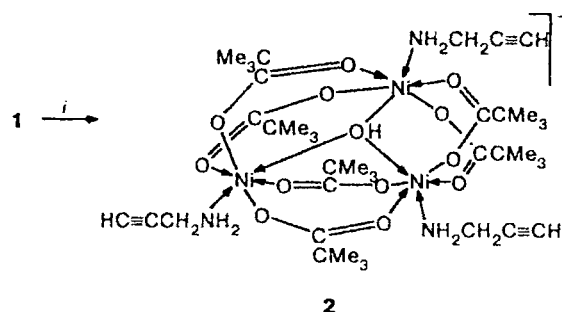


First trinuclear hydroxocarboxylate anionic complex with Ni^{II} atoms

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We found that the reaction of the nonanuclear complex $\text{Ni}_9(\text{HOCCMe}_3)_4(\mu_4\text{-OH})_3(\mu_3\text{-OH})_3(\mu\text{-O}, \text{O'-OCCMe}_3)(\mu\text{-O}, \text{O'-OCCMe}_3)_7(\mu_3\text{-O}, \text{O'-OCCMe}_3)_3(\mu_4\text{-O}, \text{O'}, \text{O'-OCCMe}_3)$ (1), which we have described recently,¹ with propargylamine (reagent ratio 1 : 9) in hexane followed by treatment of the reaction mixture with solid KOH in CH_2Cl_2 afforded the trinickel μ_3 -hydroxocarboxylate complex $[\text{K}(\text{OEt}_2)][(\text{HC}\equiv\text{CCH}_2\text{NH}_2)_3\text{Ni}_3(\mu_3\text{-OH})(\mu\text{-O}, \text{O'-OCCMe}_3)_6]$ (2). Complex 2 was isolated by recrystallization from a 1 : 2 ether—hexane solution as green prismatic crystals (the yield was 38%); space group



i. 1) $\text{NH}_2\text{CH}_2\text{CCH}$, hexane; 2) KOH (solid), CH_2Cl_2 , 22 °C

