Two Modifications of Tetraethylammonium *trans*-Diiodobis(ethanedialdioximato)cobaltate(III) with and without Intermolecular I...I Interactions

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The structures of two modifications of $[\text{C}_8\text{H}_{20}\text{N}][\text{C}_4\text{H}_6\text{CoI}_2\text{N}_4\text{O}_4]$, $M_r = 617.11$, have been determined by X-ray investigations. Form **1** is orthorhombic, *Pbcn*, $a = 8.417(2)$, $b = 12.923(3)$, $c = 18.444(3)$ Å, $V = 2006$ Å³, $Z = 4$, $d_c = 2.04$ g cm⁻³, final $R_w = 0.037$ for 1989 reflections and 124 parameters. There are no unusual intermolecular interactions in this modification. Form **2** is tetragonal, *I4₁md*, $a = 8.886(3)$, $c = 25.841(6)$ Å, $V = 2040$ Å³, $Z = 4$, $d_c = 2.01$ g cm⁻³, final $R_w = 0.027$ for 1629 reflections and 80 parameters. In this modification the metal complexes form strictly linear chains *via* short intermolecular I...I contacts, $3.722(1)$ Å.

Introduction

We have recently reported the synthesis and structure of a Co^{II}/Co^{III} mixed valence salt in which the anion is *trans*-dibromobis(ethanedialdioximato)cobaltate(III), $[\text{CoBr}_2(\text{GH})_2]^-$ [1]. Of particular interest is the easy conversion of this anion into the neutral cobaltoxime: *trans*-aquabromobis(ethanedialdioximato)cobalt(III) $\text{CoBr}(\text{H}_2\text{O})(\text{GH})_2$ [2], which may be regarded as the smallest model compound for vitamin B₁₂ and related biological substances [2, 3].

The search for analogous iodine complexes has now led to the preparation of salt involving the homologous anion: *trans*-diiodobis(ethanedialdioximato)cobaltate(III), $[\text{CoI}_2(\text{GH})_2]^-$, with Et_4N^+ counterions. This salt crystallizes in two different chain structures with and without intermolecular iodine-iodine interactions.

The linear chain ordering of atoms and molecules in solids is of crucial scientific relevance, particularly in connection with the study of anisotropic magnetic

interactions [4] and electronic properties of quasi-one-dimensional materials [5]. In this paper we describe the synthesis of the title compound and the structures of its two crystalline forms.

Experimental

Commercial $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99% pure), analytical grade tetraethylammonium triiodide, $(\text{Et}_4\text{N})\text{I}_3$, and ethanedialdioxime, GH_2 , were used for the synthesis.

$(\text{Et}_4\text{N})\text{I}_3$ (1 g ~ 2 mmol) and GH_2 (0.2 g ~ 2.3 mmol) were dissolved in acetone (150 ml). To this red solution solid $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g ~ 1 mmol) was added with stirring at room temperature. The dark-red mixture was filtered, and the filtrate was stirred for *ca.* 45 min, during which shiny crystallites were formed. The reaction mixture was left to stand over night in a loosely covered beaker. The brown crystals were separated by filtration, washed with little cold acetone and air dried. Recrystallization from warm methanol yielded emerald-green crystals (form II) which were slightly contaminated with some brown prismatic crystals. The latter were removed by dissolution in little acetone. The mother liquor of the reaction mixture was concentrated by slow evaporation at room temperature to afford mainly brown, prismatic crystals (form I).

* Correspondence about preparation and properties should be addressed to Dr. M. M.-Bélombé, about the structure to Prof. H. Endres.

For the X-ray investigations, crystals were mounted on top of glass capillaries. Lattice parameters were derived from the setting angles of 25 reflections centered on a diffractometer (Syntex R3, monochromated MoK α radiation). Data were collected by $\theta/2\theta$ scans, monitoring two check reflections at intervals of 100 reflections. Empirical absorption corrections (ψ -scans) were applied and equivalent reflections merged to a set of unique data. Table I contains additional information about the data collection and the calculations.

