ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2012, Vol. 38, No. 2, pp. 140–144. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © S.R. Garaeva, A.A. Medzhidov, O. Beukgunger, A. Aydin, B. Yalcin, M.G. Abbasov, 2012, published in Koordinatsionnaya Khimiya, 2012, Vol. 38, No. 2, pp. 147–152.

Heterovalent Trinuclear Co(III)–Co(II)–Co(III) Complexes with N-(2-Carboxyethyl)salicylaldimines

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Received February 9, 2011

Abstract—The heterovalent trinuclear cobalt complexes $[\mathrm{Co}_2^{\mathrm{III}}\mathrm{L}_4^i \cdot \mathrm{Co}^{\mathrm{II}}(\mathrm{H_2O})_4] \cdot nXmY$ (L^i are deprotonated Schiff bases derived from substituted salicylaldehydes and β-alanine; $i = 1–3$) were obtained and characterized. An X-ray diffraction study of the trinuclear cobalt complex with N-(2-carboxyethyl)salicylaldimine showed that the central Co(II) ion and the terminal Co(III) ions are linked by bridging carboxylate groups. Either terminal Co(III) atom is coordinated to two ligand molecules. They form an octahedral environment consisting of two azomethine N atoms, two phenolate O atoms, and two O atoms of two carboxylate groups. The central Co(II) atom is coordinated to four water molecules and to two O atoms of two bridging carboxylate ligands involved in the coordination sphere of the terminal Co(III) atoms.

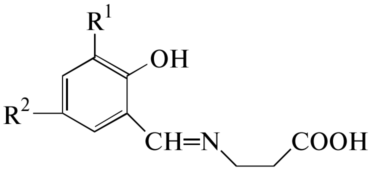
DOI: 10.1134/S1070328412010022

Heterovalent trinuclear cobalt complexes are of interest for better understanding of redox processes in the formation of polynuclear complexes of the same metal in different oxidation states.

A survey of the literature data showed that various ligands with different dentate numbers tend to form heterovalent Co(III)–Co(II)–Co(III) complexes. Such ligands include amino alcohols [1], dianionic tridentate Schiff bases derived from amino alcohols [2], amino acids [3, 4], their tridentate Schiff bases [5], pyridone oximes [6], tetradentate bisalicylidene dianions [7–10], and bridging pyrazolate ligands [11, 12].

Earlier, we have examined the structures and properties of a heterovalent trinuclear cobalt complex with N-(2-carboxyethyl)-2-hydroxynaphthaldimine and found different types of coordination of the central Co(II) ion to the terminal Co(III) complexes for α- and β-amino acid derivatives.

Here we studied the structures and properties of heterovalent trinuclear Co(III)–Co(II)–Co(III) complexes with Schiff bases derived from unsubstituted and substituted salicylaldehydes and β-alanine. The trinuclear complexes were obtained by both template synthesis and by using Schiff bases as the starting materials.



$\mathrm{L^1H_2}$: $\mathrm{R^1 = R^2 = H}$;
$\mathrm{L^2H_2}$: $\mathrm{R^1}$ = *tert*-Bu, $\mathrm{R^2 = H}$;
$\mathrm{L^3H_2}$: $\mathrm{R^1 = R^2}$ = *tert*-Bu.

EXPERIMENTAL

IR spectra were recorded on a Specord M 80 spectrophotometer for pellets with KBr. Electronic absorption spectra were recorded on an EZ 210 spectrophotometer (Perkin Elmer). Elemental analysis was performed on a LECO CHNS 932 analyzer at the Tubitak analytical laboratory (Ankara). Magnetic moments were measured at room temperature on a Faraday setup with $\mathrm{Hg[Co(SCN)_4]}$ as a standard.

An X-ray diffraction study was carried out on a STOE IPDS diffractometer at 296 K ($\mathrm{Mo}K_\alpha$ radiation). Crystallographic parameters and the data collection statistics are summarized in Table 1.

