-ray diffraction using synchrotron radiation.

## EXPERIMENTAL

All commercial reagents (Sigma-Aldrich) were used as received. Elemental analysis was performed on a Perkin Elmer CHN PE 2400 automated analyzer. The fluorine content was determined by photometry. $^1$H NMR spectra were recorded on a Bruker DRX-400 spectrometer in DMF-$d_7$. The nickel content was found by atomic emission spectroscopy using an iCAP 6300 Duo spectrometer. Fourier transform IR spectra were measured on a Spectrum One spectrometer (Perkin Elmer) with the attenuated total internal reflection attachment with a diamond crystal.

**Synthesis of 1,1,1-trifluoro-4-(2-methoxyphenyl)butane-2,4-dione (HL).** Finely ground Lithium hydride (151 mmol, 1.2 g) was added to a solution of ethyl trifluoroacetate (75 mmol, 8.9 mL) in dry tetrahydrofuran (30 mL). *ortho*-Methoxyacetophenone (82 mmol) was added with heating and stirring. The reaction was carried out under vigorous stirring and refluxing for 5 h. The reaction mixture was cooled down to room temperature, and the solvent was distilled off under reduced pressure. The residue was triturated with acetic acid, the target product was extracted from an aqueous solution into chloroform, and the organic fractions were combined, washed with water, and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under reduced pressure, and the residue was recrystallized from chloroform. The yield was 12.4 g (67%).

For $C_{11}H_9O_3F_3$

| | | | |
|---|---|---|---|
| Anal. calcd., % | C, 53.67 | H, 3.68 | F, 23.15 |
| Found, % | C, 53.90 | H, 3.80 | F, 23.21 |

$^1$H NMR (DMF-$d_7$; δ, ppm; *J*, Hz): 4.04 (s, 3H, $CH_3$); 7.07 (s, 1H, H(2)); 7.17 (m, 1H, H(5')); 7.32 (d, 1H, H(3'), $J$ = 8.5); 7.70 (dd, 1H, H(4'), $J_o$ = 11.5, $J_m$ = 4.1); 7.98 (d, 1H, H(6'), $J$ = 7.6). $^{13}$C NMR (DMF-$d_7$, δ, ppm): 56.53 ($OCH_3$); 97.80 (C(2)); 113.48 (C(3'), Ar*H*); 114.88, 117.14, 119.39, 121.56 ($CF_3$); 121.64 (C(5'), Ar*H*); 121.98 (C(1'), Ar*H*); 130.88 (C(6'), Ar*H*); 136.59 (C(4'), Ar*H*); 160.62 (C(2'), Ar*H*); 176.03, 176.30, 176.58, 176.86 (C(3)); 185.53 (C(1)). $^{19}$F NMR (DMF-$d_7$; δ, ppm; $C_6F_6$): 87.59 (s, $CF_3$).

**Synthesis of hexakis(1,1,1-trifluoro-4-(2-methoxyphenyl)butane-2,4-dionato-O,O')octa(μ$_3$-hydroxy)hexakis-ethanolheptanickel(II) monohydrate $[Ni_7(L\text{-}\kappa^2\text{-}O,O')_6(\mu_3\text{-}OH)_8(EtOH)_6]\cdot H_2O$ (I).** A solution of $Ni(CH_3COO)_2\cdot 4H_2O$ in water was added to a solution of HL and NaOH in methanol. The reaction was carried out under vigorous stirring at room temperature for 2 h. The precipitate was collected on a filter, washed with water, and dried in vacuo. The product was recrystallized from an $Et_2O$–EtOH–$Me_2CO$ mixture (8 : 1 : 1). The yield was 25%.

