Letters to the Editor

Reversible temperature-dependent structural transformations of the $Co_3(OOCBu^t)_6(NEt_3)_2$ complex in crystalline state

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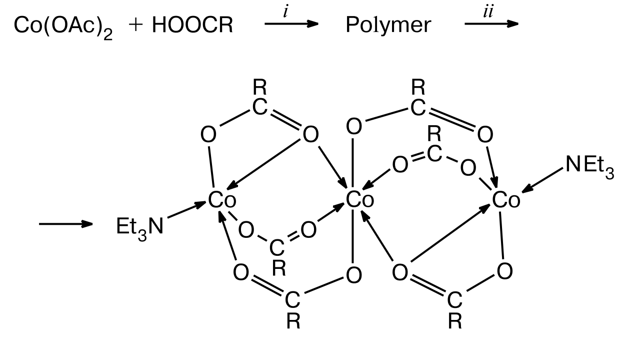
Earlier,[1] it has been demonstrated that the reaction of the polymeric cobalt complex, which was prepared by fusion of cobalt(II) acetate tetrahydrate and trimethylacetic acid,[2] with excess triethylamine in hexane at room temperature afforded the $Co_3(\mu,\eta^2\text{-}OOCBu^t)_2(\mu\text{-}OOCBu^t)_4(NEt_3)_2$ complex (**1**). Its structure has been established by X-ray diffraction analysis at 112 K.

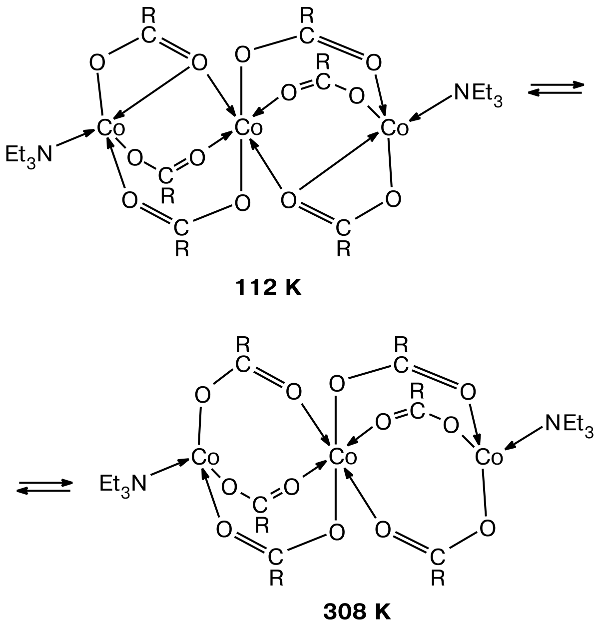


1

R = Bu^t

i. Fusion at 150 °C. *ii*. Et_3N, hexane, 22 °C

Scheme 1



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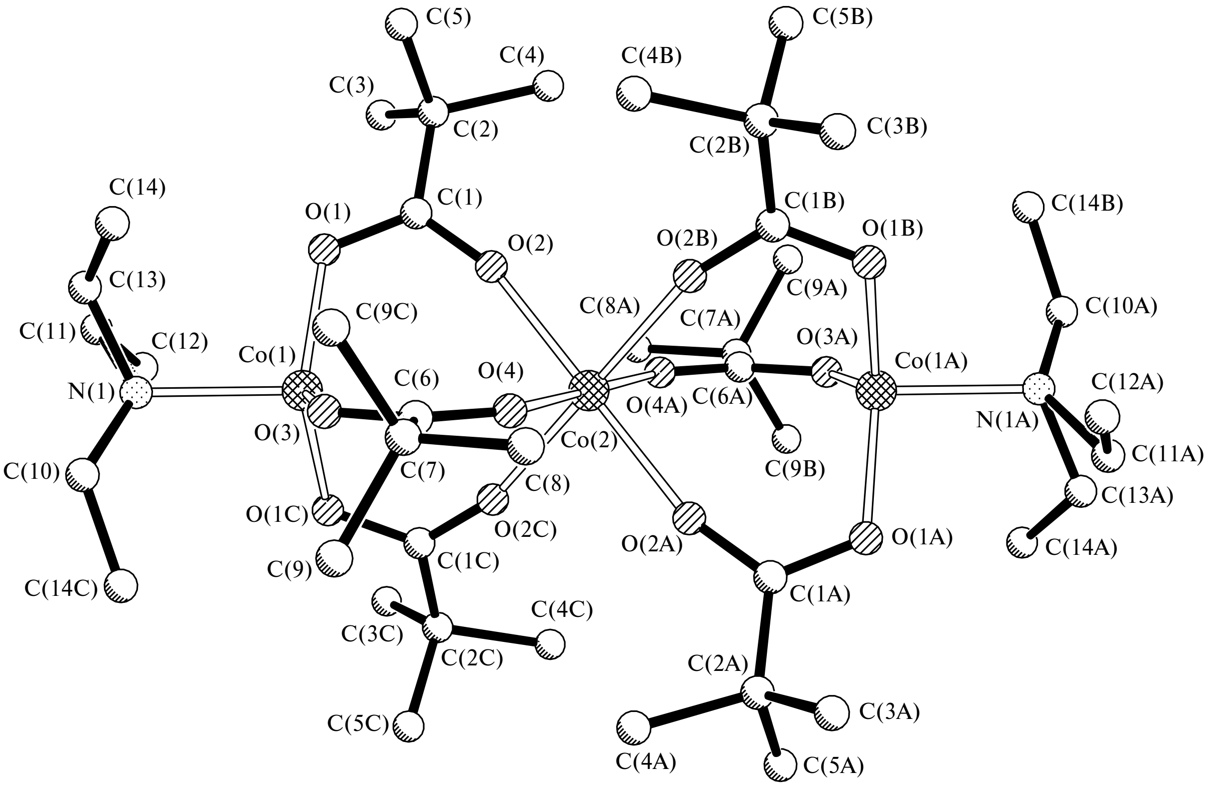

