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The Crystal and Molecular Structure of the Violet Form of Tris(β-alaninato)cobalt(III) Tetrahydrate

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The crystals of the title compound are monoclinic, space group $P2_1/n$, with four formula units in a unit cell with $a=5.666(2)$ Å, $b=12.868(1)$ Å, $c=22.215(3)$ Å, $\beta=90.66(3)°$ at 22 °C. The solution and refinement of the structure was based on 1577 unique non-zero reflections measured with a four-circle diffractometer. The full matrix least squares refinement terminated with $R=0.046$, $R_w=0.048$. The configuration of the tris(β-alaninato)cobalt complex is *meridional*. The average Co-ligator distance is 1.929 Å. No characteristic Co–O or Co–N distance is found. The bond lengths and angles of the β-alanine residue are normal. The conformations of the chelate rings are twist-boat; the sense of the twist of one ring is opposite to that of the other two. One molecule of water of crystallization connects four complex molecules by hydrogen bonds. The remaining three water molecules, which complete the tetrahydrate formula, are randomly distributed in channels around $x,0,0$ and $x,\frac{1}{2},\frac{1}{2}$.

The development of elaborate methods for calculating the minimum energy conformation of complexes of trivalent metals with bidentate ligands has created an interest in accurate structural data. Conformational analyses of tris(diamino) compounds of Co(III) have been undertaken by Niketić and Woldbye.[1] The results of the crystal structure analysis of tris(β-alaninato)cobalt(III) tetrahydrate, reported in this paper, provide data for the more complicated case of a bidentate ligand with different ligators.

EXPERIMENTAL

Needle-like, bluish-violet crystals of tris(β-alaninato)cobalt(III) tetrahydrate, henceforth called $Co(\beta\text{-ala})_3$ were prepared by S.R. Niketić, University of Beograd.[2] A single crystal, approximately $0.17\times0.12\times0.05$ mm^3, was picked directly from the mother liquor.

The unit cell dimensions, the space group extinctions as well as a unique set of reflection intensities were measured with a CAD4 four-circle diffractometer. Monochromatized (graphite) Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) was used. The crystal data and some technicalities of the collection and treatment of data are as follows:

$Co(C_3H_6NO_2)_3.4H_2O$, FW = 395.2
$a=5.666(2)$ Å, $b=12.868(1)$ Å, $c=22.215(3)$ Å,
$\beta=90.66(3)°$, $V=1619.6$ Å^3 at 22 °C.
D_m (flot.) = 1.62 g cm^{-3}, $D_x(Z=4)=1.621$ g cm^{-3}.
μ(Mo$K\alpha$) = 11.6 cm^{-1}.

Systematically absent reflections: $h0l$ for $h+l$ odd, $0k0$ for k odd. Space group $P2_1/n$. Coordinates of general positions $\pm(x,y,z)$ and $\pm(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$.

All unique reflections in the interval $4°<\theta<28°$ were $\omega/2\theta$ scanned. The width of the scan was $(1.2+0.35\tan\theta)°$. The width of the variable horizontal detector aperture was $(2.5+\tan\theta)$ mm. The intensity of a control reflection of medium intensity, remeasured at intervals of ~4000 s of exposure time, did not show significant variations.

The solution and refinement of the structure was based on 1577 unique reflections having $|F|<\sqrt{2}\sigma(F)$. The number of variables involved in the refinement was 280.

Computional details. The observed net intensities, I, were reduced to relative structure factors and assigned a standard deviation calculated from the counting statistics. The usual Lorentz and polariza-

tion corrections were applied, but no corrections were made for absorption, extinction or anomalous dispersion. All crystallographic calculations were made with the X-RAY program system,[3] which also generates atomic form factors from given constants.[4,5] Form factors for neutral atoms were used. The full matrix, least squares calculation minimizes $\Sigma w(\Delta F_o)^2$, $\Delta F = \| F_o | - | F_c \|$. During the final stages of refinement a weight function $1/w = 0.193 + 1.66(\sigma F)^1 + 0.0590|F| - 0.000220|F|^2 - 1.152 \sin\theta/\lambda$ was used. The coefficients of the function were determined by a least squares calculation[6] minimizing

$$S = 1 + \frac{\Sigma w(\Delta F)^2 \log (w(\Delta F)^2}{\log N}$$, where N is the number of reflections.

