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The Crystal and Molecular Structure of Racemic *cis*-Dinitrobis(1,3-diaminopropane)-cobalt(III) Chloride Monohydrate

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The crystals of racemic cis*-dinitrobis(1,3-diaminopropane)cobalt(III) chloride monohydrate are monoclinic:* a = *24.918(8),* b = *8.867(4),* c = *15.452(4)* Å, *β = 122.60(2)°, V = 2876 Å^3. Space group C2/c, Z = 8. The structure was solved by the heavy atom method on the basis of 1987 intensities, measured on the Nonius CAD-4 four-circle diffractometer. The full-matrix least-squares refinement of positional and anisotropic temperature factors gave $R = 0.027$, $R_w = 0.029$. The crystal structure consists of enantiomer pairs of the complex cations, chloride anions and molecules of water. The cobalt(III) ion is surrounded by two nitrogen atoms of nitro groups and four nitrogen atoms of 1,3-diaminopropane molecules in distorted octahedral arrangement. The nitro groups are in the* cis*-position. The two 1,3-diaminopropane ligands are bidentately bonded to the cobalt forming six membered chelate rings. Both rings have chair conformation in (C_1)-constellation.*

Introduction

Studying the effects of chelate rings and geometrical configuration on the position of absorption maxima in the electronic spectra, Ćelap and co-workers [1] prepared two isomers (*cis* and *trans*) of dinitrobis(1,3-diaminopropane)cobalt(III) ion, which were previously described by Kawaguchi and Kawaguchi [2]. The *trans*-isomer was identical with the *trans*-$[Co(tn)_2(NO_2)_2]^+$ (tn = 1,3-diaminopropane) ion of Kawaguchi and Kawaguchi. However, the *cis*-isomer appeared to be different from the product which was assigned as the *cis*-isomer by Kawaguchi and Kawaguchi. As described in ref. 1, the electronic absorption spectrum of Kawaguchi's *cis*-isomer is entirely different from the spectrum of Ćelap's isomer and admittedly very similar to the spectrum of the *trans*-isomer. Kawaguchi and Kawaguchi [2] used ir spectra in order to determine geometrical configuration of their isomers, while Ćelap and co-workers [1] proposed geometrical configuration by the resolution of the *cis*-isomer into enantiomers as well as by paper chromatography, electronic absorption and ir spectra. Furthermore, Kawaguchi and Kawaguchi [2] described the *cis*-isomer of nitronitritobis$(tn)_2$cobalt(III) complex, with the electronic absorption spectrum very similar to that of Ćelap's *cis*-dinitro isomer. To solve these ambiguities and to determine which of the products is really the *cis*-isomer, as well as to obtain new data about the conformation of the six-membered chelate rings, we have undertaken the X-ray diffraction analysis of the *cis*-isomer prepared by Ćelap and co-workers.

Experimental

Reddish-brown crystals of *cis*-$[Co(tn)_2(NO_2)_2]Cl \cdot H_2O$ were prepared and kindly supplied by M. B. Ćelap.

On the basis of rotation and Weissenberg photographs it was established that the crystals belong to the monoclinic system. The observed extinction h + k = 2n + 1 for hkl and l = 2n + 1 for h0l suggested the space groups C2/c or Cc. Unit cell constants which were determined from the least squares refinement of the setting angles of 21 strong reflections which had been centered on a Nonius CAD-4 diffractometer using MoK_α radiation (λ_1 = 0.70926, λ_2 = 0.71354), are *a* = 24.918(8), *b* = 8.867(4), *c* = 15.452(4) Å, and β = 122.60(2)°. The density calculated for eight formula unit weights per unit cell is 1.63 g cm^{-3} which is identical with the values of 1.63 g cm^{-3} measured by flotation in the mixture of carbon tetrachloride and bromoform.

For data collection a crystal with approximate dimensions 0.22 × 0.22 × 0.24 mm was used. The intensities were measured by the ω-scan technique and MoK_α radiation. The unique data set, having $2\theta \leqslant 50°$, was gathered; the intensities of 2640 reflections were recorded. The intensities of two standard reflections measured after every 50 reflections remained essentially constant through data collection.

The values of I and $\sigma(I)$ were corrected for the Lorentz and polarization effects. The total of 1987 reflections for which the net intensity was greater than $2\sigma(I)$ was considered as observed. The correction for absorption was not applied (the linear absorption coefficient for this compound, using MoK_α radiation, is 15.3 cm^{-1}).

