Letters to the Editor

Unusual transformation of the urea molecule giving rise to the NCO^- anion as a bridging ligand between two Co^{II} atoms

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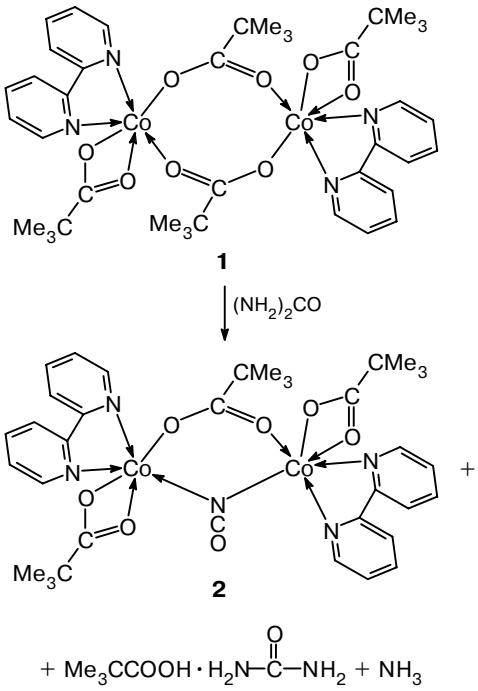
The structural similarity of metal-containing fragments of some binuclear carboxylate complexes to the fragments present in metal-containing enzymes gave impetus to the development of the chemistry of transition metal carboxylates.[1—3] As part of continuing studies of transformations of the urea molecule in the coordination sphere of the transition metal ion, we carried out the reaction of urea with the new binuclear Co^{II} complex, *viz.*, $dipy_2Co_2(\mu\text{-}OOCCMe_3)_2(OOCCMe_3)_2$ (**1**). In this reaction, the NH_2CONH_2 molecule lost the NH_4^+ ion or the NH_3 molecule and the proton to form the NCO^- anion, which is a bridging ligand between two Co^{II} atoms in the resulting binuclear complex $dipy_2Co_2(OOCCMe_3)_2(\mu\text{-}OOCCMe_3)(\mu\text{-}NCO)$ (**2**).

Complex **1** was prepared by the reaction of the polymeric complex $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$[4,5] with α,α′-dipyridyl taken in a ratio Co : dipy = 1 : 1. According to the results of X-ray diffraction analysis, the Co atoms in antiferromagnetic complex **1** (Fig. 1) (μ_{eff}/Co_{at} = 4.77—2.42 μB (295—2 K)) are located at a nonbonded distance (4.383(1) Å) and are linked only *via* two carboxylate bridges (Co—O, 2.030(2) and 2.043(2) Å; C—O, 1.249(4) and 1.240(4) Å; O—C—O, 124.8(3)°). The distorted octahedral environment around each Co atom in the dimer is completed with the coordinated dipyridyl ligand (Co—N, 2.116(3) Å) and the η^2-coordinated pivalate fragment (Co—O, 2.198(2)—2.221(3) Å).



The reaction of complex **1** with urea in anhydrous MeCN (the reagent ratio was 1 : 4) under an argon atmosphere afforded complex **2**. According to the results

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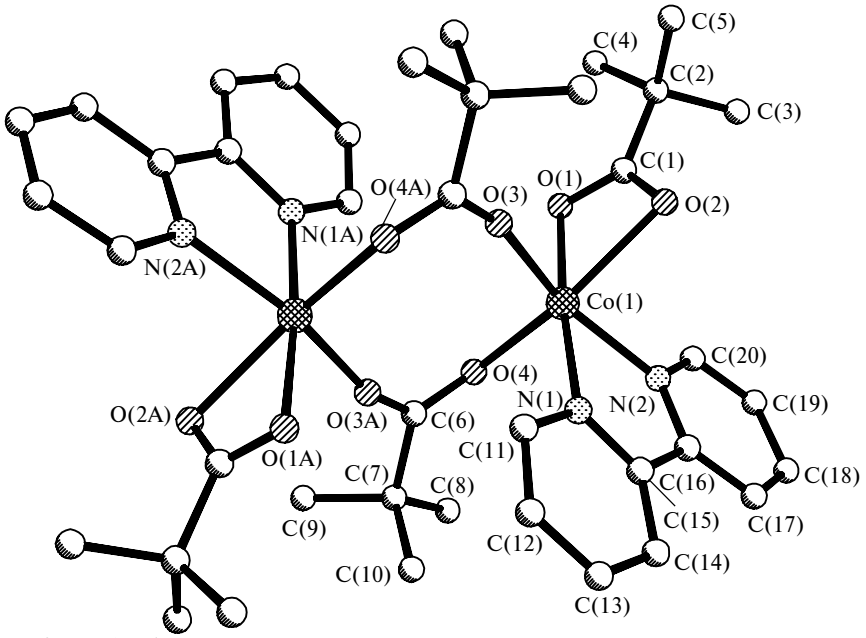

Fig. 1. Molecular structure of complex **1**.