The residual $R = \Sigma|\Delta F|/\Sigma F_0$; the weighted residual

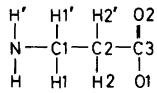
$$R_w = \left(\frac{\Sigma w(\Delta F)^2}{\Sigma w F_o{}^2}\right)^{\frac{1}{2}}.$$

SOLUTION AND REFINEMENT OF THE STRUCTURE

The sites of all non-hydrogen atoms of the complex molecule and 1 molecule of water of crystallization were determined by the heavy atom method. The refinement, which initially proceeded steadily, came to a halt at $R = 0.1$. A difference electron density map showed positive regions indicating the presence of disordered water molecules. A thermogravimetric analysis supported this interpretation; 3 water molecules out of 4 were loosely bond. When 6 oxygen half-atoms were placed in the intermolecular channels extending in the a-direction, the refinement process continued. All hydrogen atoms, except those of the disordered water molecules, showed up on another difference map. After two more cycles of least squares calculations the refinement was completed. The final residual indexes were $R = 0.046$ and $R_w = 0.048$. A final difference Fourier map did not show any

Table 1. Fractional atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms of the complex. Standard deviations in parentheses. The form of the temperature factor expression is $\exp[-2\pi^2 \Sigma_{ij} h_i h_j a_i^* a_j^* U_{ij}]$. All U-values have been multiplied by 10^3.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.2222(1)	0.06243(6)	0.034917(3)	22.3(3)	35.6(4)	27.5(4)	2.2(4)	−2.3(2)	0.4(4)
Ligand 1									
N	0.0128(8)	0.0126(4)	0.2857(2)	25(2)	40(3)	38(3)	2(2)	−4(2)	2(2)
O1	0.4755(6)	0.0942(3)	0.2964(2)	27(2)	51(3)	36(2)	−6(2)	−2(2)	5(2)
O2	0.6435(7)	0.1409(4)	0.2124(2)	38(2)	65(3)	50(3)	−10(2)	8(2)	10(2)
C1	0.115(1)	−0.0075(5)	0.2258(3)	37(3)	64(4)	35(3)	−6(3)	−4(3)	−8(3)
C2	0.246(1)	0.0857(6)	0.2042(3)	38(3)	87(3)	33(3)	−8(3)	−2(3)	7(3)
C3	0.4678(9)	0.1089(5)	0.2397(3)	29(3)	40(3)	47(4)	3(3)	2(3)	6(3)
Ligand 2									
N	0.3687(7)	−0.0712(4)	0.3599(2)	31(2)	45(3)	32(2)	6(2)	−1(2)	−1(2)
O1	−0.0299(6)	0.0332(3)	0.4031(2)	33(3)	47(2)	33(2)	10(2)	4(2)	−9(2)
O2	−0.2645(7)	−0.0573(4)	0.4610(2)	29(2)	79(3)	42(2)	4(2)	6(2)	9(2)
C1	0.226(1)	−0.1591(5)	0.3807(3)	43(4)	42(4)	47(4)	3(3)	3(3)	3(3)
C2	0.1067(11)	−0.1332(5)	0.4387(3)	45(4)	51(4)	43(4)	9(3)	11(3)	9(3)
C3	−0.0732(9)	−0.0484(5)	0.4344(2)	30(3)	53(4)	26(3)	−2(3)	−4(2)	−7(3)
Ligand 3									
N	0.4226(8)	0.1184(4)	0.4144(2)	37(3)	52(3)	34(3)	7(2)	−9(2)	−7(2)
O1	0.0771(7)	0.1947(3)	0.3325(2)	44(2)	35(2)	40(2)	5(2)	−7(2)	−1(2)
O2	−0.0546(3)	0.3522(3)	0.3487(2)	62(3)	41(3)	59(3)	12(2)	1(2)	3(2)
C1	0.448(1)	0.2307(6)	0.4169(3)	53(4)	57(5)	52(4)	−6(3)	−19(3)	−2(3)
C2	0.217(2)	0.2835(6)	0.4201(4)	102(6)	48(4)	56(5)	11(4)	−19(4)	−15(4)
C3	0.069(1)	0.2766(5)	0.3633(3)	39(3)	38(4)	41(4)	−1(3)	8(3)	9(3)



Scheme 1. Labelling scheme for the atoms of the β-alanine residue.

distinct features. The atomic coordinates and the temperature factors are listed in Tables 1 and 2. A list of observed and calculated structure factors may be obtained from this institute.