TABLE I. Final Atomic Parameters with Their e.s.d.'s. Positional parameters are given as a fraction of unit cell translations. The anisotropic temperature factors are expressed in the form: $\exp(-\Sigma_i\Sigma_j\beta_{ij}h_ih_j)$. Positional and anisotropic thermal parameters are $\times 10^4$.

Atom	x	y	z	$\beta_{1,1}$(B)	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$
Co	3343.2(2)	5006.5(5)	4681.8(3)	9.5(1)	64.2(5)	24.8(2)	2.0(2)	8.1(1)	2.1(3)
Cl	4430.5(4)	5489.2(9)	3066.0(6)	16.8(2)	112.1(2)	31.3(4)	4.7(4)	12.6(3)	4.5(6)
N(1)	2909(1)	6642(3)	3737(2)	12.0(6)	94(4)	31(2)	8(1)	7(1)	5(2)
N(2)	3735(1)	3267(3)	5652(2)	19.7(7)	70(3)	32(2)	6(1)	15(1)	3(2)
N(3)	4170(1)	5664(3)	4919(2)	10.9(6)	73(3)	30(1)	0(1)	11(1)	−2(2)
N(4)	2523(1)	4377(3)	4415(2)	16.0(7)	104(4)	74(2)	−5(1)	23(1)	−21(3)
N(5)	3466(1)	6267(3)	5836(2)	18.6(7)	69(4)	34(2)	2(1)	17(1)	−5(2)
N(6)	3194(1)	3792(3)	3496(2)	13.0(6)	104(4)	28(1)	6(1)	6(1)	−16(2)
O(1)	2573(1)	7526(3)	3863(2)	22.1(6)	137(4)	50(2)	30(1)	16(1)	8(2)
O(2)	2953(1)	6805(3)	2983(2)	26.8(7)	166(4)	45(2)	30(1)	21(1)	40(2)
O(3)	2075(1)	4165(4)	3525(2)	13.7(6)	290(7)	95(2)	−21(2)	14(1)	−74(2)
O(4)	2449(1)	4202(3)	5128(2)	31.6(8)	170(5)	114(2)	−13(2)	50(1)	−12(3)
O(W)	699(2)	4214(4)	2009(3)	30.6(9)	174(5)	114(3)	−3(2)	19(1)	−9(3)
C(1)	4093(2)	2062(4)	5503(3)	23(1)	78(5)	47(2)	12(2)	18(1)	11(3)
C(2)	3721(2)	1412(4)	4429(3)	27(1)	70(5)	62(2)	−3(2)	29(1)	−10(3)
C(3)	3619(2)	2531(4)	3616(2)	16.5(7)	89(5)	41(2)	2(2)	15(1)	−13(2)
C(4)	3773(2)	7782(4)	6055(2)	23(1)	70(4)	41(2)	1(2)	18(1)	−11(2)
C(5)	4409(2)	7716(4)	6155(3)	17.2(8)	80(1)	44(2)	−3(2)	8(1)	−12(3)
C(6)	4361(1)	7271(4)	5171(3)	14.9(8)	73(4)	51(2)	−4(1)	15(1)	4(2)
H(W1)	603	2992	1964	7.5					
H(W2)	1200	4000	2400	7.5					
H(1)	4005	3666	6416	4.0					
H(2)	3389	2758	5758	4.0					
H(3)	4220	1169	6067	4.0					
H(4)	4543	2522	5663	4.0					
H(5)	3969	420	4393	4.0					
H(6)	3268	995	4263	4.0					
H(7)	4072	2979	3800	4.0					
H(8)	3426	1957	2885	4.0					
H(9)	2716	3415	3071	4.0					
H(10)	3128	4517	2903	4.0					
H(11)	3684	5624	6514	4.0					
H(12)	3032	6356	5796	4.0					
H(13)	3840	8221	6766	4.0					
H(14)	3464	8562	5457	4.0					
H(15)	4722	6932	6756	4.0					
H(16)	4649	8803	6413	4.0					
H(17)	4813	7462	5244	4.0					
H(18)	4010	7987	4551	4.0					
H(19)	4536	4969	5457	4.0					
H(20)	4198	5341	4283	4.0					

The centrosymmetric space group C2/c was assumed. This places no restriction on the symmetry of the molecule, while the presence of the centre of symmetry in the crystal lattice ensures that both enantiomeric forms of this potentially asymmetric molecule will be present.

