Chemical assembly of a new heterometallic trimethylacetate cluster with the Co_6Ni_2 core

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Co-thermolysis of the tetranuclear trimethylacetate clusters $M_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ (M = Co or Ni; the reagent ratio was 1 : 1) in decalin (2 h, 170 °C) afforded the octanuclear heterometallic cluster $Co_6Ni_2(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$, which exhibits ferromagnetic properties at 10—8 K.

Key words: cobalt and nickel complexes, trimethylacetate complexes, heterometallic complexes, X-ray diffraction analysis, magnetic properties.

Earlier, we have demonstrated[1] that thermolysis of tetranuclear trimethylacetate $Co_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ (**1**) containing labile coordinated ethanol molecules in decalin (2 h, 170 °C) afforded the volatile antiferromagnetic octanuclear cluster $Co_8(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**2**), which was isolated as blue-violet prismatic crystals. In the course of this reaction, complex **1** lost all ethanol molecules and the water molecule to form cluster **2** with the tetradentate bridging O atoms. Unlike thermolysis of complex **1**, thermolysis of its nickel analog $Ni_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(HOEt)_6$ (**3**)[2] under the same conditions gave rise to highly soluble unidentified products. This difference in the chemical behavior of complexes **1** and **3** is, apparently, attributed to the impossibility of forming the nickel octanuclear analog of cluster **2** under these conditions (in **2**, the Co atoms are in different coordination environments formed by O atoms: two metal atoms are in a tetrahedral environment and other six atoms have a distorted trigonal-bipyramidal coordination). Unlike cobalt(II) carboxylate (trimethylacetate) derivatives, the known nickel trimethylacetates contain the metal atoms only in an octahedral and pseudooctahedral environment.[2—4] The aim of the present study was to reveal the possibility of preparing a stable heteronuclear nickel- and cobalt-containing trimethylacetate cluster isostructural to cobalt derivative **2**, whose stability is determined by the cobalt-containing moiety of the complex.

Results and Discussion

We found that co-thermolysis of tetranuclear complexes **1** and **3** (ratio between the tetramers was 1 : 1) in decalin (2 h, 170 °C) afforded the heteronuclear cluster $Co_6Ni_2(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**4**), which was isolated as prismatic blue crystals in 80% yield (Scheme 1).

Metal content analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) demonstrated that the Co : Ni ratio in complex **4** is 3 : 1.

The properties of heterometallic cluster **4** differ from those of analog **2**. For example, complex **2** readily sublimes at 100—150 °C under a stream of argon, whereas compound **4** does not sublime even on heating *in vacuo*. In addition, the magnetic properties of cluster **4** (Fig. 1) differ noticeably from those of homonuclear cluster **2**. For example, heterometallic cluster **4** exhibits ferromagnetic properties in the temperature range of 8—10 K.

In spite of these differences, X-ray diffraction study demonstrated that complexes **2** and **4** are isostructural (crystallographic parameters of their crystals are identical). Since we have already solved the crystals structure of **2**,[1] the structure of heterometallic cluster **4** becomes clear (Fig. 2). However, the positions of the Co and Ni atoms in cluster **4** cannot be correctly distinguished, because the molecule is located on a crystallographic threefold axis in the vicinity of the inversion center (crystals of **2** and **4** belong to the cubic system) due to which only