For $C_{78}H_{94}O_{33}F_{18}Ni_7$

| | | | | |
|---|---|---|---|---|
| Anal. calcd., % | C, 40.51 | H, 4.10 | F, 14.79 | Ni, 17.77 |
| Found, % | C, 40.42 | H, 4.08 | F, 14.71 | Ni, 17.82 |

IR (ν, cm$^{-1}$): 3426 ν(O–H), 2926 ν(C–$H_{Ar}$), 1618 ν(C=O, C=C), 1595 ν(C=O, C=C), 1528 ν(C=C–C=O).

**X-ray diffraction.** The unit cell parameters and reflection intensities were measured on the BELOK synchrotron station of the National Research Center, Kurchatov Institute, using a Rayonix SX165 CCD array detector ($T$ = 100 K, λ = 0.96990 Å, φ-scan mode with 1.0° step). The experimental data were processed using the iMOSFLM program included in the CCP4 package [23]. The absorption corrections for the obtained data were applied by the Scala program [24]. The structure was solved by direct methods and refined by the full-matrix least-squares method on $F^2$ in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included in the refinement with fixed positional parameters (riding model) and isotropic displacement parameters ($U_{iso}$(H) = 1.5$U_{eq}$(C) for $CH_3$ groups and $U_{iso}$(H) = 1.2$U_{eq}$(C) for other groups). All calculations were performed using the SHELXTL program package [25]. The main crystallographic data and refinement details are summarized in Table 1, and the bond lengths and bond angles are in Table 2.

The tables of atom coordinates and displacement parameters, bond lengths, and bond and torsion angles were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1861889; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

**Table 1.** Crystallographic data and X-ray experiment and structure refinements details for complex **I**

| Parameter | Value |
|---|---|
| Molecular formula | $C_{78}H_{94}O_{33}F_{18}Ni_7$ |
| $M$ | 2312.37 |
| System | Triclinic |
| Space group | $P\bar{1}$ |
| $Z$ | 1 |
| $a$, Å | 12.4011(11) |
| $b$, Å | 14.6269(13) |
| $c$, Å | 15.5965(14) |
| α, deg | 110.930(9) |
| β, deg | 107.611(9) |
| γ, deg | 102.063(8) |
| $V$, Å$^3$ | 2353.4(5) |
| ρ(calcd.), g/cm$^3$ | 1.632 |
| μ, mm$^{-1}$ | 3.435 |
| $F$(000) | 1184.0 |
| Crystal size, mm | 0.05 × 0.07 × 0.07 |
| Data collection range of θ, deg | 2.7 < θ <35.6 |
| Ranges of indices $hkl$ | $-14 \le h \le 10$, $-17 \le k \le 17$, $-18 \le l \le 18$ |
| Number of measured reflections | 22927 |
| Number of unique reflections | 8416 |
| Reflections with $I \ge 2\sigma(I)$ | 5356 |
| Number of refined parameters | 568 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0977, 0.2200 |
| $R_1$, $wR_2$ (all reflections) | 0.1339, 0.2477 |
| GOOF | 1.026 |
| Residual electron density (max/min), e/Å$^3$ | 1.721/−1.333 |

**Table 2.** Selected bond lengths (Å) and bond angles (deg) in the coordination unit of complex **I**

| Bond | $d$, Å | Angle | ω, deg |
|---|---|---|---|
| Ni(1)–O(1) | 2.044(5) | O(1)Ni(1)O(3) | 83.9(2) |
| Ni(1)–O(3) | 2.055(5) | O(1)Ni(1)O(2) | 83.60(19) |
| Ni(1)–O(2) | 2.061(5) | O(3)Ni(1)O(2) | 84.2(2) |
| Ni(2)–O(5) | 2.036(6) | O(2)Ni(2)O(6) | 95.6(2) |
| Ni(2)–O(1) | 2.059(5) | O(5)Ni(2)O(1) | 92.2(2) |
| Ni(2)–O(4) | 2.152(5) | O(6)Ni(2)O(14) | 93.0(2) |