The structure was solved by the direct method (SHELXS-97 [13]) and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 [13] and WINGX programs [14]. The positions of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms bound to carbon were located geometrically (C–H, 0.93–0.97 Å) and refined using a riding model with isotropic thermal parameters U_H that are higher by a factor of 1.2–1.5 than the thermal parameters U_C of the respective carbon atoms (CH, CH_2, and CH_3). The H atoms of water molecules were refined under the constraint that the O–H distance is 0.83 Å. In the refinement of the H atom of the hydroxy group O(10)H, the O–H distance was taken to be 0.82 Å.

The molecule of the complex was visualized with the ORTEPIII [15] and MERCURY programs [16]. Geometrical calculations were performed with the PLATON program [15–17].

Atomic coordinates and comprehensive structural data have been deposited with the Cambridge Crystallographic Data Collection (no. 778333; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of N-(2-carboxyethyl)salicylaldimine (L^1H_2). A heterogeneous mixture of β-alanine (0.891 g, 0.01 mol) and salicylaldehyde (1.22 g, 0.01 mol) in ethanol (100 mL) was refluxed until a yellow homogeneous solution formed. The solution was cooled and the yellow needle-like crystals that formed were isolated, washed with ethanol, and dried. The yield of L_1H_2 was 80%, $T_m = 205$°C.

For $C_{10}H_{11}NO_3$
anal. calcd, %: C, 62.18; H, 3.5; N, 7.2.
Found, %: C, 61.18; H, 3.4; N, 7.6.

Trinuclear cobalt complexes were obtained by template synthesis, as well as by using the Schiff bases L^1H_2, N-(2-carboxyethyl)-3-*tert*-butylsalicylaldimine (**L^2H_2**), and N-(2-carboxyethyl)-3,5-di-*tert*-butylsalicylaldimine (**L^3H_2**) as the starting materials.

Synthesis of $[Co(L^1)_2Co(H_2O)_4Co(L^1)_2] \cdot CH_3COOH \cdot H_2O$ (I). A. Cobalt acetate tetrahydrate (0.249 g, 0.01 mol) in methanol (15 mL) and potassium acetate (0.98 g, 0.01 mol) in water (5 mL) were added with stirring to L^1H_2 (0.89 g, 0.01 mol) in methanol (10 mL). The reaction mixture was heated at 50°C for 0.5 h and cooled. The rose-violet precipitate of a Co(II) complex that formed was separated. The mother liquor was left for 72 h to produce dark brown crystals of complex **I**. The yield was 30%.

For $C_{42}H_{50}N_4O_{19}Co_3$
anal. calcd, %: C, 46.21; H, 4.61; N, 5.13.
Found, %: C, 46.05; H, 4.76; N, 5.39.

Table 1. Crystallographic parameters and the data collection statistics for structure **I**

Parameter	Value
Empirical formula	$C_{42}H_{50}N_4O_{19}Co_3$
M	1091.67
Temperature, K	296
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell parameters:	
a, Å	37.5662(15)
b, Å	9.5737(4)
c, Å	13.5911(5)
β, deg	102.422(3)
V, Å^3	4773.6(3)
Z	4
ρ_{calcd}, g/cm^3	1.628
μ, mm^{-1}	1.120
F(000)	2420
Crystal dimensions, mm	0.29 × 0.24 × 0.15
θ scan range, deg	2.2 to 26.5
Ranges of h, k, and l indices	$-46 \le h \le 46$ $-12 \le k \le 11$ $-17 \le l \le 17$
Number of measured reflections	17530
Number of independent reflections	443
R_{int}	0.062
T_{min}, T_{max}	0.7091, 0.8217
GOOF on F^2	1.04
R factor ($I > 2\sigma(I)$)	$R_1 = 0.040$, $wR(F^2) = 0.107$
R factor (for all reflections)	0.051
$\Delta\rho_{min}/\Delta\rho_{max}$), e Å^{-3}	−0.43/0.82

Template synthesis of $[Co(L^1)_2Co(H_2O)_4Co(L^1)_2] \cdot CH_3COOH \cdot H_2O$ (I). B. A solution of potassium acetate (0.98 g, 0.01 mol) in water (4 mL) was added to β-alanine (0.89 g, 0.01 mol) and salicylaldehyde (1.22 g, 0.01 mol) in ethanol–water (1 : 1, 20 mL). The mixing resulted in the formation of a homogeneous solution, to which cobalt acetate (2.49 g, 0.01 mol) in methanol (5 mL) was added. On cooling, the rose-violet precipitate of a Co(II) complex that formed was separated. The dark brown mother liquor was left for three to four days to produce dark brown orthorhombic crystals suitable for X-ray diffraction. The yield of complex **I** was 12% (with respect to the starting ligand).