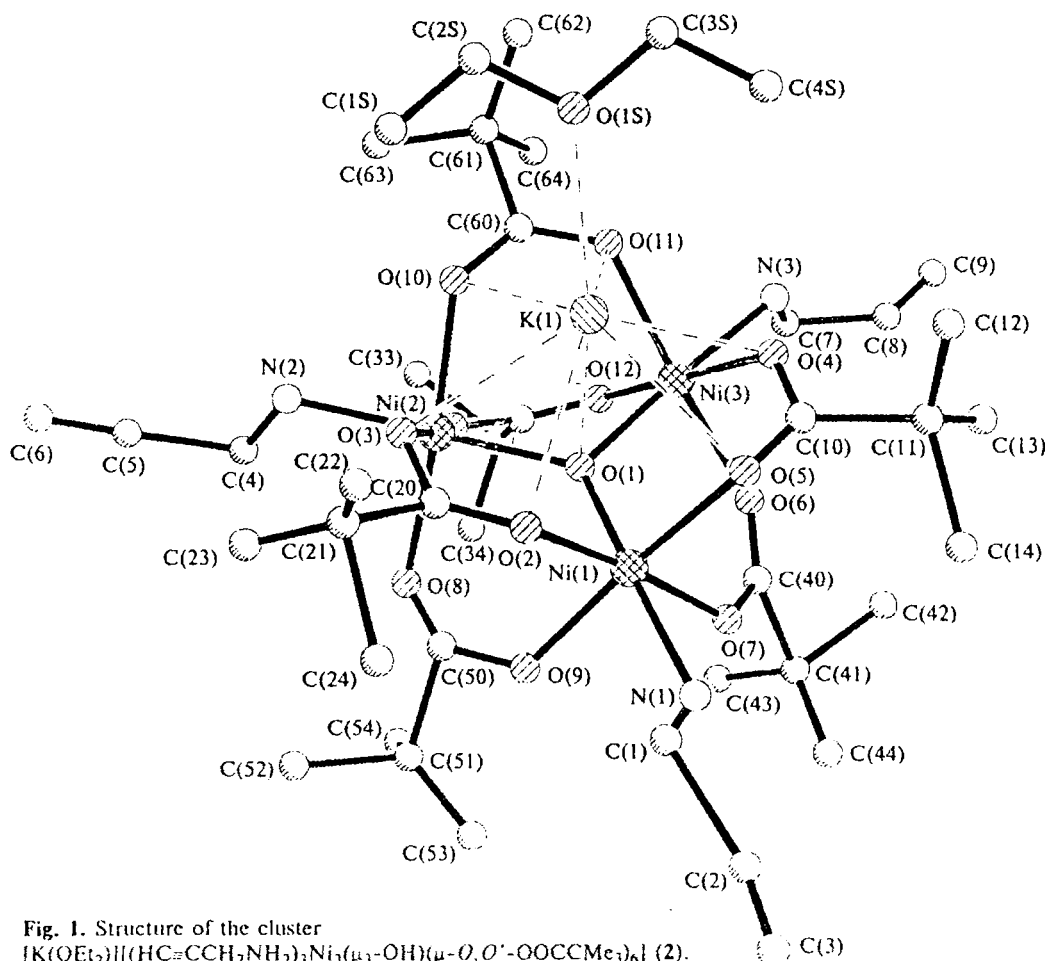


Fig. 1. Structure of the cluster $[\text{K}(\text{OEt}_2)][(\text{HC}\equiv\text{CCH}_2\text{NH}_2)_3\text{Ni}_3(\mu_3\text{-OH})(\mu\text{-O}, \text{O'-OCCMe}_3)_6]$ (2).

Pbca, $a = 13.331(3)$, $b = 22.049(5)$, $c = 40.648(9)$ Å, $V = 11947(5)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.249$ g cm⁻³, $\mu = 10.61$ cm⁻¹; weighting scheme $w^{-1} = \sigma^2(F) + 0.0066F^2$; $R = 0.059$, $R_w = 0.088$ based on 6068 reflections with $I > 4\sigma$. X-ray diffraction study demonstrated that the core of the cluster anion of **2** is the triangle formed by the nickel atoms (Ni...Ni 3.492(1), 3.517(1), and 3.494(1) Å) with the oxygen atom located in the center (Ni—O, 2.021(4)—2.027(4) Å; the deviation of the oxygen atom from the Ni₃ plane is 0.12 Å). Each side of the Ni₃ triangle contains two bridging trimethylacetate groups ($\nu(\text{OCO})$ are 1376 and 1604 cm⁻¹) located above and below the plane of the triangle (Ni—O, 2.029(5)—2.114(5) Å; C—O, 1.221(9)—1.272(8) Å). Each nickel atom is coordinated to the propargylamine molecule ($\nu(\text{NH}_2)$, 3315 cm⁻¹; $\nu(\text{C}\equiv\text{C})$, 2250 cm⁻¹; C≡C, 1.120(17)—1.167(11) Å) through the Ni—N bond (2.065(8), 2.085(5), and 2.076(7) Å) (Fig. 1). The potassium atom, which is coordinated to the ether molecule (K—O, 2.742(7) Å), is located above the Ni₃O fragment (K—O_{center}, 2.864(4) Å) and interacts with six oxygen atoms of three carboxylate groups (K—O are 2.845(5)—2.922(5) Å). This charge distribution indicates that the cluster anion formally contains Ni^{II} atoms. It is conceivable that the presence of the low-valence ions in the complex and its negative charge

result in the unusual magnetic properties of complex **2**. Thus, the effective magnetic moment of **2** increases slightly from 3.02 to 3.12 μB in the range of 290—110 K, unlike the known heterovalent neutral iron complexes, $\text{L}_3\text{Fe}_3\text{O}(\text{OOCR})_6$, which exhibit antiferromagnetic properties (see, for example, Refs. 2 and 3). In conclusion, note that complex **2** is the first hydroxohexacarboxylate triangular nickel complex as well as the first anionic representative of this class of carboxylates of 3d elements.

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References

1. I. L. Eremenko, M. A. Golubnichaya, S. E. Nefedov, A. A. Sidorov, I. F. Golovaneva, V. I. Burkov, O. G. Ellert, V. M. Novotortsev, L. T. Eremenko, A. Sousa, and M. R. Bermejo, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 725 [*Russ. Chem. Bull.*, 1998, 47, 704 (Engl. Transl.)].
2. S. M. Oh, S. R. Wilson, D. N. Hendrickson, S. E. Woehler, R. J. Wittebort, D. Inniss, and C. E. Strouse, *J. Am. Chem. Soc.*, 1987, 109, 1073.
3. K. Asamaki, T. Nakamoto, S. Kawata, H. Sano, M. Katada, and K. Endo, *Inorg. Chim. Acta*, 1995, 236, 155.

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