RESULTS AND DISCUSSION

The present crystal structure analysis confirms the result of previous, mainly spectroscopic, investigations.[2] The configuration of the complex is *meridional.*

The coordination polyhedron, shown schematically in Fig. 1, is a slightly deformed octahedron. The distances from the Co atom to the ligators O and N vary from 1.907(4) to 1.967(5) Å. No characteristic Co–N or Co–O distance is found. On the other hand, the Co–O distance is always the smaller in each particular chelate ring. The same holds for all the complexes quoted in Table 3 except for the A

Table 2. Fractional atomic coordinates and isotropic thermal parameters of hydrogen and oxygen (water) atoms. [a] Standard deviations in parentheses.

	x	*y*	*z*	*B*(Å^2)
Ligand 1				
H	−0.061(9)	−0.037(4)	0.293(2)	3.9
H′	−0.089(9)	0.059(4)	0.281(2)	3.9
H1	0.214(9)	−0.069(4)	0.230(2)	3.9
H1′	−0.020(9)	−0.030(4)	0.197(2)	3.9
H2	0.275(9)	0.075(4)	0.163(2)	3.9
H2′	0.135(9)	0.150(4)	0.210(2)	3.9
Ligand 2				
H	0.432(9)	−0.089(4)	0.327(2)	3.9
H′	0.467(4)	−0.071(4)	0.386(3)	3.9
H1	0.110(9)	−0.176(4)	0.354(2)	3.9
H1′	0.328(9)	−0.219(4)	0.389(2)	3.9
H2	0.039(9)	−0.186(4)	0.451(3)	3.9
H2′	0.226(9)	−0.112(4)	0.467(2)	3.9
Ligand 3				
H	0.361(9)	0.102(4)	0.447(3)	3.9
H′	0.550(9)	0.093(4)	0.413(2)	3.9
H1	0.555(9)	0.253(4)	0.452(2)	3.9
H1′	0.522(9)	0.250(4)	0.381(2)	3.9
H2	0.138(9)	0.250(4)	0.453(2)	3.9
H2′	0.237(9)	0.349(4)	0.431(2)	3.9
Water				
O	0.8221(8)	0.3380(4)	0.2290(2)	4.1(1)
H	0.858(9)	0.354(4)	0.254(2)	3.9
H′	0.763(9)	0.289(4)	0.221(3)	3.9
W1	0.149(3)	0.097(2)	0.039(1)	13.3(7)
W2	0.266(3)	0.103(1)	0.0345(8)	10.0(6)
W3	0.681(4)	0.050(2)	0.0950(9)	13.4(7)
W4	0.775(3)	0.166(1)	0.0922(8)	12.2(7)
W5	0.593(4)	−0.004(2)	0.0585(9)	13.2(7)
W6	0.841(4)	−0.027(2)	0.074(1)	15.0

[a] W = oxygen half-atom.

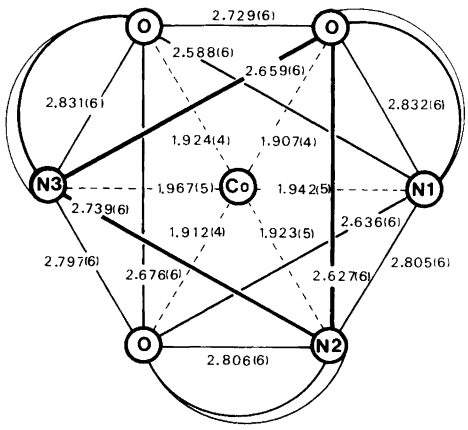


Fig. 1. Interatomic distances (Å), with standard deviations, in the coordination octahedron.

molecule in $Cu(\beta\text{-ala})_2.4H_2O$. The reversal in the A molecule is due to the repulsive force of the carbonyl O atom of the adjacent B molecules occupying the *trans* positions of the A molecule.

Bond lengths and angles involving only non-hydrogen atoms of the three β-alanine residues are shown in Fig. 2. The average N–H and C–H bond lengths are 0.82(3) and 0.95(6) Å, respectively.