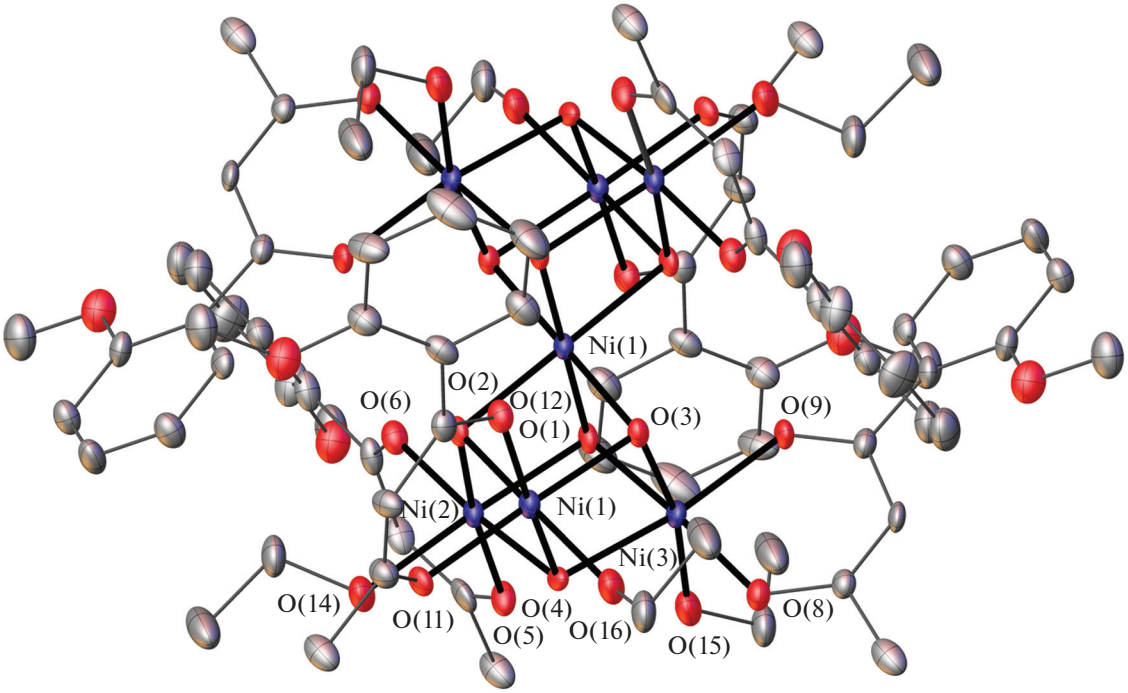
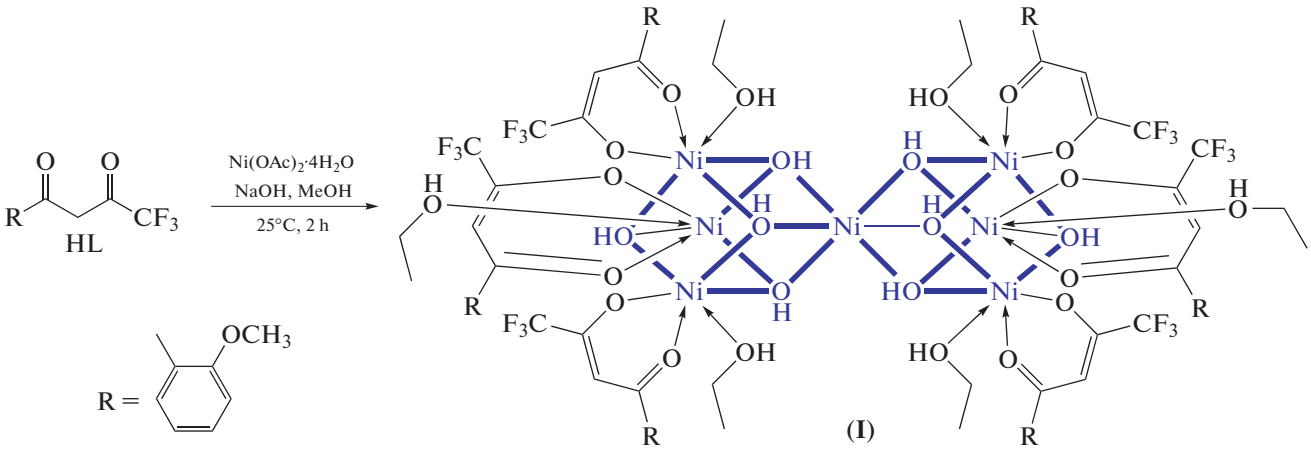



