The Crystal Structure of Potassium Dinitro–bis(R,S–alaninato)cobaltate(III) Monohydrate

Boris Kamenar, Branko Kaitner and Neven Strukan

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, P. O. Box 153, 41001 Zagreb Croatia

The crystal structure of the title complex has been determined from diffractometer X-ray intensity data by means of the heavy-atom method and refined by least-squares procedure to an R index of 0.039 (R_w = 0.055). The crystals are built up of K^+ cations, $\{Co[CH_3CH(NH_2)COO]_2(NO_2)_2\}^-$ anions and water molecules. The cobalt atom is octahedrally coordinated by two oxygen (1.899 and 1.916 Å) and two nitrogen atoms (1.945 and 1.946 Å) from two alaninato ligands, and two nitrogen atoms (1.909 and 1.913 Å) from two nitro groups in *cis* positions. The structure of the anion is disordered in the regions of the asymmetrical carbon atoms. Each potassium ion is surrounded by eight oxygen atoms from alaninato and nitro ligands as well as water molecules at the distances varying from 2.676 to 3.163 Å. The water molecules take part in the hydrogen bonding between nitro and alaninato carboxyl groups.

INTRODUCTION

Metal complexes with amino acids are interesting as possible models for studying the interactions between metal ions and proteins in biological systems.[1] Some of such complexes with cobalt as the central metal ion were prepared and thoroughly studied by Ćelap and coworkers.[2-6] In order to contribute to the structural elucidation of this class of complexes we have determined the crystal structure of the title compound.

EXPERIMENTAL

The complex was prepared as already described[2] and the crystals were given to us by Professor B. Kamberi and I. Ibrahimi, University of Priština.

Crystal data: from oscilation, Weissenberg and single crystal diffractometer, $C_6H_{14}CoKO_9N_4$, M = 384.23, monoclinic, space group $C2/c$ (No. 15), a = 16.670(2), b = 10.331(3), c = 17.250(4) Å, β = 109.17(1)°, V = 2806(1) Å^3, Z = 8, D_{obs} = 1.809 Mg m^{-3} (by flotation), D_{calc} = 1.819 Mg m^{-3}, $F(000)$ = 1568, $\mu(MoK\alpha)$ = 15.64 cm^{-1}, $\lambda(MoK\alpha)$ = 0.7107 Å.

Accurate cell parameters were obtained by least-squares treatment of 18 reflections collected on a Philips PW1100 automatic diffractometer using graphite-monochromated $MoK\alpha$ radiation. Intensity data ware collected from a crystal of dimensions $0.20 \times 0.30 \times 0.60$ mm^3 with the ω -2Θ scan technique. A total of 3455 reflections were measured in the interval $2.0 < \Theta < 30.0°$. The final set contained 3330 independent reflections of which 2601 with $I > 3\sigma(I_0)$ (obtained from counting statistics) were used for the structure analysis. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by heavy-atom method and the atomic parameters of non-hydrogen atoms refined anisotropically by full-matrix least-squares procedure. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 3.03/\sigma^2(F_0)$. The structure of the anion is disordered in the regions of the asymmetrical carbon atoms C(2) and C(5). Indeed, in the regions of C(2) and C(5) two well resolved peaks occur at the distances of 0.80(1) and 0.83(1) Å, respectively. In Figure 1 they are labelled as C(2a) and C(2b), and C(5a) and C(5b), respectively. Although the refinement of the occupancy factors for the two possible positions of these carbon atoms gave their values of 0.58 and 0.42, the refinement of both alternative positions was continued with the occupancy factors 0.5 bearing in mind that the complex was prepared from the racemic *R,S*-alanine. The amino as well as methyl hydrogen atom positions are, of course, also affected by this disorder. However, although all alternative H-atom positions were proved in the difference Fourier map their final positions were generated at the geometrical grounds and included in the structure factors calculation. The water hydrogen atoms were not positioned. The refinement converged at the reliability indices R and R_w of 0.039 and 0.055, respectively. The atomic scattering factors

TABLE I

Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for
$K\{Co[CH_3CH(NH_2)COO]_2(NO_2)_2\}\cdot H_2O$ *with estimated standard deviations*
(e.s.d.'s) in parentheses[*]