The position of the cobalt atom was found from a three-dimensional Patterson synthesis and was used to phase the F_o values for three-dimensional Fourier synthesis. From these maps all the atoms except the hydrogen were located. The refinement of the positional and individual isotropic thermal parameters of the atoms by a full-matrix least-squares procedure minimizing $\Sigma w(|F_o| - |F_c|)^2$ and using unit weights, w, gave the convergence at R = 0.074. Individual anisotropic thermal parameters were then assumed for all the atoms and the refinement led to R = 0.046. A three-dimensional difference electron density synthesis, calculated at this point, clearly revealed all the hydrogen atoms in the complex and the water molecules as the most significant features of the map. The positions of the hydrogens in the 1,3-diaminopropane ligands were calculated from the C and N atom positions, and their scattering amplitudes were added as the fixed contributions to the calculated structure factors in the subsequent refinement. The contribution of water hydrogens was also included with fixed positional parameters and isotropic temperature factors. The final refinement converged at $R = 0.027$ and $R_w = 0.029$ ($R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

The highest function values in the final difference synthesis was 0.7 e/Å^3 and the minimum peak height of a carbon atom in the final synthesis of electron density was 6.5 e/Å^3.

Values for the atomic scattering factors and anomalous terms (for cobalt) were taken from the international Tables for X-ray Crystallography [3].

The main computer programs used on a CDC-3600 computer include FORDAP, Zalkin's Fourier program, NUCLS, full matrix least squares program of Ibers and Deodens and ORFFE, Busing and Levy's function and error program.

A tabulation of F_o and F_c values for the reflections used in the refinement is given in a Table available from the Editor. The positional and thermal parameters derived from the last cycle of least-squares refinement are given in Table I along with the associated standard deviations as estimated from the inverse matrix.

Results and Discussion

The structure consists of the discrete enantiomer pairs of $[Co(tn)_2(NO_2)_2]^+$ cations, chloride anions and molecules of water. The complex cations are arranged in layers parallel to (001). Between these layers the sheets of chloride anions and molecules of water are alternately repeated along the *a* and *c* axis.

The atomic packing in the crystals, in the projection (010) of the unit cell, is shown in Fig. 1. Table II gives a selection of the interatomic distances and bond angles.

The cobalt atom is surrounded nearly octahedrally by four nitrogen atoms from the 1,3-diaminopropane ligands and two nitrogen atoms of the nitro groups. The nitro groups are in the *cis*-positions. The two 1,3-diaminopropane ligands are bidentately bonded to the cobalt, forming six-membered chelate rings. Both chelate rings have chair-conformation. They fold in the same direction, there is no symmetry relation between them; hence, the constellation of the chairs is C_1^4. Two chairs which are *cis* to one another have three possible arrangements: *syn, anti* and C_1. Geue and Snow [5] have calculated the relative energy for these isomers by the conformational strain energy minimization technique. They have found that the isomer in which the chairs fold apart, *i.e. anti* isomer, has the lowest strain energy. The difference in energy between *anti* and C_1 isomers is however only 2.0 kcal mol^{-1} so that the conformation of the rings in the crystal may be easily affected by the requirement of the crystal lattice. The less favoured C_1 constellation of the chairs has also been found in the crystal structure of *cis*-$[Co(tn)_2(CO_3)]ClO_4$ [5].

The molecular geometry of the rings is similar. None of the bond lengths and bond angles within one chelate ring is significantly different from that for the other or from their expected values. The greatest difference occurs in the values defining the conformation of the rings, *i.e.* in the torsional angles (given in Table II) as well as in the angles D_1 (D_1 = dihedral