For $C_{42}H_{50}N_4O_{19}Co_3$
anal. calcd, %: C, 46.21; H, 4.61; N, 5.13.
Found, %: C, 46.58; H, 4.28; N, 4.91.

Synthesis of $[Co(L^3)_2Co(H_2O)_4Co(L^3)_2] \cdot CH_3COOH \cdot H_2O$ (III). β-Alanine (0.89 g, 0.01 mol) and potassium acetate (0.98 g, 0.01 mol) were dis-

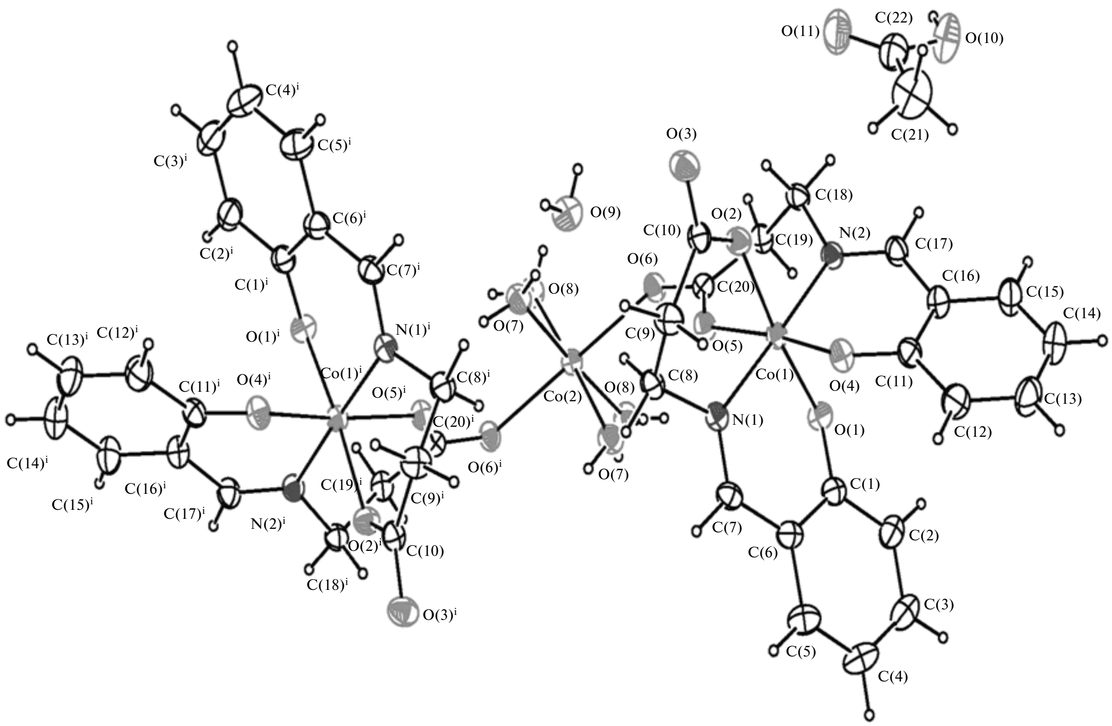


Fig. 1. Molecular structure of complex **I** with atomic thermal displacement ellipsoids (30% probability).

solved in water (3 mL). Then a solution of L^3H_2 (2.34 g, 0.01 mol) in ethanol (10 mol) was added. The resulting solution was mixed with a solution of cobalt acetate tetrahydrate (2.45 g, 0.01 mol) in methanol (10 mL) to produce a dark red homogeneous solution, which was heated at 60°C for 30 min and left for slow crystallization. The dark brown fine crystalline precipitate that formed was isolated, washed with ethanol, and dried in vacuo. The yield of complex **III** was 41% (with respect to the ligand), $T_m > 250°C$. Complex **III** is well soluble in ethanol, DMF, acetonitrile, and water.