Atom	x/a	y/b	z/c	U_{eq}
K(1)	0	0.5	0	0.0418(2)
K(2)	0	0.4675(1)	0.25	0.0472(2)
Co	0.20090(2)	0.19652(4)	0.31797(2)	0.0277(1)
N(1)	0.2449(2)	0.2145(2)	0.2271(2)	0.034(1)
N(2)	0.1401(2)	0.1662(2)	0.3952(2)	0.035(1)
N(3)	0.3059(2)	0.1357(3)	0.3929(2)	0.045(1)
N(4)	0.2292(2)	0.3715(3)	0.3524(2)	0.045(1)
O(1)	0.0958(1)	0.2493(2)	0.2408(1)	0.032(1)
O(2)	0.0327(1)	0.3125(2)	0.1132(1)	0.041(1)
O(3)	0.1752(1)	0.0194(2)	0.2868(1)	0.032(1)
O(4)	0.1079(2)	−0.1524(2)	0.3094(2)	0.052(1)
O(5)	0.3167(2)	0.1188(3)	0.4655(2)	0,068(1)
O(6)	0.3632(2)	0.1035(4)	0.3655(2)	0.082(1)
O(7)	0.3006(3)	0.3977(3)	0.3976(3)	0.126(1)
O(8)	0.1811(2)	0.4589(3)	0.3274(3)	0.096(1)
O(9)	−0.0312(4)	0.6539(4)	0.1311(3)	0.141(3)
C(1)	0.0954(2)	0.2700(3)	0.1674(2)	0.032(1)
C(2a)[#]	0.1706(4)	0.2064(6)	0.1488)4)	0.026(1)
C(2b)	0.1832(4)	0.2812(9)	0.1581(4)	0.041(2)
C(3)	0.1883(3)	0.2585(5)	0.0765(2)	0.059(1)
C(4)	0.1276(2)	−0.0382(3)	0.3209(2)	0.038(1)
C(5a)[#]	0.0789(3)	0.0585(6)	0.3589(4)	0.024(1)
C(5b)	0.1182(6)	0.0292(7)	0.3977(6)	0.050(2)
C(6)	0.0438(3)	−0.0022(4)	0.4183(3)	0.068(1)

[*] Equivalent isotropic U is defined as $U_{eq} = \frac{1}{3} \sum_i \sum_j \alpha_i{}^* \alpha_j{}^* \mathbf{a}_i \mathbf{a}_j$.

[#] Atoms C(2) and C(5) are disordered.

as well as the corrections for anomalous scattering for cobalt and potassium were taken from International Tables for X-ray Crystallography.[7] Final values of atomic coordinates are given in Table I. A list of the observed and calculated structure factors can be obtained from the authors on request.

All calculations were carried out either on the UNIVAC 1100/42 computer or using IBM PC/AT compatible microcomputer (processor 80386/25MHz, coprocessor 80387), using SHELX76 computer programme.[8]

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure of the complex anion is shown in Figure 1, the potassium ions surroundings in Figure 2. The selected interatomic distances and angles are given in Table II.
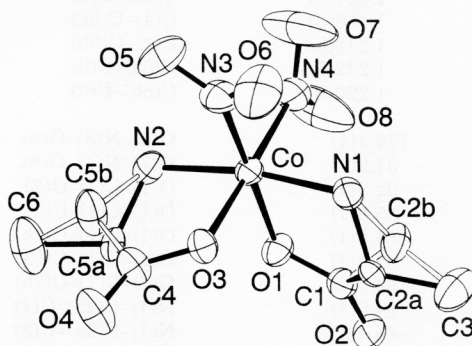

Figure 1. View of the complex anion [Co(ala)$_2$ (NO$_2$)$_2$]$^-$ showing the occupational disorder of the carbon atoms C(2) and C(5) and the atom numbering scheme. The alternative structures are represented either by heavy or by light lines. Ellipsoids are shown at the 50% probability level; H atoms are omitted for clarity.
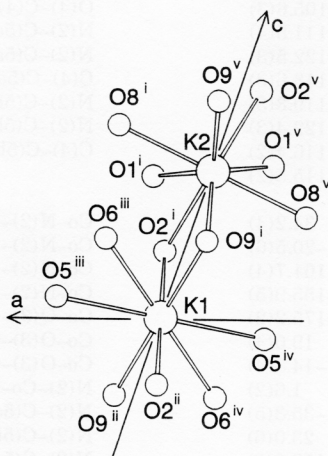

Figure 2. Potassium ions surroundings. Symetry code is given in Table II.