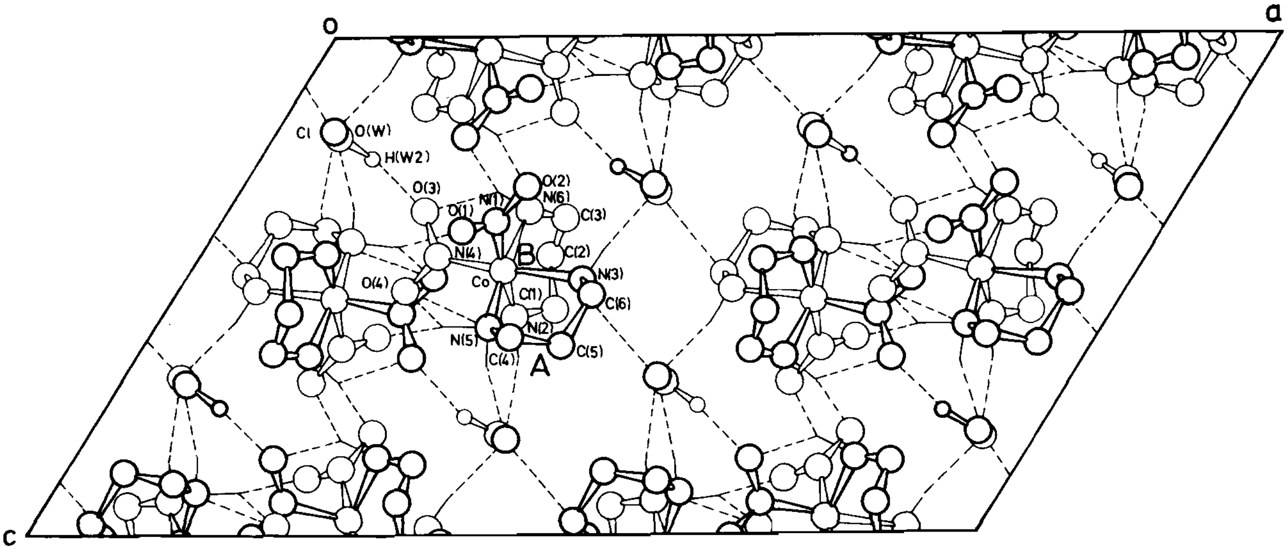

Fig. 1. The crystal structure viewed down the *b* axis. The hydrogen atoms of the complex ion are omitted. The broken lines represent hydrogen bonds.

angle between the N–Co–N and least squares N–C–C–N planes). The unique strain relieving mechanism for chair rings appears to be the flattening of the inner fragment (C–N–M–N–C) and the slight puckering of the outer one (N–C–C–C–N), accompanied by the opening of the N–M–N angle and closing of the C–C–C angle [15]. D_1 values of 146.8° and 154.1° for the rings denoted as A and B respectively indicate pronounced intermolecular interaction in the rings. The dihedral angles D_1 found in other metal–tn complexes are in the range from 132.5 to 160.5° (Table XIX in ref. 14 and Table 6 in ref. 5).

N–O distances in the nitro groups average to 1.235 Å, the average O–N–O angles being 119.0°. They are in agreement with those found in other nitro complexes [6–12]. Both groups are coplanar with the cobalt atom (Table III). Least-squares mean planes through the cobalt atom and corresponding nitro groups are inclined to each other at the angle of 68°. The Co–NO_2 distance is significantly shorter than the Co–NH_2 distance. This difference is also apparent in a number of Co nitro-complexes recently investigated [6–13] and may give some evidence for the π-bonding character of the Co–NO_2 bond.

Table IV lists the interatomic distances involving the hydrogen atoms. The hydrogen bonds exist between the complex and chloride ions, between the complex cations and water molecules, between the water molecules and chloride ions and between the amino groups and nitro-oxygens in the same molecule too, giving a variety of O–H...O, O–H...Cl, N–H...O and N–H...Cl simple and bifurcated predominantly weak intra- and intermolecular interactions.

As evident from this work, the investigated compound is really the *cis*-dinitro complex as predicted by Ćelap and co-workers [1]. Therefore, it has been established that Kawaguchi and Kawaguchi were mistaken when they claimed that they had isolated the *cis*-isomer of $[Co(tn)_2(NO_2)_2]^+$ ion.

TABLE II. Molecular Geometry of the *Cis*-$[Co(tn)_2(NO_2)_2]\cdot Cl\cdot H_2O$.

a) Bond lengths (Å)

Co–N(1)	1.924(3)	N(4)–O(4)	1.232(4)
Co–N(2)	2.001(3)	N(2)–C(1)	1.487(4)
Co–N(3)	1.977(2)	C(1)–C(2)	1.512(5)
Co–N(4)	1.936(3)	C(2)–C(3)	1.511(5)
Co–N(5)	1.984(2)	C(3)–N(6)	1.481(4)
Co–N(6)	1.980(2)	N(5)–C(4)	1.493(4)
N(1)–O(1)	1.237(3)	C(4)–C(5)	1.509(5)
N(1)–O(2)	1.234(3)	C(5)–C(6)	1.512(5)
N(4)–O(3)	1.232(4)	C(6)–N(3)	1.487(4)

b) Bond angles (°)

