ANALYTICAL SCIENCES 2008, VOL. 24 x269

Crystal Structure of Tetrakis(alaninato)di(μ)aquadicobalt(II) monohydrate

Onur Şahin,*† Orhan Büyükgüngör,* Dursun Ali Köse, and Hacali Necefoğlu*****

**Ondokuz Mayis University, Faculty of Arts and Sciences, Department of Physics, TR-55139, Kurupelit, Samsun, Turkey*
***Hacettepe University, Department of Chemistry, TR-06532, Ankara, Turkey*
****Kafkas University, Department of Chemistry, TR-36100, Kars, Turkey*

The title compound, tetrakis(alaninato)di(μ)aquadicobalt(II)monohydrate, is a three-dimensional hydrogen-bonded supramolecular complex, which crystallizes in the monoclinic space group $P2_1/c$ with unit-cell parameters a = 13.7266(7), b = 4.9866(2), c = 19.4759(10)Å and Z = 2. The Co(II) ion is in an octahedral coordination environment comprising two amino N atoms, two carboxylate O atoms and two O atoms from water molecules. The molecules are linked principally by N–H···O hydrogen bonds involving the amino NH_2 groups and carboxylate O atoms, forming $R_2^2(8)$ and $R_2^2(12)$ rings that link to give a one-dimensional network of molecules. The N–H···O hydrogen bonding is supported by three different O–H···O hydrogen bonds from the water O atoms to either a carboxylate O atom or water O atoms in neighbouring molecules. The combination of the intermolecular N–H···O and O–H···O hydrogen bonds produce $R_2^2(4)$, $R_2^2(8)$, $R_2^2(12)$ and $R_6^6(32)$ rings, which lead to three-dimensional polymeric chains.

(Received February 28, 2008; Accepted September 22, 2008; Published on web November 25, 2008)

An investigation of coordination polymers has attracted increasing interest over the past decade because of the intriguing structural motifs of these compounds and their potential applications in catalysis, host-guest chemistry and magnetism. The self-assembly of coordination-based entities is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites, and of metal ions reading out the structural information through an algorithm defined by their coordination geometry. Water, carboxylate and amine as Co(II) coordination groups are selected as competitive partners in coordination or hydrogen-bonding events. Some interesting coordination polymers assembled with alanine have been reported, showing various structural motifs, including two-dimensional layers.[1,2] We report here on the structure of tetrakis(alaninato)di(μ)aquadicobalt(II) monohydrate, in which hydrogen-bond interactions lead to a three-dimensional supramolecular network.

Firstly, alanine sodium salts were prepared according to the following equation:

$$2\text{Alanine} + 2\text{NaHCO}_3 \longrightarrow 2\text{Na(alanine)} + 2\text{CO}_2 + 2\text{H}_2\text{O}$$

After removing of CO_2 gas, a $CoSO_4{\cdot}6H_2O$ salt solution was added to the main solution and stirred for two hours. After three weeks, the obtained product was filtered off and dried in air. *Analysis* calcd. for $C_{12}H_{30}Co_2N_4O_{11}$: C 31.37, H 6.54, N 12.20%; found: C 31.88, H 6.83, N 12.31%.

Table 1 summarizes the crystal and experimental data. The structure was solved by direct methods with SHELXS-97,[3] and

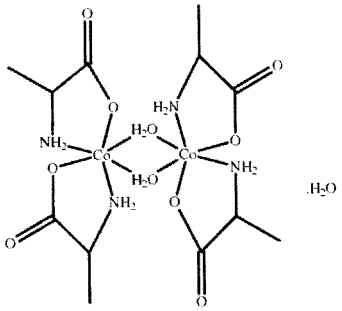

Fig. 1 Schematic diagram of the title compound.

Table 1 Crystal and experimental data

Formula: $C_{12}H_{32}Co_2N_4O_{12}$	
Formula weight: 534.28	
Crystal system: monoclinic	
Temperature (K): 296	
Space group: $P2_1/c$	Z = 2
a = 13.7266(7)Å	
b = 4.9866(2)Å	β = 131.125(3)°
c = 19.4759(10)Å	
V = 1004.20(9)Å^3	
D_c = 1.767 g cm^{-1}	
No. of reflections used = 8399	
θ_{max} = 26.0° Mo K_α	
R = 0.038	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.55 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.31 eÅ^{-3}	
Measurement: STOE IPDS II	
Program system: STOE X-RED	
Structure determination: direct methods	
Refinement: full matrix	
CCDC number: CCDC 670569	

† To whom correspondence should be addressed.
E-mail: onurs@omu.edu.tr

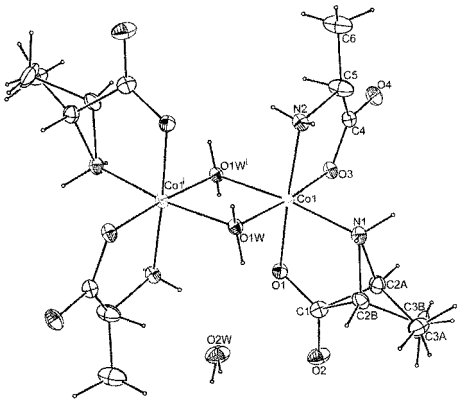

Fig. 2 Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at 40% probability. Symmetry transformation used to generate equivalent atoms (i) $-x$, $-y+1$, $-z+1$.