For $C_{72}H_{116}N_4O_{20}Co_3$			
anal. calcd, %:	C, 56.6;	H, 7.65;	N, 3.66.
Found, %:	C, 56.9;	H, 7.55;	N, 3.85.

The complex $[Co(L^2)_2Co(H_2O)_4Co(L^2)_2] \cdot H_3COOH \cdot H_2O$ (**II**) was obtained from L^2H_2 as described for complex **III**.

For $C_{56}H_{80}N_4O_{20}Co_3$			
anal. calcd, %:	C, 51.76;	H, 6.2;	N, 4.3.
Found, %:	C, 52.06;	H, 6.08;	N, 4.2.

RESULTS AND DISCUSSION

Heterovalent trinuclear cobalt complexes $[Co^{III}(L^i)_2Co^{II}(H_2O)_4Co^{III}(L^i)_2] \cdot CH_3COOH \cdot H_2O$ ($i = 1–3$) with Schiff bases derived from α- and β-amino acids (L^iH_2) can be obtained by template synthesis from cobalt acetate, 2-hydroxyarenecarbaldehyde, and an amino acid in the presence of alkali metal acetates.

If a Schiff base of an amino acid is stable (as in the case of the Schiff bases derived from β-alanine and salicylaldehyde and 2-hydroxynaphthaldehyde [4]), the above complexes can be obtained directly from cobalt acetate and an appropriate Schiff base.

The electronic absorption spectra of cobalt complexes **I–III** in the visible range show two absorption bands at 15400–14300 and 19200–18700 cm^{-1}, which can be assigned to the $^1A_{1g}–T_{1g}$ and $^1A_{1g}–T_{2g}$ transitions in octahedral Co(III) complexes. The electronic transitions in the Co(II) centers of heterovalent complexes are masked by more intense transitions in the Co(III) centers [2].

The magnetic moments of complexes **I–III** (4.4–4.8 μ_B) measured at room temperature suggest the presence of the Co(II) ion.

The IR spectra of complexes **I–III** show absorption bands at 1600 ν_{as} (COO^-) and 1400 cm^{-1} $\nu_s(COO^-)$) due to the monodentate carboxylate group and at 1570 $\nu_{as}(COO^-)$ and 1430 cm^{-1} $\nu_s(COO^-)$ due to the bridging carboxylate group.

The formation of heterovalent trinuclear cobalt complexes is usually accompanied by the formation of Co(II) complexes [4], which precipitate at the beginning of the reaction because of their poor solubility in common organic solvents.

Table 2. Selected bond lengths and bond angles in structure **I***

Bond	*d*, Å	Bond	*d*, Å
Co(1)–O(1)	1.8842(19)	Co(1)–N(2)	1.911(2)
Co(1)–O(2)	1.9211(18)	Co(2)–O(6)	2.1282(19)
Co(1)–O(4)	1.8767(19)	Co(2)–O(7)	2.083(2)
Co(1)–O(5)	1.9622(19)	Co(2)–O(8)	2.092(2)
Co(1)–N(1)	1.921(2)		
Angle	ω, deg	Angle	ω, deg
O(1)Co(1)O(2)	173.01(8)	O(5)Co(1)N(1)	85.12(8)
O(1) Co(1)O(4)	88.91(8)	O(5)Co(1)N(2)	93.43(8)
O(1)Co(1)O(5)	91.05(8)	N(1)Co(1)N(2)	178.23(9)
O(1) Co(1) N(1)	92.60(9)	O(6)Co(2)O(7)	91.69(7)
O(1)Co(1)N(2)	88.44(8)	O(6)Co(2)O(8)	93.11(8)
O(2)Co(1)O(4)	91.32(8)	O(6)Co(2)O(6)$^{\#1}$	178.47(7)
O(2)Co(1)O(5)	89.55(8)	O(6)Co(2)O(7)$^{\#1}$	89.38(7)
O(2)Co(1)N(5)	94.39(9)	O(6)Co(2)O(8)$^{\#1}$	85.80(8)
O(2)Co(1)N(2)	84.58(8)	O(7)Co(2)O(8)	90.11(8)
O(4)Co(1)O(5)	173.11(8)	O(7)Co(2)O(7)$^{\#1}$	90.80(8)
O(4)Co(1)N(1)	88.00(9)	O(7)Co(2)O(8)$^{\#1}$	177.33(8)
O(4)Co(1)N(2)	93.46(8)	O(8)Co(2)O(8)$^{\#1}$	89.09(8)