TABLE II

Interatomic distances (Å), angles and selected torsion angles (°) for
$K\{Co[CH_3CH(NH_2)COO]_2(NO_2)_2\} \cdot H_2O$

a) Complex anion

Co–N(1)	1.945(4)	N(4)–O(8)	1.190(4)
Co–N(2)	1.946(4)	O(1)–C(1)	1.282(4)
Co–N(3)	1.909(3)	O(2)–C(1)	1.232(3)
Co–N(4)	1.913(3)	O(3)–C(4)	1.279(4)
Co–O(1)	1.899(2)	O(4)–C(4)	1.223(4)
Co–O(3)	1.916(2)	C(1)–C(2a)	1.540(8)
N(1)–C(2a)*	1.506(6)	C(1)–C(2b)	1.528(8)
N(1)–C(2b)	1.465(7)	C(2a)–C(3)	1.474(9)
N(2)–C(5a)*	1.501(6)	C(2b)–C(3)	1.457(8)
N(2)–C(5b)	1.466(8)	C(4)–C(5a)	1.561(8)
N(3)–O(5)	1.218(5)	C(4)–C(5b)	1.549(11)
N(3)–((6)	1.242(5)	C(5a)–C(6)	1.476(9)
N(4)–O(7)	1.220(5)	C(5b)–C(6)	1.435(12)
N(1)–Co–N(2)	170.4(1)	O(5)–N(3)–O(6)	118.7(4)
N(1)–Co–N(3)	94.2(1)	O(7)–N(4)–O(8)	117.6(4)
N(1)–Co–N(4)	92.3(1)	O(1)–C(1)–O(2)	122.5(3)
N(1)–Co–O(1)	85.0(1)	O(1)–C(1)–C(2a)	113.2(3)
N(1)–Co–O(3)	88.5(1)	O(1)–C(1)–C(2b)	114.9(4)
N(2)–Co–N(3)	92.9(1)	O(2)–C(1)–C(2a)	122.7(4)
N(2)–Co–N(4)	94.0(1)	O(2)–C(1)–C(2b)	119.8(4)
N(2)–Co–O(1)	87.6(1)	N(1)–C(2a)–C(1)	106.0(4)
N(2)–Co–O(3)	85.4(1)	N(1)–C(2a)–C(3)	113.9(5)
N(3)–Co–N(4)	91.3(1)	C(1)–C(2a)–C(3)	115.0(5)
N(3)–Co–O(1)	177.3(1)	N(1)–C(2b)–C(1)	108.7(5)
N(3)–Co–O(3)	86.9(1)	N(1)–C(2b)–C(3)	117.5(6)
N(4)–Co–O(1)	91.3(1)	C(1)–C(2b)–C(3)	116.8(6)
N(4)–Co–O(3)	178.1(1)	O(3)–C(4)–O(4)	123.2(3)
O(1)–Co–O(3)	90.4(1)	O(3)–C(4)–C(5a)	112.5(3)
Co–N(1)–C(2a)*	107.5(3)	O(3)–C(4)–C(5b)	115.9(4)
Co–N(1)–C(2b)	110.5(3)	O(4)–C(4)–C(5a)	122.4(4)
Co–N(2)–C(5a)*	105.6(3)	O(4)–C(4)–C(5b)	118.4(4)
Co–N(2)–C(5b)	111.5(4)	N(2)–C(5a)–C(4)	105.9(4)
Co–N(3)–O(5)	122.5(3)	N(2)–C(5a)–C(6)	113.3(4)
Co–N(3)–O(6)	118.6(3)	C(4)–C(5a)–C(6)	113.5(4)
Co–N(4)–O(7)	119.8(3)	N(2)–C(5b)–C(4)	108.2(6)
Co–N(4)–O(8)	122.4(3)	N(2)–C(5b)–C(6)	118.0(7)
Co–O(1)–C(1)	116.4(2)	C(4)–C(5b)–C(6)	116.6(7)
Co–O(3)–C(4)	115.5(2)		
Co–N(1)–C(2a)–C(1)*	34.2(4)	Co–N(2)–C(5a)–C(4)*	39.2(4)
Co–N(1)–C(2b)–C(1)	−20.5(6)	Co–N(2)–C(5b)–C(4)	−16.1(7)
Co–N(1)–C(2a)–C(3)	161.7(4)	Co–N(2)–(C5a)–C(6)	164.2(4)
Co–N(1)–C(2b)–C(3)	−155.9(5)	Co–N(2)–C(5b)–C(6)	−151.3(5)
Co–O(1)–C(1)–O(2)	−175.2(2)	Co–O(3)–c(4)–O(4)	−177.5(3)
Co–O(1)–C(1)–C(2a)	19.0(4)	Co–O(3)–C(4)–C(5a)	17.7(4)
Co–O(1)–C(1)–C(2b)	−14.3(4)	Co–O(3)–C(4)–C(5b)	−15.9(4)
N(1)–Co–O(1)–C(1)	1.6(2)	N(2)–Co–O(3)–C(4)	5.0(2)
N(1)–C(2a)–C(1)–O(1)	−35.3(5)	N(2)–C(5a)–C(4)–O(3)	−38.3(5)
N(1)–C(2b)–C(1)–O(1)	23.0(6)	N(2)–C(5b)–C(4)–O(3)	21.1(7)
N(1)–C(2a)–C(1)–O(2)	159.0(3)	N(2)–C(5a)–C(4)–O(4)	156.7(4)
N(1)–C(2b)–C(1)–O(2)	−175.5(4)	N(2)–C(5b)–C(4)–O(4)	−176.3(4)

