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The Crystal Structure of *trans, trans, trans*-Potassium Dinitrobis(β-Alaninato)Cobaltate(III)

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The crystal structure of trans, trans, trans – *potassium dinitrobis(β–alaninato)cobaltate(III),* $K[Co(NH_2CH_2CH_2COO)_2(NO_2)_2]$ *was determined by X-ray diffraction technique. The crystals belong to the monoclinic system,* $a = 12.38(1)$, $b = 13.12(1)$, $c = 8.27(1)$, $\beta = 115.2(2)$, $z = 4$, $D_m = 2.03(2) gcm^{-3}$, $D_x = 2.00 gcm^{-3}$, *space group C2/c. A total of 1008 independent nonzero reflexions was collected by multiple film Weissenberg technique and the model was refined by least squares method to a conventional R–factor of 11.8%. The coordination around the* Co^{III} *atom is octahedral, with two nitro groups in a* trans *arrangement. The β–alaninato ligands form six–membered chelate rings through the use of the amino nitrogen and the carboxylate oxygen atoms, both in the* trans *position too.*

Introduction

Studying the reactions between potassium hexanitrocobaltate(III) and aminoacids, Ćelap and coworkers[1] have obtained a new class of complex compounds: dinitrobis(aminoacidato)cobaltate(III) salts.

These compounds could exist as five geometrical isomers. Four of them have already been isolated, i.e. two *cis*–NO_2 isomers and two *trans* – isomers. By analyzing electronic and NMR spectra the configurations of these isomers were postulated[2]. To prove the configuration of the *trans, trans, trans* isomer, the X-ray diffraction study of the corresponding potassium salt was undertaken.

Experimental Section

The purple red, optically inactive, small prismatic crystals were supplied by M. B. Ćelap. The crystal data were determined from zero layer Weissenberg photographs (h0ℓ) and (hk0), taken at 18 °C with CuKα radiation ($\lambda = 1.5418$ Å). Values for the cell dimensions and their standard deviations were derived from a least squares treatment of a number of high order reflexions. The density was measured by flotation in $ZnCl_2$ solution.

The systematic absences, from Weissenberg hk0, hkℓ and h0ℓ photographs are:

hkℓ: h+k = 2n+1
h0ℓ: ℓ = 2n+1; (h = 2n+1)
0k0: (k = 2n=1)

The space groups Cc and C2/c are consistent with such absences. On the basis of the electronic and NMR spectra it was postulated that the configuration of the investigated compound is *trans, rans, trans.*[2] This assumption requires that the molecule possesses the centre of symmetry and indicated the choice of C2/c as a space group. The crystal habit also clearly revealed the holoedry of the crystal class.

The crystal data are as follows: $K[Co(NH_2CH_2CH_2COO)_2(NO_2)_2]$, $C_6CoH_{12}KN_4O_8$, M = 366.24. Monoclinic, space group C2/c, a = 12.38(1)*, b = 13.12(1), c = 8.27(1), β = 115.2(2)*, z = 4, D_m = 2.03(2) gcm^{-3}, D_x = 2.00 gcm^{-3}, μMoKα = 18.95 cm^{-1}.

Acrystal whose dimensions varied between 0.25 and 0.37 mm was used for data collection. As the crystals were very small and mechanically sensitive, they could not be ground into spherical or cylindrical forms. Equi–inclination Weissenberg photographs h0ℓ → h8ℓ and hk0 → hk2 were obtained using the multiple film technique with MoKα radiation and Nonius camera. The intensities were measured visually with standard calibrated scale and corrected for Lorentz and polarization factors. The correction for absorption was not applied, introducing in the observed intensity a maximum error ±11.5%. The interlayer scaling was made using the average of F_o's ratios of hk0 data which appear in both settings as a scaling factor for each level. A total of 1008 independent nonzero reflexions was collected.

From threedimensional Patterson synthesis the positions of cobalt and potassium atoms were determined. With electron density and difference synthesis, followed by a series of least squares refinement cycles, all nonhydrogen atoms were located. The function $\Sigma w(F_o - F_c)^2$ was minimized. The weights were assumed as 1 for all reflexions. With anisotropic