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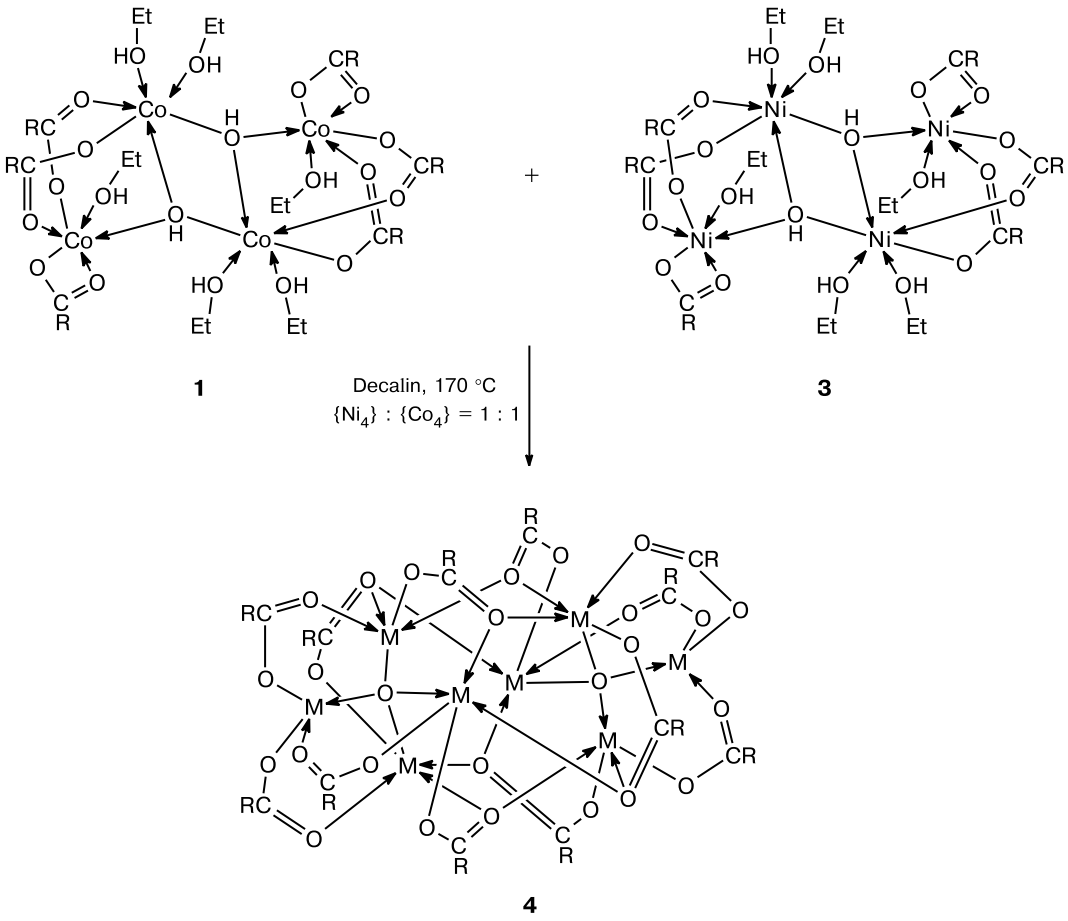
Scheme 1



two atoms are crystallographically independent. The multiplicity of one of the metal atoms in a tetrahedral oxygen environment (M(1) or M(1a)) is 1/3. However, it is reasonably safe to suggest that this position is occupied by the Co atom, because carboxylate complexes with tetracoordinated nickel are presently unknown. The positions of the Ni and Co atoms in the triangle located above and below this tetracoordinated metal atom (Fig. 3, the M(2),

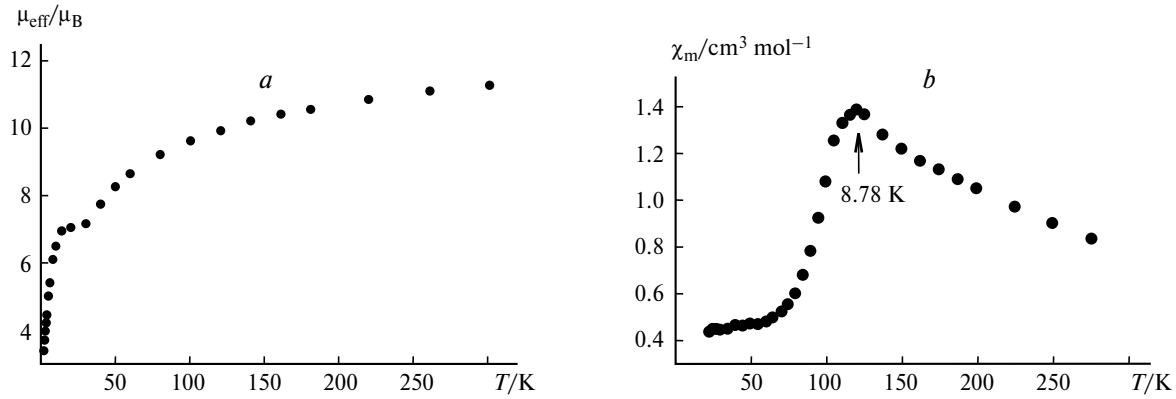


Fig. 1. Magnetic properties of heterometallic cluster **4**: the effective magnetic moment (μ_{eff}) (*a*) and static magnetic susceptibility (χ_m) at $H = 10$ Oe (*b*).