Table II continued

O(1)–Co–N(1)–C(2a)	−21.4(3)	O(3)–Co–N(2)–C(5a)	−26.0(3)
O(1)–Co–N(1)–C(2b)	11.6(4)	O(3)–Co–N(2)–C(5b)	7.5(4)
O(1)–C(1)–C(2a)–C(3)	−162.0(4)	O(3)–C(4)–C(5a)–C(6)	−163.3(4)
O(1)–C(1)–C(2b)–C(3)	158.8(5)	O(3)–C(4)–C(5b)–C(6)	157.0(5)
O(2)–C(1)–C(2a)–C(3)	32.2(7)	O(4)–C(4)–C(5a)–C(6)	31.8(6)
O(2)–C(1)–C(2b)–C(3)	−39.7(7)	O(4)–C(4)–C(5b)–C(6)	−40.4(8)

b) Potassium coordination

K(1)···O(2)[i,ii]	2.676(2)	K(2)···O(1)[i,v]	2.797(2)
K(1)···O(5)[iii,iv]	3.163(3)	K(2)···O(2)[i,v]	3.045(2)
K(1)···O(6)[iii,iv]	2.873(3)	K(2)···O(8)[i,v]	2.874(3)
K(1)···O(9)[i,ii]	2.947(6)	K(2)···O(9)[i,v]	2.736(5)

Symmetry code:
i = x,y,z
ii = −x,1−y,−z   iv = −1/2+x,1/2−y,−1/2+z
iii = 1/2−x,1/2+y,1/2−z   v = −x,y,1/2−z

* Atoms C(2) and C(5) are disordered.

The crystal structure is built up of potassium cations, $[Co(ala)_2(NO_2)_2]^-$ anions and water molecules. The cobalt atom is octahedrally coordinated by two oxygen and two nitrogen atoms from two alaninato ligands, and two nitrogen atoms from two nitro groups. The alaninato ions have a role of the bidentate ligands and the nitro groups are in *cis* positions. The coordination polyhedron around the cobalt atom is distorted with the angles at Co varying from 85.0 to 94.2°. The cobalt oxygen bond lengths are 1.899 and 1.916 Å. The cobalt-nitrogen bond lengths from the alaninato ligands of 1.945 and 1.496 Å are, as expected, significantly longer than those from the nitro groups amounting to 1.909 and 1.913 Å. Such values are close to those previously established in the similar cobalt complexes with amino acids.[4,5] Also, bond lengths and angles as well as the torsion angles in the five-membered chelate rings are within the expected values and may be compared with the values found not only in the structures of the analogous cobalt complexes[4,6] but also, for example, in the corresponding nickel[9] and copper[10,11] complexes. The nitro groups are planar with the O–N–O angles of 117.6 and 118.7°.