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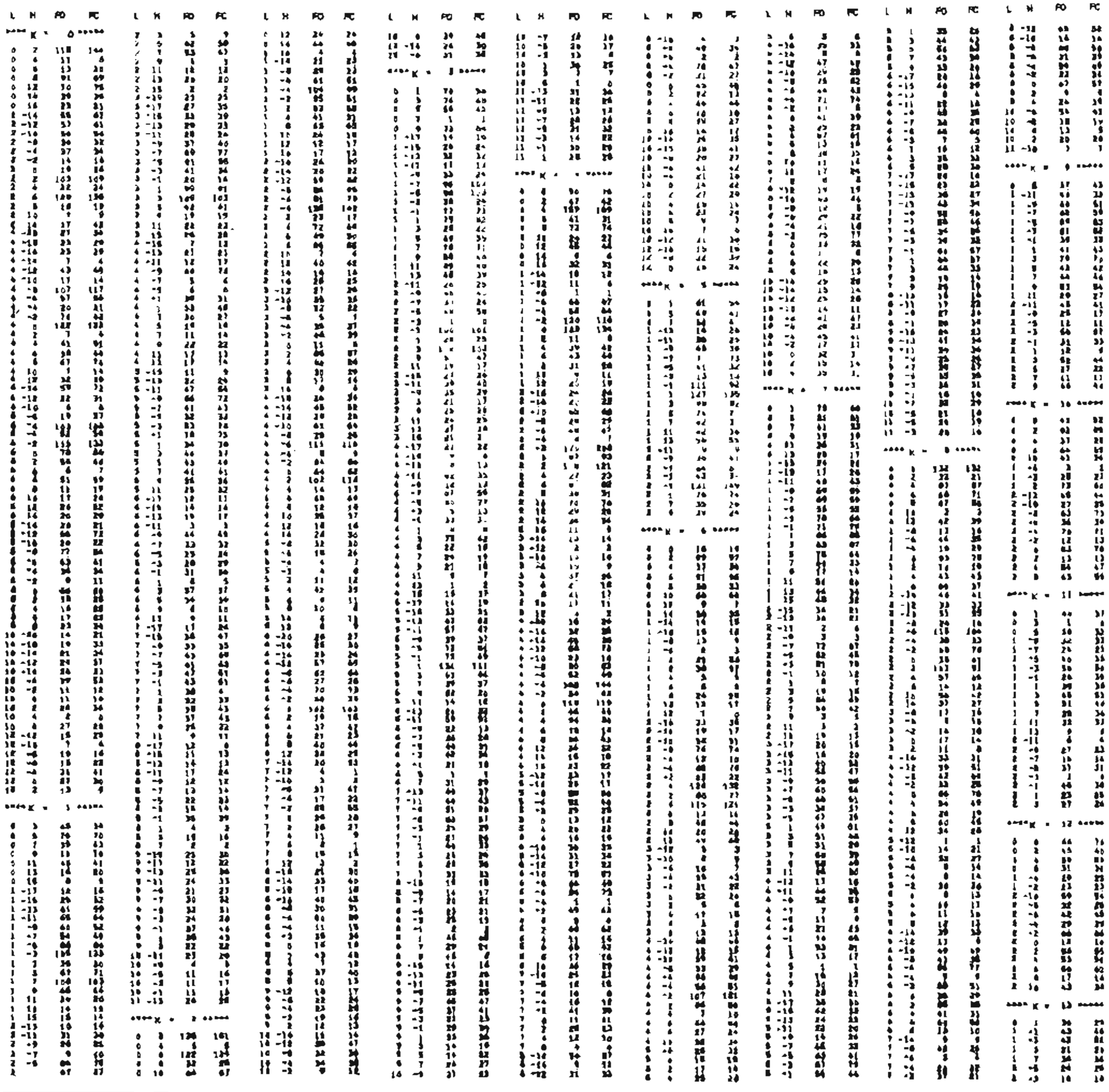
(1) M. B. Ćelap, D. J. Radanović, T. I. Nikolić, and T. I. Janjić. *Inorg. Chim. Acta, 2,* 52 (1968).

(2) R. G. Danning, M. B. Ćelap, and D. J. Radanović, *Inorg. Chim. Acta,* 2, 58 (1968). M. B. Ćelap, R. G. Denning, D. J. Radanović, and T. I. Janjić, *Inorg. Chim. Acta,* 5, 9 (1971). M. B. Ćelap, M. J. Malinar, S. M. Nešić, T. I. Janjić, and P. N. Radivojša. Proceedings of the III Conference on Coordination Chemistry, Smolenice-Bratislava (ČSSR), p. 59 (1971).

* Here, and elsewhere in this paper, e.s.d's in the last significant figure are in the parentheses.

Table I.



temperature factors for all a atoms the refinement converged to the conventional R factor, $\Sigma|F_o-F_c|/\Sigma|F_o|$, of 11.8% and the weighted R factor, $\sqrt{\Sigma w(F_o-F_c)^2}/\sqrt{\Sigma w(F_o)^2}$, of 12.0%. The refinement with anisotropic thermal parameters gave no improvement in the R-factor. In the final difference Fourier synthesis the five major peaks are between 1.88 and 1.15 e/A^3. The first value represents 2.2, 4.4, 15.1, 18.0 and 18.3% of the height of the peaks of Co, K, O, N and C atoms in the final Fourier map. Atomic scattering factors were taken from the International Tables for X-ray Cristallography.[3] Table I lists the observed and calculated structure amplitudes based on the final atomic parameters given in Table II.