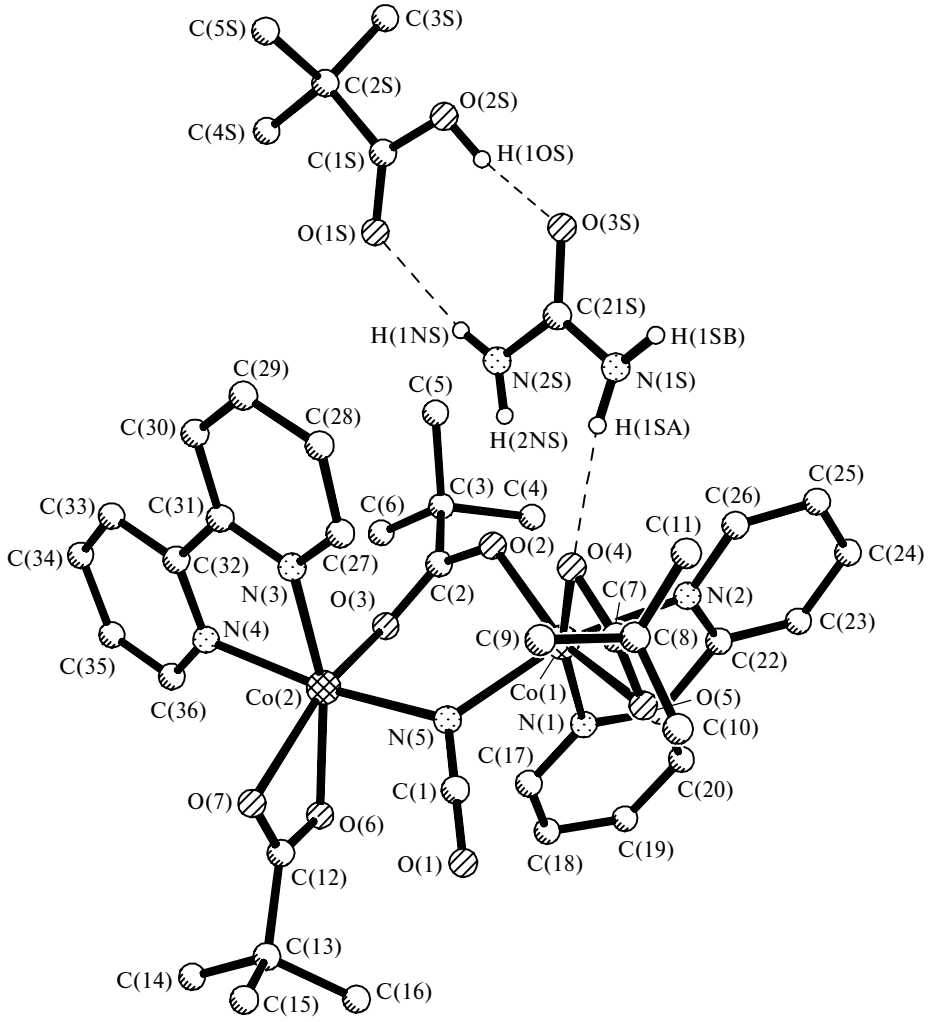

Fig. 2. Molecular structure of the solvate $2 \cdot HOOCCMe_3 \cdot (H_2N)_2CO$.

of X-ray diffraction analysis (Fig. 2), two cobalt(II) atoms in complex **2** are located at a nonbonded distance (3.594(1) Å) and are linked *via* the carboxylate (Co—O, 2.035(4) and 2.048(4) Å) and cyanate (Co—N, 2.106(4) and 2.130(4) Å; N—C, 1.179(5) Å; C=O, 1.190(5) Å) bridging groups. Each metal atom is coordinated by the dipyridyl ligand (Co—N, 2.100(4)—2.136(5) Å) and the pivalate anion (Co—O, 2.208(3)—2.224(4) Å), both ligands being coordinated in the chelate mode. In addition, the crystal contains the associate of the pivalic acid with the urea molecule, *viz.*, $HOOCCMe_3 \cdot (H_2N)_2CO$, formed *via* hydrogen bonds (RCOO—H...O=C$(NH_2)_2$, 1.93(4) Å; N—H...O=C(OH), 2.13(5) Å). This associate is linked to the oxygen atom of the chelate carboxylate fragment of complex **2** through the hydrogen atom of the amino group of the urea molecule (N—H...OCO, 2.04(4) Å).

