Synthesis and structure of dinuclear trimethylacetate complex $Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2[NH_2CH(CHMe_2)COOMe]_4$ containing coordinated molecules of valine methyl ester

*Z. P. Zubreichuk,[a] T. O. Denisova,[b] V. A. Knizhnikov,[a] and S. E. Nefedov[b]**

[a] *Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, 13 ul. Surganova, 220072 Minsk, Belarus*
[b] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 954 1279. E-mail: snef@igic.ras.ru*

Synthetic modeling of dinuclear fragments of the active sites of metalloenzymes responsible for various chemical processes occurring in nature (redox reactions, oxygen transfer, peptide bond hydrolysis, fixation and transformations of small molecules, *etc.*) is a priority area of research in modern coordination chemistry.[1—3] The aim of this modeling is to study the characteristic features of natural enzymatic reactions, including the possible stepwise isolation of their intermediates and final products.[3] Earlier,[4—7] we have studied the target formation of the dinuclear complex $[M_2(\mu\text{-}OOCR)_2L_4]^{2+}$ ($M = Co^{II}$), which serves as a model of fragments of the active sites of metalloenzymes, with the use of 3,5-dimethylpyrazole (L) and trimethylacetate anions as imidazole analogs in the histidine molecule and carboxylate anions in amino acids, respectively. We attempted to extend these ideas directly to L-amino acid derivatives containing the protected carboxylate group, in particular, by replacing 3,5-dimethylpyrazole with L-valine methyl ester.

It appeared that the reaction of the compound, which was prepared by fusion of cobalt(II) acetate tetrahydrate and trimethylacetic acid,[8] with an excess of $NH_2CH(CHMe_2)COOMe$ at room temperature afforded the red-violet $Co_2(\mu\text{-}OH_2)(\mu\text{-}OOCBu^t)_2(OOCBu^t)_2[NH_2CH(CHMe_2)COOMe]_4$ complex (**1**) in 70% yield.

According to the results of single-crystal X-ray diffraction study of complex **1** (Fig. 1), two Co^{II} atoms located at a nonbonded distance (Co(1)...Co(2), 3.5081(9) Å) are linked by two bridging carboxylate ligands (Co(1)—O(2), 2.078(3) Å; Co(1)—O(4), 2.077(3) Å; Co(2)—O(3), 2.081(3) Å; Co(2)—O(5), 2.074(3) Å) and the bridging water molecule (Co(1)—O(1), 2.101(3) Å; Co(2)—O(1), 2.104(3) Å; Co(1)—O(1)—Co(1A), 113.1(2)°). A distorted octahedral environment about each metal atom in the dinuclear complex involves also two N atoms belonging to two molecules of valine methyl ester and the O atom of the terminal trimethylacetate anion (Co(1)—N(1), 2.178(3) Å; Co(1)—N(2), 2.192(4) Å; Co(2)—N(3), 2.157(4) Å; Co(2)—N(4), 2.184(3) Å; Co(1)—O(6), 2.128(3) Å; Co(2)—O(8), 2.124(3) Å).

The uncoordinated O atoms of the terminal trimethylacetate ligands form hydrogen bonds with the H atoms of the bridging water molecule (O(9)...H(1), 1.72 Å; O(9)...O(1), 2.523 Å; O(7)...H(2), 1.71 Å; O(7)...O(1), 2.519 Å). In addition, there are both intraligand and interligand short contacts between the H atoms of the coordinated NH_2 fragments and the O atom of the C=O group of the amino acids (H...O, 2.11—2.59 Å). The Co...Co distance in complex **1** is somewhat shorter than the distances observed in the dinuclear cobalt complexes $Co_2(\mu\text{-}OOCR)_2(\mu\text{-}OH_2)(OOCR)_2L_4$ containing the bridging water molecule, which have been prepared earlier (Co...Co, 3.569(1) Å; R = Bu^t, L = py;[9] Co...Co, 3.59 Å; R = Ph, L = γ-picoline;[10] Co...Co, 3.596 Å; R = Me, $L_2 = Me_2NC_2H_4NMe_2$ (tmeda);[11] Co...Co, 3.621 Å; R = CH_2Cl, L_2 = tmeda;[12] Co...Co, 3.675 Å; R = $CHCl_2$, L_2 = tmeda;[13] Co...Co, 3.696 Å; R = CCl_3, L_2 = tmeda;[14] Co...Co, 3.692 Å; R = CF_3, L_2 = tmeda[15]).

Complex **1** is the first structurally characterized dinuclear cobalt(II) carboxylate complex containing coordinated molecules of amino acid derivatives.

All operations were carried out under argon in anhydrous solvents. The IR spectra were recorded on a Specord M-80 spectrophotometer in KBr pellets in a frequency range of 392—4000 cm^{-1}.