**Fig. 1.** Molecular structure of complex **I** with the thermal ellipsoids shown at 30% probability. The hydrogen atoms and the solvation water molecule are omitted. Only major components are given for disordered groups.

## RESULTS AND DISCUSSION

The complex $[Ni_7(L\text{-}\kappa^2\text{-}O,O')_6(\mu_3\text{-}OH)_8(EtOH)_6]\cdot H_2O$ (**I**) was obtained by treatment of an aqueous methanol solution of NaL with a solution of nickel(II) acetate followed by drying and crystallization (Scheme 1).




**Scheme 1.**

The homometallic heptanuclear nickel complex **I** has a dicubane structure with a common vertex (Fig. 1). The Ni(1) atom is located at the inversion center and linked to the other crystallographically independent metal centers (Ni(2), Ni(3), Ni(4)) via three oxygen atoms of the bridging $\mu_3$-OH groups (O(1), O(2), O(3)). The fourth $\mu_3$-OH group binds three peripheral metal centers through the O(4) atom. Thus, the six-coordinate nickel atoms, together with oxygen atoms of the hydroxy groups, form the $\{Ni_4O_4\}$ cubane moieties (Fig. 2).

Each of the peripheral metal centers coordinates two oxygen atoms of one chelating moiety of the deprotonated ligand HL, one oxygen atom of ethanol,

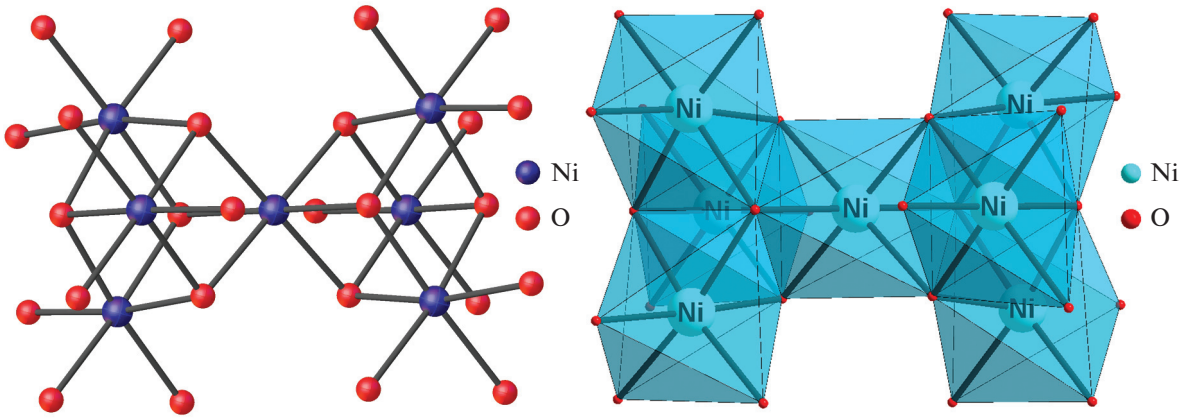



**Fig. 2.** Structure of the inorganic core and the coordination polyhedron of complex **I** according to X-ray diffraction data.

and three oxygen atoms of the bridging hydroxyl groups, thus forming a distorted octahedral environment (Fig. 3). The lengths of the Ni–O bonds with the oxygen atoms located in the equatorial plane are 2.035 to 2.056 Å, while the distances to the oxygen atoms located on the axial axis are 2.060 to 2.152 Å. Due to distortion of the $\{Ni_4\}$ cubane moiety, the Ni...Ni distances between the central and outer Ni atoms (on average, 3.033 Å) are shorter than the distances between outer atoms (on average, 3.118 Å). Table 3 gives the minimum and maximum Ni–O and Ni–Ni bond lengths for complex **I** in comparison with those in heptanuclear dicubanes containing hexafluoroacetylacetone ligands. As it follows from the presented data, the HL ligand has weaker donor properties than hexafluoroacetylacetone, since the Ni–O bond length increases.