In Table 3 average values of the bonds are compared with results from the recent literature. The C3–O1 bond, as well as the N–C1 bond, in the cited complexes is the same as in the pure amino acid. The C3–O2 bond, as well as the bonds C1–C2 and C2–C3, is significantly shorter in the complexes, (except C2–C3 in $KCo(\beta\text{-ala})_2(NO_2)_2$). In addition to the complexes mentioned above only two other β-alaninato compounds have been reported,[11] *viz.* $Ni(\beta\text{-ala})_2.2H_2O$ and $Cu(\beta\text{-ala})_2$.-

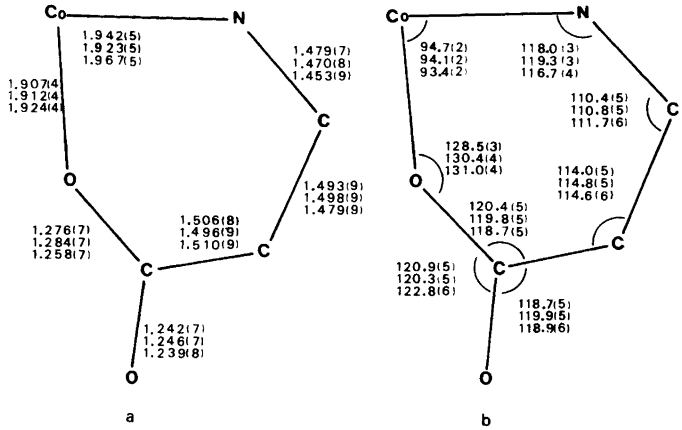


Fig. 2. a. Bond lengths (Å), and *b.* bond angles (°) in the chelate rings. Standard deviations in parentheses.

Table 3. Bond lengths in (Å) in β-alanine and some β-alaninato complexes. $\tilde{\beta}$ = β-alaninato. tn = 1,3-diaminopropane. Standard deviations in parentheses.

Bond	β-Alanine Ref. 7	$KCO\tilde{\beta}_2(NO_2)_2$ Ref. 8	$Co\tilde{\beta}tn(NO_2)_2$ Ref. 9	$Cu\tilde{\beta}_2.4H_2O$ Ref. 10 A	B	$Co\tilde{\beta}_3.4H_2O$ This paper		
Co–O1		1.913(8)	1.912(5)	2.015(3)	1.960(4)	1.907(4)	1.812(4)	1.924(5)
Co–N		1.956(9)	1.962(6)	1.967(4)	1.987(3)	1.942(5)	1.923(4)	1.967(5)
N–C1	1.478(10)	1.463(14)	1.469(9)	1.473(6)	1.483(7)	1.467(14)		
C3–O1	1.287(9)	1.279(13)	1.272(8)	1.276(6)	1.274(7)	1.273(13)		
C3–O2	1.292(9)	1.227(13)	1.238(8)	1.250(7)	1.247(5)	1.242(4)	Average[a]	
C1–C2	1.551(10)	1.521(15)	1.492(10)	1.511(8)	1.503(8)	1.490(10)		
C2–C3	1.553(10)	1.543(15)	1.513(10)	1.507(8)	1.507(8)	1.504(7)		

[a] Sample standard deviation = $[\sum_i (d_i - \bar{d})^2/(n-1)]^{\frac{1}{2}}$.

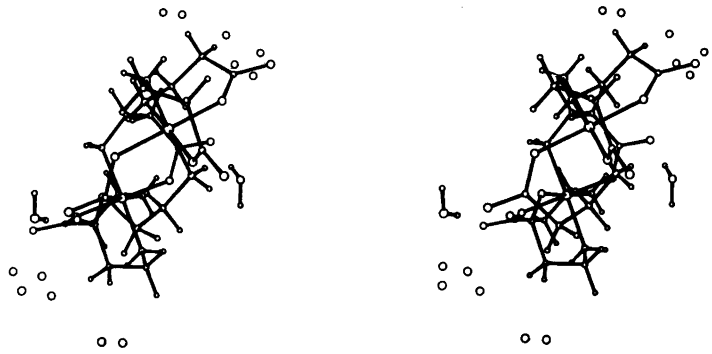


Fig. 3. Stereo pair showing two Co(β-ala)$_3$.4H_2O units related by a center. The disordered water molecules, W in Table 2, are shown as isolated open circles.

6H_2O. In general the structures of these compounds are in agreement with the results of this investigation. A detailed comparison, however, is prohibited by the low accuracy of the reported data.