N(1)–Co–N(2)	175.9(1)	Co–N(1)–O(1)	120.6(2)
N(1)–Co–N(3)	91.2(1)	Co–N(1)–O(2)	120.3(2)
N(1)–Co–N(4)	87.6(1)	O(1)–N(1)–O(2)	119.1(3)
N(1)–Co–N(5)	90.6(1)	Co–N(4)–O(3)	120.0(3)
N(1)–Co–N(6)	87.7(1)	Co–N(4)–O(4)	120.0(3)
N(2)–Co–N(3)	92.8(1)	O(3)–N(4)–O(4)	120.0(3)
N(2)–Co–N(4)	88.3(1)	Co–N(2)–C(1)	121.9(2)
N(2)–Co–N(5)	89.1(1)	N(2)–C(1)–C(2)	112.2(3)
N(2)–Co–N(6)	92.7(1)	C(1)–C(2)–C(3)	113.0(3)
N(3)–Co–N(4)	178.6(2)	C(2)–C(3)–N(6)	112.9(3)
N(3)–Co–N(5)	91.6(1)	Co–N(6)–C(3)	122.0(2)
N(3)–Co–N(6)	89.4(1)	Co–N(5)–C(4)	121.5(2)
N(4)–Co–N(5)	89.3(1)	N(5)–C(4)–C(5)	111.8(3)
N(4)–Co–N(6)	89.8(1)	C(4)–C(5)–C(6)	113.4(3)
N(5)–Co–N(6)	177.9(1)	C(5)–C(6)–N(3)	110.8(3)
		C(6)–N(3)–Co	119.0(2)

c) Torsional angles (°)

Co–N(2)–C(1)–C(2)	51.2(3)
N(2)–C(1)–C(2)–C(3)	66.7(4)
C(1)–C(2)–C(3)–N(6)	67.3(4)
C(2)–C(3)–N(6)–Co	52.0(3)
C(3)–N(6)–Co–N(2)	30.7(2)
N(6)–Co–N(2)–C(1)	30.6(2)
Co–N(5)–C(4)–C(5)	52.7(3)
N(5)–C(4)–C(5)–C(6)	64.7(4)
C(4)–C(5)–C(6)–N(3)	69.5(3)
C(5)–C(6)–N(3)–Co	60.8(3)
C(6)–N(3)–Co–N(5)	40.8(2)
N(3)–Co–N(5)–C(4)	37.3(2)

TABLE III. Equatons of the Least-Squares Mean Planes through Selected Groups of Atoms. The equation of the plane is expressed as $Ax + By + Cz - D = 0$, where x, y, z are the monoclinic coordinates.

Plane	A	B	C	D
(1): Co, N(1), O(1), O(2)	0.596	0.590	0.138	8.584
(2): Co, N(4), O(3), O(4)	−0.277	0.958	0.090	2.592
(3): N(3), N(5), C(4), C(6)	0.371	0.308	0.539	6.372
(4): N(2), N(6), C(1), C(3)	0.725	0.651	−0.202	6.871

Plane	Distances of atoms from the planes (Å)							
1	Co	−0.002,	N(1)	0.007,	O(1)	−0.003,	O(2)	−0.002
2	Co	0.001,	N(4)	−0.005,	O(3)	0.002,	O(4)	0.002
3	N(3)	0.023,	N(5)	−0.024,	C(4)	0.027,	C(6)	−0.028
4	N(2)	0.001,	N(6)	−0.001,	C(3)	0.001,	C(1)	−0.001

TABLE IV. Possible Hydrogen Bonds.[a]

A	H	B	A...B	A...H	H...B	∢A...H...B
O(W)	H(W1)	Cl^{iii}	3.315	1.104	2.220	170.8
O(W)	H(W2)	O(3)	2.931	1.072	1.927	156.6
N(2)	H(1)	Cl^{i}	3.342	1.056	2.297	170.1
N(2)	H(2)	O(4)	2.984	1.061	2.383	114.6
N(3)	H(19)	Cl^{ii}	3.348	1.052	2.372	153.8
N(3)	H(20)	Cl	3.260	1.059	2.250	158.9
N(5)	H(11)	Cl^{i}	3.339	1.050	2.320	163.3
N(5)	H(12)	O(1)^{iv}	3.059	1.051	2.095	151.3
N(5)	H(12)	O(4)	2.836	1.051	2.289	110.7
N(6)	H(9)	O(2)^{iii}	3.077	1.058	2.133	147.3
N(6)	H(9)	O(3)	2.832	1.058	2.166	118.8
N(6)	H(10)	O(2)	2.760	1.058	2.093	118.5

[a] The superscripts refer to the following transformation of the coordinates x, y, z:

i	x	1 – y	1/2 – z
ii	1 – x	1 – y	1 – z
iii	1/2 – x	1/2 + y	1/2 – z
iv	1/2 – x	1/2 – y	1/2 – z

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