The crystal of **I** has numerous intramolecular hydrogen bonds and intermolecular contacts (OH···O, OH···F, CH···F, and CH···O) (Table 4). In addition, the solvated water molecule present in **I** is held by classical OH···O hydrogen bonds.

The IR spectrum of complex **I** (Fig. 4) exhibits characteristic asymmetric stretching bands for the C=C–C=O vibrations at 1618 $cm^{-1}$, which are also manifested at 1595 $cm^{-1}$ due to the coordination to the metal. In the free ligand, these vibrations are manifested as an intense broad band with a maximum at

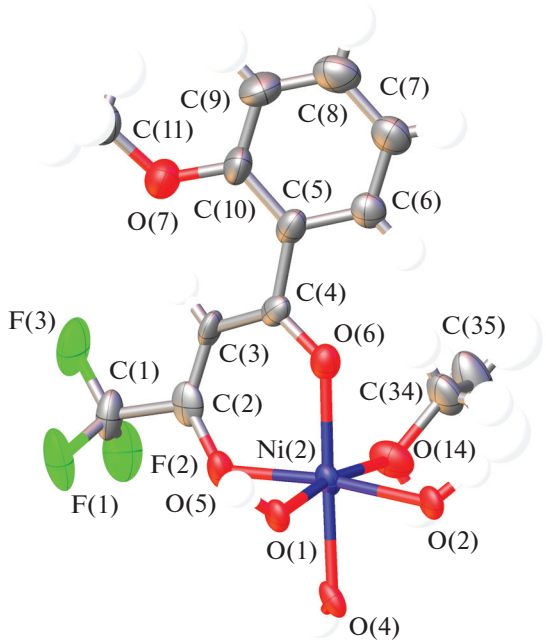



**Fig. 3.** Coordination environment of the peripheral metal center in complex **I** according to X-ray diffraction data.

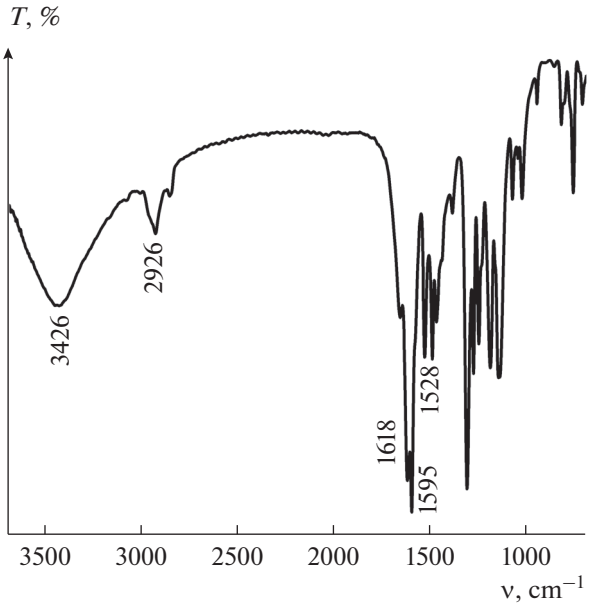



**Fig. 4.** Fourier transform IR spectra of complex **I**.

**Table 3.** Minimum and maximum bond lengths in the coordination unit of dicubane nickel(II) complexes in the series of 1,3-diketones