Table II. Atomic and thermal parameters.

	x	y	z	B
Co	0.2500(0)	0.2500(0)	0.5000(0)	0.84(3)
K	0.0000(0)	0.0000(0)	0.2500(0)	1.88(6)
O(1)	0.1544(6)	0.1714(7)	0.2936(10)	1.46(12)
O(2)	0.3230(9)	0.4202(9)	0.3675(14)	3.06(20)
O(3)	0.0953(7)	0.1383(7)	0.0102(11)	1.82(14)
O(4)	0.1326(10)	0.3939(10)	0.2354(14)	3.36(21)
N(1)	0.4015(7)	0.2160(8)	0.4924(12)	1.31(14)
N(2)	0.2323(9)	0.3684(9)	0.3501(13)	1.74(16)
C(1)	0.1760(9)	0.1579(11)	0.1571(17)	1.44(17)
C(2)	0.3060(10)	0.1561(11)	0.1783(15)	1.58(18)
C(3)	0.3953(10)	0.1338(11)	0.3692(15)	1.80(19)

(3) "International Table for X-ray Crystallography" Vol. III, Kynoch Press, Birmingham, p. 202 (1962).

Table III. Intramolecular and intermolecular distances (Å) and angles (deg.). Standard deviations do not include cell parameters errors. Superscripts refer to the following transformation of atomic coordinates:

No symbol	x	y	z
i	½+x	½+y	z
ii	−x	−y	−z
iii	½−x	½−y	1−z
iv	−x,	y,	½−z
v	x	−y,	½+z
vi	½−x,	½+y,	½−z
vii	½+2,	½−y,	½+z

Co-O(1)	1.913(8)	N(2)-O(4)	1.241(14)
Co-N(1)	1.956(9)	N(2)-O(2)	1.268(14)
Co-N(2)	1.941(11)	K^i-$O(1)^{i,vi}$	2.873(9)
O(1)-C(1)	1.279(13)	K^i-$O(2)^{o,iv}$	2.943(11)
C(1)-C(2)	1.543(15)	K^i-$O(3)^{iii,vii}$	2.675(9)
C(2)-C(3)	1.521(15)	K^i-$O(2)^{ii,v}$	3.162(10)
C(1)-O(3)	1.227(13)	K^i-$O(3)^{i,vi}$	3.258(9)
N(1)-Co-N(2)	90.6(4)	C(2)-C(3)-N(1)	112.4(1.1)
O(1)-Co-N(2)	90.2(4)	C(3)-N(1)-Co	115.1(7)
O(1)-Co-N(1)	94.9(4)	O(1)-C(1)-O(3)	121.0(1.0)
Co-O(1)-C(1)	125.4(8)	O(3)-C(1)-C(2)	118.6(1.0)
O(1)-C(2)-C(2)	120.2(9)	O(2)-N(2)-O(4)	119.2(1.1)
C(1)-C(2)-C(3)	112.5(9)	O(2)-N(2)-Co	120.2(8)

In the analysis the programs VINČA 1 (local data reduction program), FORDAP, NUCLS, SADIAN and ORFFE (from Ibers's system of crystallographic programs) at the CDC-3600 computer were used.

Results and Discussion

The projection of the crystal structure of *trans, trans, trans*—potassium dinitrobis(β—alaninato)cobaltate(III) down the c-axis is shown in Fig. 1. The interatomic distances and angles are given in Table III.

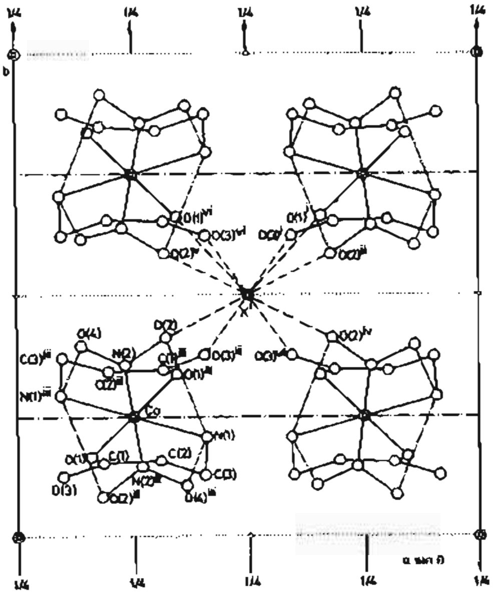


Figure 1. The structure projected down the c-axis.