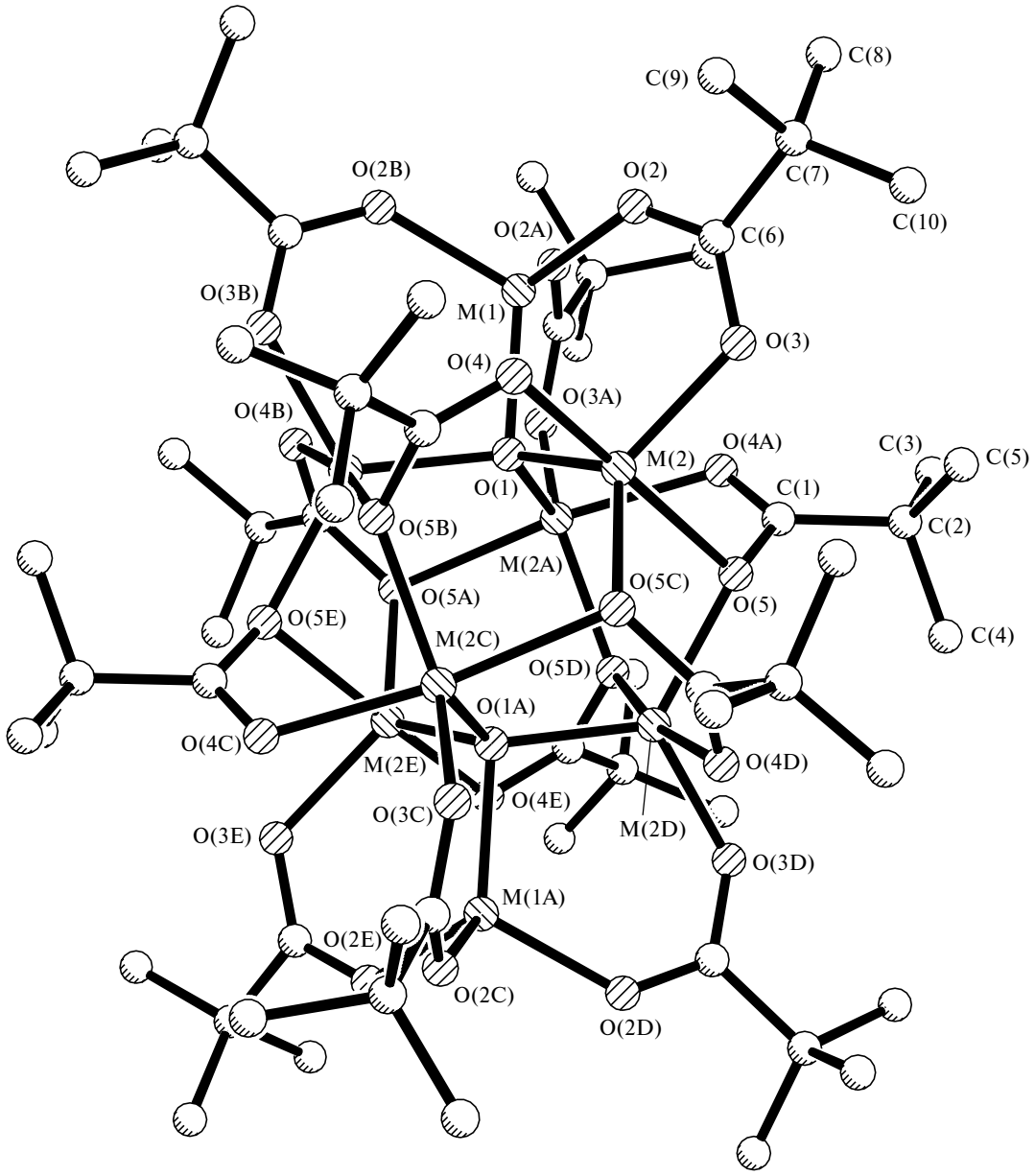


Fig. 2. Molecular structure of $Co_6Ni_2(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (**4**).

M(2a), and M(2b) atoms, and, correspondingly, M(2c), M(2d), and M(2e)) should be disordered with occupancies of approximately 2/3 for Co and 1/3 for Ni.

Presumably, the formation of complexes containing a larger number of Ni atoms than that present in cluster **4** is unfavorable because, as mentioned above, the structure has no metal sites in an octahedral oxygen environment, which is very stable for Ni atoms in polynuclear trimethylacetates.[2–4] As a result, the self-assembly of a heteronuclear molecule always culminates in the formation of the most stable structure, *viz.*, a cluster with the Co_6Ni_2 core, regardless of the ratio between the Co and Ni atoms in the starting reagents. It should be noted that this reaction produced virtually no homonuclear cobalt derivatives (only traces of cluster **2** were detected), which, apparently, indicates that the Co_8 core is less stable than the heterometallic system.