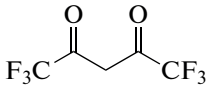
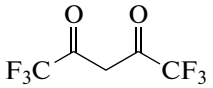
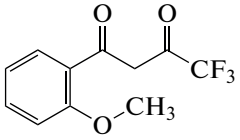
| Formula of the ligand | Formula of the coordination compound | Bond length, Å | | Ref. |
|---|---|---|---|---|
| | | Ni–O | Ni–Ni | |
|  | $[Ni_7(OH)_8(Hfac)_6(Py)_6]\cdot Py$ | 2.022<br>2.095 | 3.034<br>3.119 | [17] |
|  | $[Ni_7(Hfac)_6(OH)_8(H_2O)_6]\cdot 2H_2O$ | 2.020<br>2.095 | 3.024<br>3.093 | [20] |
|  | $[Ni_7(L\text{-}\kappa^2\text{-}O,O')_6(\mu_3\text{-}OH)_8(EtOH)_6]\cdot H_2O$ | 2.036<br>2.152 | 3.026<br>3.217 | This work |

**Table 4.** Intramolecular hydrogen bonds and intermolecular contacts in the crystal of **I***

| D–H···A | Distance, Å | | | D–H···A angle, deg |
|---|---|---|---|---|
| | D–H | H···A | D···A | |
| O(1)–H(1O)···O(12)$^{i}$ | 0.90 | 2.40 | 3.098(8) | 135 |
| O(2)–H(O)···O(9)$^{i}$ | 0.90 | 2.42 | 3.117(7) | 135 |
| O(3)–H(3O)···O(6)$^{i}$ | 0.90 | 2.54 | 3.236(8) | 135 |
| O(4)–H(4O)···O(17) | 0.90 | 2.32 | 3.068(13) | 140 |
| O(14)–H(14O)···O(11) | 0.90 | 2.19 | 3.001(9) | 149 |
| O(15)–H(15B)···O(5) | 0.90 | 1.97 | 2.837(8) | 160 |
| O(16)–H(16A)···O(8) | 0.90 | 2.40 | 3.209(8) | 150 |
| O(16)–H(16B)···O(17)$^{ii}$ | 0.90 | 1.67 | 2.461(14) | 145 |
| O(17)–H(17A)···O(8)$^{ii}$ | 0.91 | 2.12 | 2.815(13) | 133 |

* Symmetry codes: $^{i}$ $-x+1, -y+1, -z+1$; $^{ii}$ $-x, -y+1, -z+1$.

1604 $cm^{-1}$ [22]. The symmetric stretching modes of the C=C–C=O groups in complex **I** give rise to a band at 1528 $cm^{-1}$, whereas in the free ligand, this absorption band occurs at 1490 $cm^{-1}$.

Thus, the dicubane complex $[Ni_7(L\text{-}\kappa^2\text{-}O,O')_6(\mu_3\text{-}OH)_8(EtOH)_6]\cdot H_2O$ (**I**) was prepared in one step using 1,1,1-trifluoro-4-(2-methoxyphenyl)butane-2,4-dione. The structure of the product was confirmed by X-ray diffraction analysis using synchrotron radiation. Considering published data, it can be noted that among the few dicubane Ni(II) complexes, the obtained compound **I** is the first example of homometallic heptanuclear dicubane involving asymmetric 1,3-diketone ligand, which is a weaker donor than symmetric 1,3-diketones.

ACKNOWLEDGEMENTS

$^{1}$H NMR and FT-IR spectra were recorded using the equipment of the Center for Collective Use "Spectroscopy and Analysis of Organic Compounds."

FUNDING

This study was supported by the Ministry of Education and Science of Russia within the state assignment of the Postovsky Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences (subject state reg. no. 124020500039-0) and performed using the equipment of the Center for Collective Use "Spectroscopy and Analysis of Organic Compounds", in the part related to the synthesis and analysis of the composition and structure, and within the state assignment of the Ural Federal University

(subject state reg. no. 123031300049-8), in the part related to problem formulation and discussion of spectral data.

## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

## REFERENCES

1. Shiga, T., Newton, G.N., and Oshio, H., *Dalton Trans.*, 2018, vol. 47, no. 22, p. 7384.
2. Kirillov, A.M., Kirillova, M.V., and Pombeiro, A.J.L., *Coord. Chem. Rev.*, 2012, vol. 256, nos. 23–24, p. 2741.
3. Ungur, L., Lin, S.Y., Tang, J., et al., *Coord. Chem. Rev.*, 2014, vol. 43, no. 20, p. 6894.
4. Nesterov, D.S., Nesterova, O.V., and Pombeiro, A.J.L., *Coord. Chem. Rev.*, 2018, vol. 355, p. 199.
5. Wang, K. and Gao, E., *Anticancer Agents Med. Chem.*, 2014, vol. 14, no. 1, p. 147.
6. Muetterties, E.L., Rhodin, T.N., Band, E., et al., *Chem. Rev.*, 1979, vol. 79, no. 2, p. 91.
7. Zhao, Q., Harris, T.D., and Betley, T.A., *J. Am. Chem. Soc.*, 2011, vol. 133, no. 21, p. 8293.
8. Sanz, S., O'Connor, H.M., Martí-Centelles, V., et al., *Chem. Sci.*, 2017, vol. 8, no. 8, p. 5526.
9. Horiuchi, S., Tachibana, Y., Yamashita, M., et al., *Nat. Commun.*, 2015, vol. 6, p. 6742.
10. Zaleski, C.M., Tricard, S., Depperman, E.C., et al., *Inorg. Chem.*, 2011, vol. 50, no. 22, p. 11348.
11. Engelhardt, L.P., Muryn, C.A., Pritchard, R.G., et al., *Angew. Chem., Int. Ed. Engl.*, 2008, vol. 47, no. 5, p. 924.
12. Schäfer, B., Greisch, J.F., Faus, I., et al., *Angew. Chem. Int. Ed.*, 2016, vol. 55, no. 36, p. 10881.
13. Shvachko, Y.N., Starichenko, D.V., Korolev, A.V., et al., *Inorg. Chim. Acta*, 2018, vol. 483, p. 480.
14. Murrie, M., Stoeckli-Evans, H., and Güdel, H.U., *Angew. Chem. Int. Ed.*, 2001, vol. 40, no. 10, p. 1957.
15. Aromí, G., Parsons, S., Wernsdorfer, W., et al., *Chem. Commun.*, 2005, no. 40, p. 5038.
16. Keene, T.D., Hursthouse, M.B., and Price, D.J., *New J. Chem.*, 2004, vol. 32, no. 9, p. 1.
17. Petit, S., Neugebauer, P., Pilet, G., et al., *Inorg. Chem.*, 2012, vol. 51, no. 12, p. 6645.
18. Dong, W.K., Zhu, L.C., Dong, Y.J., et al., *Polyhedron*, 2016, vol. 117, p. 148.
19. Mameri, S., *Inorg. Chim. Acta*, 2017, vol. 455, p. 231.
20. Kuznetsova, O.V., Fursova, E.Y., Letyagin, G.A., et al., *Russ. Chem. Bull.*, 2018, vol. 67, no. 7, p. 1202.
21. Hameury, S., Kayser, L., Pattacini, R., et al., *ChemPlusChem*, 2015, vol. 80, no. 8, p. 1312.
22. Khamidullina, L.A., Puzyrev, I.S., Glukhareva, T.V., et al., *J. Mol. Struct.*, 2019, vol. 1176, p. 515.
23. Battye, T.G.G., Kontogiannis, L., Johnson, O., et al., *Acta Crystallogr., Sect. D: Biol. Crystallogr.,* 2011, vol. 67, no. 4, p. 271.
24. Evans, P., *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2006, vol. 62, no. 1, p. 72.
25. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.

*Translated by Z. Svitanko*