Both potassium ions are in the special positions of the space group $C2/c$: K(1) occupying centre of symmetry and K(2) two fold axis. Each potassium ion is eight-coordinated being surrounded by four pairs of the symmetrically related oxygen atoms. In such a way the potassium ion K(1) is surrounded by four nitro-oxygens [O(5)[iii],O(5)[iv],O(6)[iii],O(6)[iv]], two alaninato carboxyl-oxygens [0(2)[i],O(2)[ii]] and two oxygens from the water molecules [O(9)[i],O(9)[ii]], while the potassium ion K(2) is surrounded by two nitro-oxygens [O(8)[i],O(8)[v]], four alaninato carboxyl-oxygens [O(1)[i],O(1)[v],O(2)[i],O(2)[v]] and by two water-oxygen atoms [O(9)[i],O(9)[v]]. The potassium-oxygen distances range from 2.676 to 3.163 Å. These coordination polyhedra around K(1) and K(2) sharing the atoms O(2)[i] and O(9)[i] as their common edge thus forming a column extended along the c-axis direction.

The water molecule is hydrogen bonded to one oxygen atom [O(6)] of the nitro group at 2.830(8) Å and at the same time to the alaninato carboxyl-oxygen [O(4)] at 2.749(6) Å.

REFERENCES

1. H. C. Freeman, *Inorg. Biochem.* **1** (1973) 121.
2. M. B. Ćelap, D. J. Radanović, T. I. Nikolić, and T. J. Janjić, *Inorg. Chim. Acta* **2** (1968) 52.
3. R. G. Denning, M. B. Ćelap, and D. J. Radanović, *Inorg. Chim. Acta* **2** (1968) 58.
4. W. H. Watson, D. R. Johnson, M. B. Ćelap, and B. Kamberi, *Inorg. Chim. Acta* **6** (1972) 591.
5. B. Prelesnik, M. B. Ćelap, and R. Herak, *Inorg. Chim. Acta* **7** (1973) 569.
6. R. Herak, B. Prelesnik, Lj. Manojlović-Muir, and K. W. Muir, *Acta Cryst.* **B30** (1974) 229.
7. *International Tables for X-Ray Crystallography*, Vol. 3. p. 149 and Vol. 4. p. 99, Kynoch Press, Birmingham, 1974.
8. G. M. Sheldrick, SHELX76, *Program for Crystal Structure Determination,* Univ. of Cambridge, 1976, England.
9. S. G. Teoh, B. T. Chan, H. K. Fun, and M. E. Kamwaya, *Z. Kristallogr.* **181** (1987) 199.
10. B. Kaitner, B. Kamenar, N. Paulić, N. Raos, and Vl. Simeon, *J. Coord. Chem.* **15** (1987) 373.
11. B. Kamenar, M. Penavić, A. Škorić, N. Paulić, N. Raos, and Vl. Simeon, *J. Coord. Chem.* **17** (1988) 85.

SAŽETAK

Kristalna struktura kalij dinitro–*bis*(R,S–alaninato)kobalta(III) monohidrata

Boris Kamenar, Branko Kaitner i Neven Strukan

Kristalna struktura kompleksa navedenog u naslovu određena je iz intenziteta refleksa prikupljenih na automatskom difraktometru, riješena postupkom teškog atoma i utočnjena metodom najmanjih kvadrata do faktora pouzdanosti R = 0.039 (R_w = 0.055). Kristali su izgrađeni od kationa K^+, aniona $\{Co[CH_3CH(NH_2)COO]_2(NO_2)_2\}^-$ i molekule vode. Atom kobalta oktaedarski je koordiniran s dva atoma kisika (1.899 i 1.916 Å) i dva atoma dušika (1.945 i 1.946 Å) iz dva alaninato-liganda, te dva atoma dušika (1.909 i 1.913 Å) iz dvije nitro-skupine u *cis*-položaju. Struktura aniona neuređena je u područjima asimetričnih ugljikovih atoma. Svaki je ion kalija okružen s osam atoma kisika iz alaninato- i nitro-liganda i iz molekula vode na udaljenostima od 2.676 do 3.163 Å. Molekule vode u strukturi sudjeluju u vodikovim vezama između nitro- i karboksilnih skupina.