* The symmetry operation code is $^{\#1}$ x, $1 - y$, $z - 1/2$.

However, if the oxidation rate of Co(II) is high (this is indicated by an increasing intensity of the absorption band at 19000 cm^{-1} with time) or if a primary Co(II) complex is well soluble in the reaction medium, heterovalent trinuclear cobalt complexes are major reaction products. For instance, because Co(II) complexes with L^1H_2 are poorly soluble and the Co(II) to Co(III) oxidation rate is low, no trinuclear cobalt complex with this ligand can be obtained under normal conditions. In contrast, L^2H_2 and L^3H_2 form soluble Co(II) complexes and the yields of the corresponding trinuclear complexes are high (up to 65%), regardless of the low Co(II)–>Co(III) oxidation rate.

According to X-ray diffraction data, complex **I** {[Co(Sal-β-ala)$_2$]$_2$Co(H$_2$O)$_4$}, where Sal-β-ala = L^1–L^3) consists of three cobalt centers (Fig. 1). In the trinuclear complex (on the axis 2), the terminal Co(1) and Co(1)^i ions are each coordinated by two tridentate ligands Sal-β-ala. The central Co(2) ion is coordinated by four O atoms of four water molecules and two O atoms of two carboxylate groups which bridge the central Co(2) atom and the terminal Co(1) and Co(1)^i atoms. The di-deprotonated ligands L^1 make an octahedral environment around the terminal cobalt ion, coordinating in a tridentate fashion through two O atoms of two phenolic groups, two azomethine N atoms, and two O atoms of the carboxylate groups. One carboxylate group acts as a monodentate ligand, while the other acts as a bridging bidentate ligand. The terminal complex anion can be regarded as a monoanionic monodentate ligand to the central Co atom. From stoichiometric considerations, the oxidation state distribution in the trinuclear cobalt complex with four di-deprotonated ligands L^1 must be as follows: Co(III)–Co(II)–Co(III). This is confirmed by comparison of the C–O bond lengths. Because the ionic radius of Co(II) is larger than that of Co(III), the Co(2)–O(6) bond (2.1282(19) Å) is substantially longer than the Co(1)–O(2) and Co(1)–O(5) bonds (1.9211(18) and 1.9622(19) Å, respectively (Table 2)). According to the literature data [3, 4, 18], the Co(II)–O bond length is ~2.1 Å, while the Co(III)–O bond length is ~1.94 Å, which agrees with our data.

Structure **I** is stabilized by several types of hydrogen bonds (HBs) (Table 3). The strongest HB (H(10)···O(1)^i, 1.87 Å) links the coordinated acetic acid molecule with the phenolate O atom of the ligand of an adjacent complex. Through the second O atom,

Table 3. Geometrical parameters of the hydrogen bonds in structure **I***

Hydrogen bond, Å	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(10)–H(10)···O(1)$^{\#1}$	0.82	1.87	2.629(3)	153.2
O(7)–H(71)···O(9)	0.827(18)	1.927(18)	2.751(3)	175(4)
O(7)–H(72)···O(5)$^{\#2}$	0.810(18)	1.99(2)	2.727(3)	151(4)
O(8)–H(81)···O(11)$^{\#3}$	0.830(18)	1.902(18)	2.730(3)	175(4)
O(8)–H(82)···O(3)$^{\#3}$	0.823(18)	2.13(3)	2.874(3)	151(5)
O(9)–H(91)···O(3)$^{\#4}$	0.843(18)	1.957(18)	2.797(3)	174(4)
O(9)–H(92)···O(6)$^{\#3}$	0.809(18)	2.23(2)	3.008(3)	161(4)

* The symmetry operation codes are $^{\#1}$ x, $1 - y$, $z - 1/2$; $^{\#2}$ $1 - x$, y, $-z + 3/2$; $^{\#3}$ $1 - x$, $1 - y$, $1 - z$; $^{\#4}$ $-x$, $2 - y$, $1 - z$.