Experimental

The complexes were synthesized under an inert atmosphere using anhydrous solvents. The starting tetranuclear compounds **1** and **3** were synthesized according to known procedures.[1,2] The IR spectra of the complexes were recorded on a Specord M-80 instrument in KBr pellets. The static magnetic susceptibilities (χ_m) were measured on a SQUID MPMS-5S (Quantuim De-

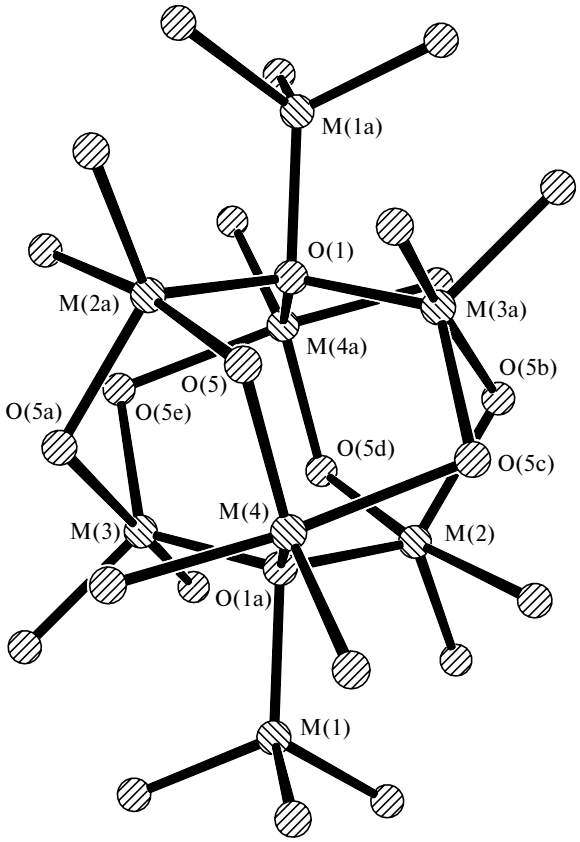


Fig. 3. Metal oxygen core of cluster **4**.

sign) magnetometer in the temperature range of 300—2 K. Metal content analysis was carried out by inductively coupled plasma atomic emission spectrometry on an IRIS Advantage instrument.

Heterometallic cluster di(μ_4-oxo)hexa(μ_3-*O*,*O*,*O*´-trimethylacetato)hexa(μ_2-*O*,*O*´-trimethylacetato)hexacobalt(II)dinickel(II), $Co_6Ni_2(\mu_4\text{-}O)_2(\mu_2\text{-}OOCCMe_3)_6(\mu_3\text{-}OOCCMe_3)_6$ (4). A solution of $Co_4(\mu_3\text{-}OH)_2(\mu\text{-}OOCCMe_3)_4(OOCCMe_3)_2(HOEt)_6$ (**1**) (0.25 g, 0.22 mmol) and $Ni_4(\mu_3\text{-}OH)_2(OOCCMe_3)_6(EtOH)_6$ (**3**) (0.25 g, 0.22 mmol) in anhydrous decalin (30 mL) was kept at 100 °C under argon until elimination of EtOH vapor ceased. The resulting blue-violet solution was heated to 170 °C, kept at this temperature for 2 h, and slowly cooled to ~20 °C to prepare large blue crystals of cluster **4** suitable for X-ray diffraction analysis. The crystals were separated by decantation and dried under argon. The yield was 0.32 g (80%). Found (%): C, 41.7; H, 6.4. $C_{60}H_{108}Co_6Ni_2O_{26}$. Calculated (%): C, 42.02; H, 6.30. IR, ν/cm^{-1}: 2968 s, 2928 m, 2872 m, 1668 w, 1664 w, 1584 v.s, 1488 s, 1432 v.s, 1360 m, 1344 m, 1232 m, 1032 w, 936 w, 896 m, 800 m, 616 w, 536 w, 530 w, 440 w, 408 w. The crystallographic data for cluster **4**: space group *Pa*3, a = 20.142(2) Å, V = 8171(2) Å^3, Z = 4, Bruker AXS SMART 1000 diffractometer (CCD detector), Mo-Kα radiation (λ = 0.71073 Å).

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