Table 2 Selected geometric parameters (Å)

Bond lengths (Å)			
Co1–O1	1.902 (2)	Co1–N1	1.937 (3)
Co1–O3	1.895 (2)	Co1–N2	1.921 (3)
Co1–O1W	1.899 (2)	Co1–O1W^{i}	1.913 (2)
Bond angles (°)			
O1W-Co1–O1W^{i}	82.96 (10)	O1-Co1–O3	90.60 (10)
N1–Co1–N2	93.40 (14)	N1–Co1–O3	92.38 (11)

Symmetry code: (i) $-x$, $-y+1$, $-z+1$.

refined by full-matrix least-squares procedures on F^2, using the program SHELXL-97.[3] All non-hydrogen atoms were refined anisotropically. Atoms C2 and C3 were disordered over two sites, with refined occupancies of 0.5 and 0.5. Water hydrogen atoms were located in difference maps and refined subject to a DFIX restraint. The hydrogen atoms of the amino groups were located in a difference map and refined freely. All other hydrogen atom positions were refined using a riding model.

The molecular structure (Fig. 1) and the atom-numbering scheme are shown in Fig. 2. Table 2 shows selected bond lengths and angles. Compound (I) crystallizes in the space group $P2_1/c$ with $Z' = 1/2$. The coordination motif of the Co(II) ion is a distorted octahedron in which two amino N atoms [N1 and N2], two carboxylate O atoms [O1 and O3] and two water O atoms [O1W and O1W^{i} (i: $-x$, $-y+1$, $-z+1$)] occupy the vertices. Thus, one Co(II) ion is bound to two alanine ligands. One of these ligands is joined to the Co(II) atom *via* the amino N atom and one of the O atoms of the carboxylate group, thus generating five-membered chelate rings: (-C1–O1–Co1–N1–C2-) and (-C4–O3–Co1–N2–C5-). One of the O atoms of a water molecule acts as a bridge to connect two Co(II) atoms in a μ_2 mode, thus forming a rhomboidal Co_2O_2 ring. The Co···Co^{i} distance is 2.8555(7)Å, and the dihedral angle between the rhomboid ring and the five-membered chelate rings are 87.56(3)° and 85.59(2)°. The Co–O bond distances [Co–O1 = 1.902(2)Å, Co–O3 = 1.895(2)Å, Co–O1W = 1.899(2)Å, and Co–O1W^{i} = 1.913(2)Å] and the Co–N bond distances [Co–N1 = 1.937(3)Å and Co–N2 = 1.921(3)Å] have also been observed in other cobalt complexes. The geometry about the carboxylate carbon atoms in this structure indicates that the delocalized electron density

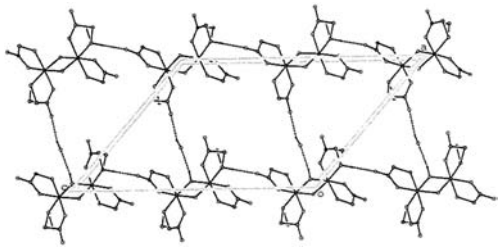

Fig. 3 Stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet built from $R_6^6(32)$ rings. H atoms not involved in these interactions have been omitted for clarity.

representation is more appropriate; that is, the four C–O bonds are almost equal in length. The C–O distances are similar to those found in a related structure.[4]

Molecules are linked by intermolecular hydrogen bonding, and we employ graph set notation[5] to describe the patterns of hydrogen bonding. Lattice water molecules stabilize the structure, also with hydrogen bonds, by playing the roles of both acceptors from ligand water molecules and donors to the exocyclic oxygen atoms. Water atom O1W in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H6, respectively, to atom O1W in the molecule at ($-x$, $-y+2$, $-z+1$), thus forming a C(4)[$R_2^2(4)$] chain of rings running parallel to the [010] direction and a centrosymmetric $R_2^2(4)$ ring centred at (0, n, 1/2) (n = zero or integer). Amino atom N1 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H2, respectively, to atom O1 in the molecule at (x, $y+1$, z), thus forming a C(4) chain running parallel to the [010] direction. At the same time, amino atom N2 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H4, respectively, to atom O3 in the molecule at (x, $y+1$, z), thus forming a C(4) chain running parallel to the [010] direction. The combination of the C(4) chains along [010] generates a chain of edge-fused $R_2^2(8)$ and $R_2^2(12)$ rings.

Amino atom N1 in the reference molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H1, respectively, to atom O4 in the molecule at ($-x$, $y+1/2$, $-z+1/2$), thus forming a C(8) chain running parallel to the [001] direction. Similarly, water atom O1W in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H5, to O2W at (x, $1+y$, z), while O2W at (x, $1+y$, z) acts as a donor to O2 at ($1-x$, $1/2+y$, $3/2-z$). In this manner a $C_2^2(8)$ chain running parallel to the [101] direction is generated. The combination of the C(8) and $C_2^2(8)$ chains along [101] generates a chain of edge-fused $R_6^6(32)$ rings (Fig. 3). The combined effect of the linked $R_2^2(4)$, $R_2^2(8)$, $R_2^2(12)$ and $R_6^6(32)$ motifs is to generate a three-dimensional network of molecules.

References

1. O. Versiane, B. L. Rodrigues, J. M. Ramos, C. A. Tellez, and J. Felcman, *Spectrochim. Acta Part A*, **2006**, *65*, 1112.
2. H. M. Haendler, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, **1994**, *50*, 1419.
3. A. L. Spek, *J. Appl. Cryst.*, **2003**, *36*, 7.
4. O. Şahin, O. Büyükgüngör, D. A. Köse, E. F. Ozturkkan, and H. Necefoğlu, *Acta Cryst.*, **2007**, *C63*, m243.
5. J. Bernstein, R. E. Davis, L. Shimoni, and N.-L. Chang, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 1555.