For form I, the space group is unambiguously determined by the systematic extinctions. For form II the centric space group is not possible due to the point symmetry of the special fourfold positions required for Ni. Both structures were solved by Patterson methods and completed by Fourier syntheses. In form I, the H positions of the complex were taken from a difference Fourier map and refined with individual isotropic temperature factors. In the cation, the $-\text{CH}_2-$ and $-\text{CH}_3$ groups were refined as rigid groups with calculated H positions. In form II the cation is disordered over two orientations, with N at a special position of symmetry mm. Therefore, the H atoms of the cation were not included in the calculations. Those of the metal complex could be found in a difference Fourier map. They were held fixed in the refinement, with temperature factors $U=0.08$, as they would not behave well when refined. Non-H atoms were refined with anisotropic temperature factors in both structures.

The refinement ("cascade matrix" least squares for form I, full-matrix least squares for form II) was based on F with weights $w = 1/\sigma^2(F)$. The calculations were carried out on a Nova 3 minicomputer with the SHELXTL program system [6], which uses

scattering factors from "International Tables" [7] and takes anomalous dispersion into account. Plots were drawn on a Tektronix plotter with SHELXTL*.

Description of the Structures and Discussion

Atom coordinates of form I and II are listed in Tables II and III, respectively. Bond lengths and angles in the metal complexes of both forms are given in Tables IV and V. The numbering schemes are shown in Figs. 1 and 2.

In form I the Co atom occupies a crystallographic inversion center, the N atom of the cation lies on a twofold axis. In form II the central metal occupies a special position of symmetry mm (and so does the N atom of the disordered cation). The iodine atoms lie in one mirror plane, the atoms of the organic ligand in the other mirror plane intersecting at the Co position.

It is obvious that the chemical reaction leading to the formation of the present product is a redox process where Co^{II} becomes oxidized to Co^{III} by molecular iodine. The resulting distorted octahedral *trans*-diiodobis(ethanedialdioximato)cobaltate(III) anions determined the crystal structure in the solid – depending on their ordering mode – and are, thus, responsible for the solid state electronic behavior.

* Lists of observed and calculated structure factors, anisotropic thermal parameters and H coordinates have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2. Copies may be obtained quoting the deposition number CSD 52131, the authors, and the journal reference.

	Form I (brown)	Form II (emerald green)
Crystal shape and size	Rectangular prism 0.07×0.14×0.23 mm	Bicapped tetragonal column 0.1×0.1×0.35 mm
Max. 2θ	66°	66°
Possible indep. reflections	3782	1924
Reflections observed $I > 2.5\sigma(I)$	1989	1629
Refl. for ψ -scans	8	9
2θ range	6.6–55°	13–51°
Min. transmission (max. = 1)	0.68	0.82
μ (cm ⁻¹)	39.2	36.6
Intensity variation of checks	±3%	±2.3%
R_{int} (from merging)	0.048	0.019
Parameters	124	80
R_w, R	0.037, 0.041	0.027, 0.031
Goodness-of-fit	1.67	1.75
Max. shift/error	0.007	0.001
Extremes in diff. Fourier	+1.48, -0.77 eÅ ⁻³	+0.83, -0.82

Table I. Experimental and computational details.

Table II. Form I: Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$) equivalent to the refined anisotropic values and defined as 1/3 of the trace of the orthogonalized U_{ij} -tensor. Atoms N(3) to C(6) form the cation.

Atom	x	y	z	U
I	4820(1)	5760(1)	1298(1)	40(1)
Co	5000	5000	0	22(1)
N(1)	7259(5)	5036(5)	51(3)	29(1)
N(2)	5324(5)	6341(4)	-375(2)	31(1)
O(1)	8096(4)	4230(3)	303(2)	40(1)
O(2)	4135(6)	6971(3)	-583(3)	45(2)
C(1)	7903(7)	5886(6)	-159(3)	35(2)
C(2)	6791(7)	6644(5)	-401(3)	35(2)
N(3)	0	4464(4)	2500	26(2)
C(3)	1008(8)	5113(6)	2992(4)	50(2)
C(4)	98(8)	5956(5)	3418(4)	54(2)
C(5)	1054(9)	3812(6)	2033(4)	55(3)
C(6)	2208(9)	3103(5)	2468(5)	70(3)

Table IV. Bond distances ($\text{\AA}$) and angles ($^\circ$) in the complex anion in form I.