The structure is built up of $[Co(\beta\,ala)_2(NO_2)_2]^-$ and K^+ ions. A perspective drawing of the complex anion is presented in Fig.2. A cobalt atom is situated in the centre of symmetry and surrounded octahedrally by two oxygen atoms from β—alanine ligands and four nitrogen atoms, two of them being from β—alanine ligands and the other two from the nitro groups. The nitro groups are in the *trans*—position. The coordination polyhedar around cobalt is nearly regular octahedron. The shortest distance in octahedron is cobalt-oxygen (1.913 Å), the longest one is cobalt-nitrogen from β—alanine ligand (1.956 Å). The most pronounced displacement from the right angle (94.6°)is also in β—alanine ring. The six-membered β—alanine ring has a skew boat conformation. The same conformation is found in the structure of complexes with six—membered β—alanine rings so far investigated, namely $Cu(NH_2CH_2CH_2COO)_2.6H_2O$[4] and $Ni(NH_2CH_2CH_2COO)_2 . 2H_2O$[5]. The bond lengths and angles in the ring are normal and may be

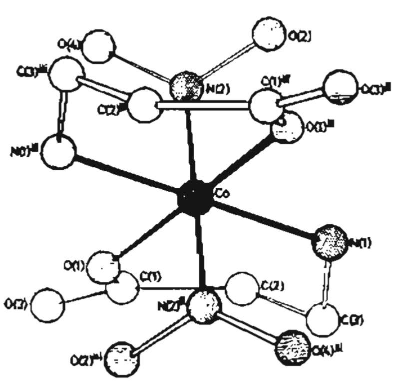


Figure 2. The configuration of dinitrobis(β-alaninato)cobaltate(III) ion.

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(4) R. F. Bryan, R. J. Poljak, and K. Tomita, *Acta Cryst.*, 14, 1125 (1961).

(5) Parimala Jose, L. M. Pant, and B. W. Biswas, *Acta Cryst.*, 17, 24 (1964).

compared with the corersponding ones found in the mentioned complexes.

The mean plane defined by C(2), C(1), O(1) and O(3) atom is given by the equation: $-0.0119\ x - 0.9799\ y + 0.1990\ z + 1.7867 = 0$. Distances of C(2), C(1), O(1)and O(3) atoms from this plane are 0.0081, – 0.0285, 0.0103 and 0.0101 Å, respectively. This indicates that C(2), C(1), O(1) and O(3) atoms are nearly coplanar, as in the structure of $Ni(NH_2CH_2CH_2COO)\ .\ 2H_2O$ (1.c.4). The angle between the plane passing through O(1)–C(1)–C(2) and the one containing C(1)–C(2)–C(3) is 20.3°; the angle between C(1)–C(2)–C(3) and C(2)–C(3)–N(1) planes is 66.9°. In $Ni(NH_2CH_2CH_2COO)_2\ .\ 2H_2O$ these angles are 30.3° and 73.7°, respectively.

The nitro group is planar, with the angles practically equal to 120°. N–O distances average to 1.25 Å. These values are comparable to those found in the nitro complexes.

The potassium ion is on the twofold axis. It is surrounded by five pairs of symmetry related oxygen atoms, three pairs carboxylate oxygen and two pairs oxygen atoms from the nitro groups. The six nearest neighbours are at the potassium–oxygen distances of 2.67, 2.87 and 2.94 Å. Two other pairs of oxygen atoms are away from the potassium ion at 3.16 and 3.26 Å and according to the data (1.c.3,p.258) it appears that they are also included in the coordination of the potassium ion.

Itis to be expected that the nitrogen atom from β–alanine ring is included in two N–H ... O hydrogen bonds. There are six oxygen atoms (O(4)^{iii}, O(4)^{vii}, O(3)^{vii}, O(2), O(1) and O(1)^{iii}) at the distances between 2.6 and 3.1 Å which may be with the N(1) atom hydrogen bonded. They form (in pairs) 15 possible "tetrahedra" together with Co and C(3) atoms around the nitrogen atom. The mean deviations of the angles from 109°28' in these sets vary from 16.2 to 40.6°. The former of these values respects to the Co, O(3), O(4)^{iii}, O(3)^{vii} set, giving the most probable hydrogen bonds N(1)–N(1) ..... O(4)^{iii} and N(1)–H(2) ..... O(3)^{vii}. Some other sets may be probable too. In every case, hydrogen bonds to O(1), O(1)^{iii}, O(2) and O(4)^{iii} would be intramolecular, and those to O(3)^{vii} and O(4)^{vii} would be intermolecular. It is possible that one (or both) of the hydrogen bonds might be bifurcated.

The results obtained in this work showed that the configuration of the investigated salt, proposed by M. B. Ćelap and coworkers[2], is correct, i.e. the potassium dinitrobis(β–alaninato)cobaltate(III) really represents *trans, trans, trans*, geometrical isomer.