Fig. 1. Structure of complex **1** based on X-ray diffraction data at 308 K.

Single-crystal X-ray diffraction study of complex **1** at 308 K (Scheme 1) showed that all six Bu^tCOO^- anions in this structure serve as μ bridges without additional η^2 coordination, in contrast to the structure of complex **1** at 112 K (Fig. 1).

The Co—Co and Co—N distances (corresponding distances at 308 K are given; the distances at 112 K are presented in parentheses: Co...Co, 3.558(1) Å (3.546(1) Å); Co(1)—N(1), 2.110(5) Å (2.130(2) Å)) and the Co—O distances in the bridging Bu^tCOO^- anions, which occupy the equatorial positions of the octahedron about the central Co(2) atom (Co(2)—O, 2.062(3), 2.062(3), 2.074(5), 2.074(5) Å (2.067(2), 2.067(2), 2.087(2), 2.087(2) Å)), change only slightly with temperature. At 308 K, the distances from the Co(2) atom to the remaining two axial oxygen atoms, which act as bridges at 112 K, are shortened (Co(2)—O(2), 2.062(3), 2.062(3) Å (2.108(2), 2.108(2) Å)). Similar changes in the Co—O bond lengths are observed also at the Co(1) atom. Two bond lengths remain virtually unchanged (Co(1)—O, 1.945(4), 1.945(4) Å (1.947(2), 1.950(2) Å)), whereas the third bond is shortened (Co—O, 1.937(5) Å (2.014(2) Å)). An increase in the temperature leads to changes in the distances from the Co(1) atom to other oxygen atoms of the trimethylacetate anions. These distances are 3.351(3), 3.237(3), and 2.316(2) Å (η^2 bond) at 112 K and 2.860(4), 2.860(4), and 3.256(5) Å, respectively, at 308 K. It should also be noted that the nitrogen atoms of the NEt_3 ligands disordered over two positions are at an angle of 6.3° (13.8°) with respect to the Co(1)Co(2)Co(1A) line.

An increase in the temperature is accompanied by a change of the space group from *Pbca* to *Cmca*; whereas the unit cell parameters change only slightly.

Supposedly, such a change in the coordination environment about the cobalt atoms resulting in the formal change in the electronic nature of the metal center (Co^{II} atom has 17 valence electrons at 112 K and 15 valence electrons at 308 K) should be reflected in the magnetic susceptibility curve. It seems likely that the point of inflection on this curve will allow one to determine the temperature of the observed structural transformation with precision. These studies are underway.

It should be noted that the spectroscopic data for compound **1** [1] correspond, apparently, to the structure established in the present study, because the spectra were measured at room temperature.

X-ray diffraction analysis. X-ray diffraction study was carried out in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) using a standard procedure[3] on a Bruker AXS SMART 1000 diffractometer equipped with a

CCD detector (λMo-Kα, graphite monochromator, 308 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 60°$). For complex **1**: $C_{42}H_{84}Co_3N_2O_{12}$, $M = 985.90$; at $T = 112$ K, space group *Pbca*, $a = 14.4787(8)$, $b = 16.5647(9)$, $c = 22.0891(12)$ Å, $V = 5297.7(5)$ Å^3 $Z = 8$;[2] at $T = 308$ K, space group *Cmca*, $a = 16.774(5)$, $b = 22.398(7)$, $c = 14.731(4)$ Å, $V = 5535.7(3)$ Å^3, $Z = 4$, 13232 measured reflections of which 3224 reflections were with $F^2 > 2\sigma(I)$, $\rho_{calc} = 1.236$ g cm^{-3}, $\mu = 9.81$ cm^{-1}, $R_1 = 0.0639$, $wR_2 = 0.1638$.

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References

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