I—Co	2.592(1)	Co—N(1)	1.904(4)
Co—N(2)	1.885(5)	N(1)—C(1)	1.285(9)
Co—N(1a)	1.904(4)	N(2)—C(2)	1.296(7)
N(1)—O(1)	1.341(7)		
N(2)—O(2)	1.346(6)		
C(1)—C(2)	1.426(9)		
I—Co—N(1)	90.2(2)	I—Co—N(2)	89.9(1)
N(1)—Co—N(2)	81.5(2)	Co—N(1)—O(1)	121.5(4)
Co—N(1)—C(1)	115.3(4)	O(1)—N(1)—C(1)	123.2(4)
Co—N(2)—O(2)	123.6(4)	Co—N(2)—C(2)	115.4(4)
O(2)—N(2)—C(2)	121.0(5)	N(1)—C(1)—C(2)	113.9(5)
N(2)—C(2)—C(1)	114.0(5)		

Table III. Form II: Atom coordinates analogous to Table II. The cation is disordered over two orientations.

Atom	x	y	z	U
I	5000	7906(1)	0	44(1)
Co	5000	5000	5(1)	32(1)
N(1)	3618(7)	5000	557(2)	38(2)
N(2)	6416(8)	5000	-543(2)	46(2)
O(1)	2115(7)	5000	495(2)	61(2)
O(2)	7892(7)	5000	-474(2)	61(2)
C(1)	4196(8)	5000	1017(3)	46(2)
C(2)	5807(10)	5000	-999(3)	59(3)
N(3)	0	0	612(2)	36(2)
C(4)	0	1948(10)	-110(4)	88(4)
C(6)	0	2204(10)	1276(4)	96(4)
C(3)	1038(11)	930(11)	273(3)	54(3)
C(5)	1061(13)	994(12)	931(4)	63(4)

Table V. Bond distances ($\text{\AA}$) and angles ($^\circ$) in the complex anion in form II.

I—Co	2.583(1)	Co—N(1)	1.882(6)
Co—N(2)	1.896(6)	N(1)—O(1)	1.345(8)
N(1)—C(1)	1.294(8)	N(2)—O(2)	1.323(10)
N(2)—C(2)	1.297(9)	C(1)—C(1a)	1.429(15)
C(2)—C(2a)	1.435(18)		
I—Co—N(1)	90.2(1)	I—Co—N(2)	89.8(1)
N(1)—Co—N(2)	179.1(3)	I—Co—Ia	179.4(1)
N(2)—Co—N(1a)	97.7(3)	N(1)—Co—N(1a)	81.5(3)
N(2)—Co—N(2a)	83.2(4)	Co—N(1)—O(1)	123.9(4)
Co—N(1)—C(1)	115.9(5)	O(1)—N(1)—C(1)	120.2(6)
Co—N(2)—O(2)	123.8(4)	Co—N(2)—C(2)	113.7(6)
O(2)—N(2)—C(2)	122.5(7)	N(1)—C(1)—C(1a)	113.4(4)
N(2)—C(2)—C(2a)	114.7(5)

Fig. 1. Section of a chain of complex anions in Form I. Thermal ellipsoids are drawn at 50% probability. Symmetry codes are: i) 1-x, 1-y, -z; ii) 1-x, y, 0.5-z.

Fig. 2. View of form II analogous to Fig. 1. Symmetry codes are: i) $1-x, 1-y, z$; ii) $x, 2-y, z$.

In form I, the anionic complexes are disposed in infinite zigzag chains involving very large $\text{I}\cdots\text{I}$ contacts ($4.44 \text{ \AA}$) and, therefore, virtually no interionic interactions. The brown color of these crystals is consistent with the absence of any dramatic collective electronic phenomena. By contrast, form II is characterized by the strictly linear ordering of the complex anions, thus giving rise to the formation of the heteroatomic, polymeric straight chains $\cdots\text{I}-\text{Co}-\text{I}\cdots\text{I}-\text{Co}-\text{I}\cdots$, where the intermolecular $\text{I}\cdots\text{I}$ contacts of $3.72 \text{ \AA}$ are short

enough to warrant considerable covalent bonding effects between the iodides of adjacent complex ions. Extended orbital overlapping along the heteroatomic chain results this way, and considerable anisotropic electronic properties may be expected for this type of solid. This is reflected in the beautiful emerald green lustre of the strongly dichroic crystals.

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