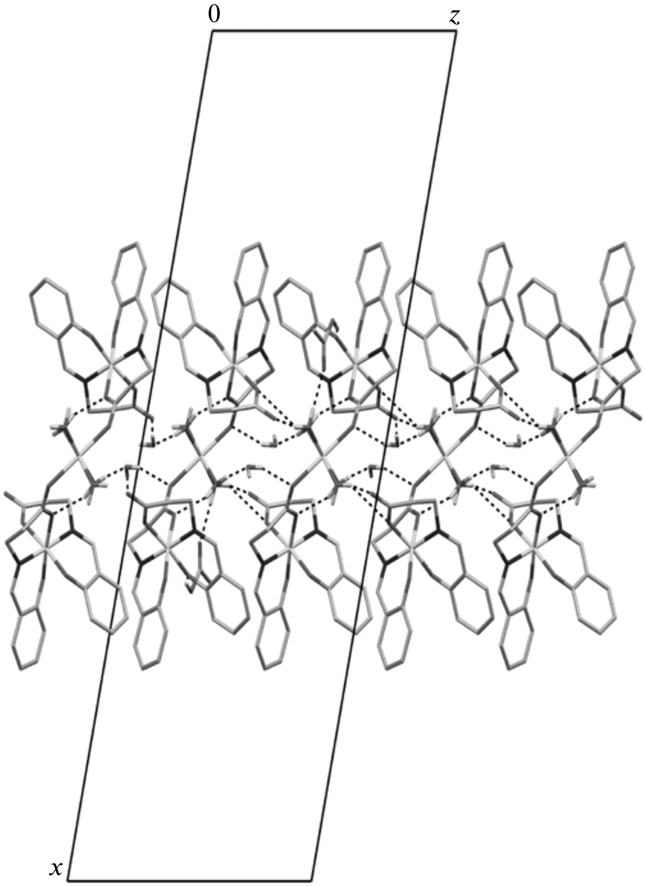


Fig. 2. Packing of the structural units in the crystal of complex **I**.

the coordinated acetic acid molecule is hydrogen-bonded to the water molecule coordinated by the central Co(II) ion (H(81)···0(11)^{iii} 1.90 Å) of an adjacent complex molecule (Fig. 2). The intramolecular HB O(7)–H(72)–O(5)^{ii} links the coordinated water molecule with the carboxylate O atom of the β-alaninate fragment coordinated by the terminal Co(III) ion (H···O 1.99 Å). The same coordinated water molecule is hydrogen-bonded (O(8)–H(82)···O(3)^{iii}) to the uncoordinated carboxylate O atom of the β-alaninate fragment of an adjacent trinuclear complex molecule (H···O 2.13 Å). The coordinated and outer-sphere water molecules are linked by the sufficiently strong HB O(7)–H(71)···O(9) (H···O 1.93 Å).

Two HBs link the uncoordinated water molecule with the carboxylate O atoms of the β-alaninate fragments of two adjacent trinuclear complex molecules: O(9)–H(91)···0(3)^{iv} (H···O 1.96 Å) and O(9)–H(92)···O(6)^{iii} (2.23 Å).

It is thus safe to say that Schiff bases derived from β-alanine and 2-hydroxyarenecarbaldehydes form heterovalent complexes in which the terminal Co(III) ions are linked to the central Co(II) ion (the cation $[Co(H_2O)_4]^{2+}$) by carboxylate bridges. In the case of α-amino acids, the central Co(II) ion is hydrogen-bonded to the terminal Co(III) ions [3].

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