The chelate rings of Co(β-ala)$_3$.4H_2O have the twist-boat conformation. The twisting is easily seen on the ORTEP[12] stereo drawing, Fig. 3. The sense of the twist of one ligand (No. 3 in Table 1) is opposite to that of the other two. Quantitatively, the twist may be expressed in terms of the torsion angles listed in Table 4. Inspection of all available data on torsion angles reveals rather large varia-

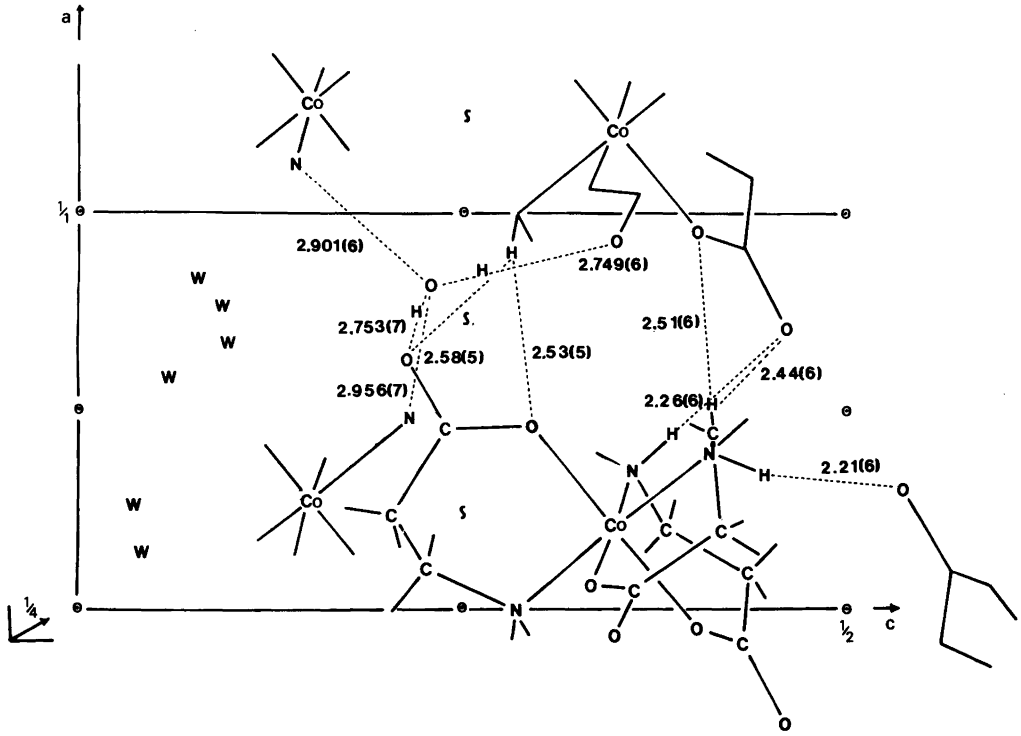


Fig. 4. Schematic projection of the structure on the *ac*-plane, showing the hydrogen bonds and the short *inter*-complex contacts (Å). Standard deviations in parentheses. The disordered water molecules, W in Table 2, have been calculated as oxygen half-atoms.

Table 4. Torsion angles with standard deviations. Signs as recommended by the IUPAC-IUB commission.[13]

Atoms	Angles (°) Ligand 1	Ligand 2	Ligand 3
N–Co–O1–C3	19.8(5)	0.7(5)	−16.7(5)
Co–O1–C3–C2	−9.6(8)	9.2(7)	8.4(8)
O1–C3–C2–C1	−36.8(8)	−42.2(8)	36.6(9)
C3–C2–C1–N	68.5(7)	65.4(7)	−69.2(8)
C2–C1–N–Co	−53.0(6)	−55.4(6)	55.7(6)
C1–N–Co–O1	12.8(4)	22.8(4)	−16.2(4)

tions. There is no fixed standard conformation of the β-alaninato chelate ring. A constant feature, though, is the coplanarity of the atoms C2, C3, O1, O2.

The packing of the complexes and the water molecules in the unit cell is illustrated in Fig. 4. The short *inter*-complex contacts are all of the type H···O. One molecule of water connects four complexes by hydrogen bonds. The remaining three water molecules, which complete the tetrahydrate formula, are randomly distributed in the channels around $x,0,0$ and $x,\frac{1}{2},\frac{1}{2}$.

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