Tetra(methylvalinate)di(μ-*O*,*O*′-trimethylacetato)(μ-aqua)di(trimethylacetato)dicobalt(II) (1). A solution of L-valine methyl ester (0.52 g, 4 mmol) in hexane (15 mL) was added

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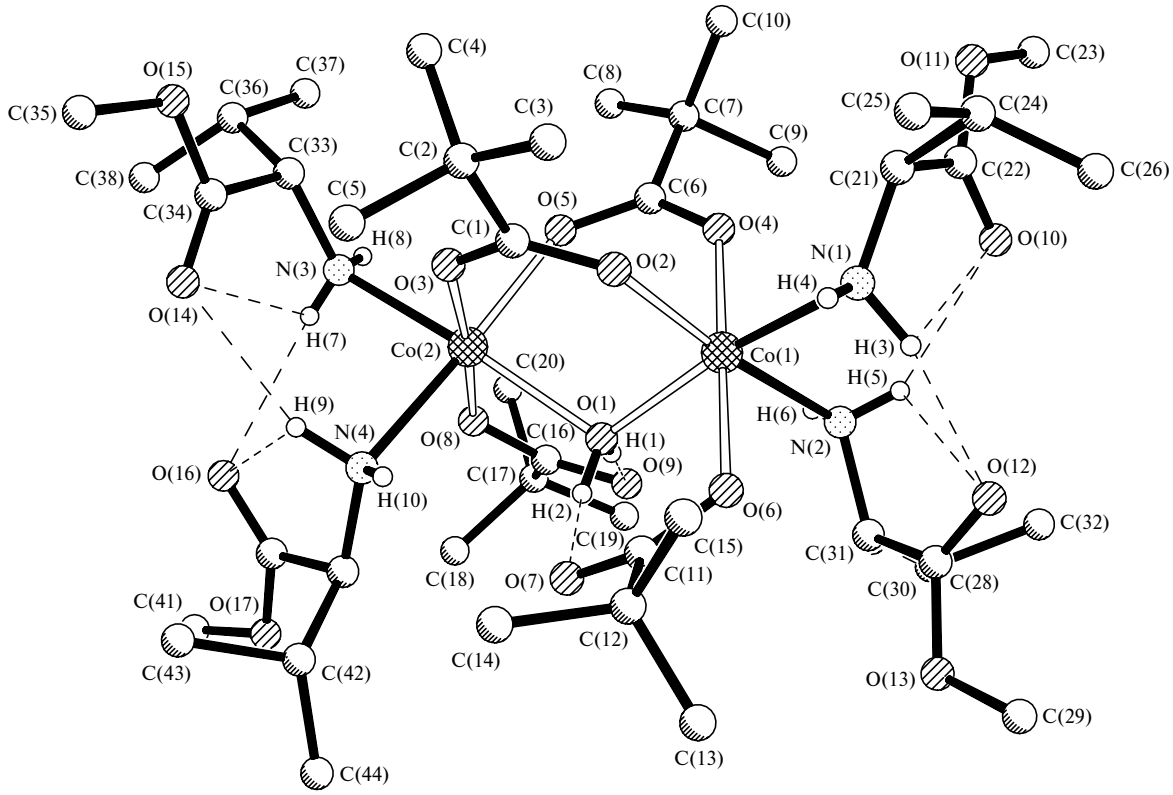

Fig. 1. Structure of complex **1**.

to a hexane-insoluble solid polymer (0.5 g, 1.9 mmol with respect to $Co(OOCBu^t)_2$), which was prepared by fusion of cobalt(II) acetate tetrahydrate and trimethylacetic acid,[8] at ~20 °C. After 20 min, the violet-blue solution that formed was filtered, concentrated to 5 mL, and kept at −18 °C for 2 days. Large violet-red prismatic crystals were separated from the solution by decantation, washed with cold hexane (−10 °C), and dried under argon at ~20 °C. The yield was 0.71 g (70%). Found (%): C, 49.81; H, 8.64. $C_{44}H_{90}Co_2N_4O_{17}$. Calculated (%): C, 49.62; H, 8.52. IR, ν/cm^{-1}: 3366 m.br, 3340 w, 3284 m, 2962 m, 2864 w, 1600 s, 1536 s, 1452 s, 1372 s, 1324 s, 1228 s, 1176 m, 1100 w, 936 w, 912 w, 896 m, 808 w, 788 m, 752 m, 616 m, 548 w, 496 w, 476 w, 436 m.

X-ray diffraction study of complex 1. X-ray diffraction study was carried out at the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) according to a standard procedure[16] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λ(Mo), graphite monochromator, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max}$= 60°). The molecular formula is $C_{44}H_{90}Co_2N_4O_{17}$, M = 1065.06, space group *P*2(1), a = 11.7141(6) Å, b = 20.8008(10) Å, c = 13.0095(6) Å, β = 107.842(1)°, V = 3017.5(3) Å^3 (120 K), Z = 2, a total of 25213 reflections were measured, of which 10398 reflections were independent with $F^2 > 2\sigma(I)$, d_{calc} = 1.172 g cm^{-3}, μ = 6.11 cm^{-1}, R_1 = 0.0481, wR_2 = 0.1176.

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