It should be noted that the possibility of such a transformation of the urea molecule in anhydrous ethanol has been demonstrated previously using the $[\{Ni_2L(OH)(MeOH)\}_2(CO_3)]^{2+}$ complex (L is the 2-[*N*,*N*-di(2-pyridylmethyl)aminomethyl]-6{*N*-[2-(dimethylamino)ethyl]iminomethyl}-4-methylphenoxide ion) as the starting compound.[6] However, we carried out the reaction in anhydrous MeCN, *i.e.*, under the conditions excluding the generation of the hydroxy group or the water molecule.

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

Synthesis of the complexes. Bis(η^2-2,2′-dipyridyl)di(μ-*O*,*O*′-pivalato)di(η^2-pivalato)dicobalt(II), dipy$_2$Co$_2$(μ-OOCCMe$_3$)$_2$(OOCCMe$_3$)$_2$ (1). A mixture of the polymer $[Co(OH)_n(OOCCMe_3)_{2-n}]_x$ (1 g, 3.83 mmol) and α,α′-dipyridyl (0.6 g, 3.83 mmol) in acetonitrile (or toluene) (50 mL) was refluxed for 1 h until the stable violet color appeared. The resulting solution was concentrated to 10 mL and cooled to −5 °C. Violet crystals of **1** were separated from the mother liquor, washed with cold hexane (−10 °C), and dried *in vacuo*. The yield was 1.36 g (85%). Found (%): C, 57.7; H, 6.5; N, 6.9. $C_{40}H_{52}Co_2N_4O_8$. Calculated (%): C, 57.85; H, 6.24; N, 6.71. IR, ν/cm^{-1}: 2976 m, 2958 m, 2920 m, 2864 m, 1592 s, 1528 s, 1472 s, 1424 s, 1360 s, 1312 m, 1280 w, 1224 s, 1152 m, 1104 w, 1056 s, 1016 s, 976 w, 936 w, 896 v.s, 792 v.s, 776 v.s, 736 v.s, 648 s, 632 m, 616 m, 608 v.s, 560 s, 536 m.

Bis(η^2-2,2′-dipyridyl)-μ-cyanato-μ-*O*,*O*′-pivalatodi(η^2-pivalato)dicobalt(II), dipy$_2$Co$_2$(OOCCMe$_3$)$_2$(μ-OOCCMe$_3$)(μ-NCO) (2). A solution of urea (0.055 g, 0.928 mmol) in anhydrous MeCN (5 mL) was added dropwise to a solution of complex **1** (0.193 g, 0.232 mmol) in anhydrous MeCN (15 mL) under an argon atmosphere at 0 °C. The resulting solution was slowly heated to ~20 °C with stirring during 1 h. The solvent was distilled off *in vacuo* and the dry residue was extracted with benzene (10 mL). The extract was concentrated to 3—4 mL and kept at 20 °C for one day. The red-raspberry crystals of the solvate $\mathbf{2} \cdot HOOCCMe_3 \cdot (H_2N)_2CO \cdot 2.5C_6H_6$ that precipitated were separated from the solution by decantation and dried under a steam of argon. The yield was 0.086 g (48%). Found (%): C, 71.8; H, 6.7; N, 9.8. $C_{57}H_{72}Co_2N_7O_{10}$. Calculated (%): C, 71.30; H, 6.73; N, 9.71. IR, ν/cm^{-1}: 3512 w, 3424 w, 3192 w, 3080 w, 2960 m, 2910 m, 2864 m, 2176 v.s, 1704 m, 1672 m, 1600 s, 1576 s, 1536 m, 1480 v.s, 1448 s, 1416 s, 1360 m, 1319 w, 1296 w, 1224 m, 1192 w, 1104 w, 1056 w, 1024 m, 936 w, 896 w, 872 w, 768 v.s, 736 m, 688 s, 632 s, 608 m, 560 w, 416 w.

X-ray diffraction investigation was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) according to a standard procedure[7] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, 110 K, ω scan technique, the scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max}$ = 60°). For complex **1**: $C_{40}H_{52}Co_2N_4O_8$, M = 834.72, space group $P2_1/c$, a = 11.125(2) Å, b = 17.578(4) Å, c = 10.412(2) Å, β = 103.97(3)°, V = 1975.9(7) $Å^3$, Z = 2, 5363 reflections were measured of which 3216 reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.789 g cm^{-3}, μ = 8.96 cm^{-1}, R_1 = 0.0620, wR_2 = 0.1391. For complex **2**: $C_{57}H_{72}Co_2N_7O_{10}$, M = 1133.08, space group $P\bar{1}$, a = 11.929(2) Å, b = 15.408(2) Å, c = 17.852(2) Å, α = 101.111(3)°, β = 99.668(4)°, γ = 108.240(3)°, V = 2964.9(6) $Å^3$, Z = 2, 9327 reflections were measured of which 7769 reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.687 g cm^{-3}, μ = 6.19 cm^{-1}, R_1 = 0.0676, wR_2 = 0.1786.

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