Synthesis and X-Ray Crystal Structure of the Double Salt, Bis(tetramethylammonium) Triiodide

trans-Diiodobis(ethanedial dioximato(1-)N,N')cobaltate(III).
(N(CH₃)₄)₂I₃(CoI₂(GH)₂)

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Structure, Double Salt, Cobaloximate, Iodine Interactions

A "one-pot" reaction involving cobalt(II) nitrate hexahydrate, iodine, tetramethylammonium iodide and ethanedial dioxime (or glyoxime, GH₂) in water/methanol solution has afforded the novel double salt, bis(tetramethylammonium) triiodide trans-diiodobis(ethanedial dioximato) cobaltate(III), (N(CH₃)₄)₂I₃(CoI₂(GH)₂). The structure of the salt was determined from single crystal X-ray diffraction data. Crystal data: orthorhombic space group Pnma; C₃H₅CoI₁₃O₆N₆; Mᵣ = 1015.84; a = 10.60(1), b = 12.53(1), c = 21.47(2) Å; V = 2851.83 Å³; Z = 4; Dᵣ = 2.36 Mg m⁻³. The structure consists of three distinctive molecular species, namely, (N(CH₃)₄)⁺, I⁻, and (CoI₂(GH)₂)⁻. The cobaloximatic anion contains Co¹¹¹ in the usual "stripes" that propagate throughout the structure, parallel to the crystallographic ac plane. There are no interactions amongst ICoI triads in this material.

Introduction

"Cobaloximes" (which are cobalt complexes based on α,β-dione dioximes as the main ligands) are of special scientific interest, since they may be regarded as convenient model compounds for the systematic study of the highly important biological system, cyanocobalamin or vitamin B₁₂ [1]. With ethanedial dioxime as the smallest member of this series of organic ligands, we have recently reported a few salts involving the cobaloximatic anion, trans-diiodobis(ethanedial dioximato)cobaltate(III), (CoI₂(GH)₂)⁻ [2, 3]. In an effort to further our research along these lines, we have carried out a chemical reaction aimed at fabricating a homologous salt with tetramethylammonium, (N(CH₃)₄)⁺, as the cation. In lieu of the initially expected single salt, however, we have isolated the novel double salt of this cation with I⁻ and (CoI₂(GH)₂)⁻ as the counterions. We report here synthesis and X-ray crystal structure of this double salt.

Experimental

Commercial Co(NO₃)₂·6H₂O (>99% pure), analytical grade N(CH₃)₄I and GH₂, and doubly sublimed I₂ were used to prepare the material.

Co(NO₃)₂·6H₂O (900 mg, 3 mmol) and I₂ (380 mg, 1.5 mmol) were dissolved at room temperature in 99.5% pure methanol (50 ml). N(CH₃)₄I (605 mg, 3 mmol) and GH₂ (530 mg, 6 mmol) were dissolved separately at about 50 °C in methanol/water (70/30 ml). The two solutions were filtered, mixed (red-brown solution) and stirred at room temperature over two nights. The resulting solution was filtered into a porcelain dish and allowed to evaporate slowly and undisturbed at room temperature. After a few days, the redbrown, elongated crystals that had appeared in large quantity were separated by filtration, washed...
with little methanol/water (1:1, v/v), then dried in air between filter papers.

A suitable crystal (see Table I) mounted on top of a glass capillary was used for X-ray diffraction at ambient temperature. Data were collected on an automatic Siemens AED II diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.7107 Å). Lattice parameters were derived from the setting angles of 17 reflections in the range 5 < 2θ < 22°. Table I summarises further experimental and computational details.

The structure was solved by Patterson and Fourier methods, and refined by full matrix least-squares, based on F with weights w = 1/σ²(F). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were treated with fixed isotropic temperature factors as rigid CH₃ or CH groups, respectively. Calculations were carried out with SHELXTL PLUS program [4] which uses scattering factors from “International Tables” [5] and takes anomalous dispersion into account*.

**Results and Discussion**

Table II lists fractional atomic coordinates and equivalent isotropic thermal parameters (defined as 1/3 of the trace of the orthogonalized Ueq tensor) for (N(CH₃)₄)₂I₃(CoI₂(GH)₂). Table III lists bond distances and angles.

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* Lists of observed and calculated structure factors, along with anisotropic and isotropic thermal parameters for C₁₅H₂₆CoI₃N₂O₂ have been deposited with the Fachinformationszentrum Karlsruhe GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG). Copies may be ordered quoting the deposition number CSD 54739, the authors and the journal reference.
The structure of this double salt is made up of three distinctive molecular species which are the cation tetramethylammonium, \((\text{N(CH}_3\text{)}\text{)}^+\), the cobaloximate anion trans-diiodobis(ethanedian
dioxidamato)cobaltate(III), \((\text{CoI}_2\text{(GH)}\text{)}^2\text{)}_\text{2}^\text{-}\), and the triiodide ion, \(I_3^-\). There are four formula units in the orthorhombic unit cell, i.e. 8 cations and 4 of each anionic species.

In the cation, the CH\(_3\) groups are asymmetrical­ly oriented around the central nitrogen (N\(_3\)) atom which occupies a general position. Fig. 1 displays an ORTEP perspective view (ellipsoids drawn at 40% probability) with atom numbering for the cobaloximatic anion. The central Co\(^{\text{III}}\) lies at the molecular center of symmetry. The separations of 2.492 Å between O1 and O1a, and of 2.516 Å between O2 and O2a are well within the usual range (2.40—3.00 Å) for classical intramolecular O—H—O bridges. The coordination geometry around Co is, like in homologous cases established previously [2, 3], a distorted (4+2) octahedron of four equa­torial N atoms and two equidistant apical iodide ligands. Unlike the observation made in previous materials, however, the \(1—\text{Co—I}\) triads in the present material turn out to be slightly bent (by an angle of 177.3°), instead of being rectilinear as usually observed [2, 3]. Fig. 2 depicts a projection of the structure down the \(b\) axis onto the mirror plane \(y = 1/4\). The cations and the organic parts of the cobaloximatic anions have been omitted for clarity. The \(I_3^-\) ions, too, are bent by an angle of

![Fig. 1. Molecular structure of the cobaloximatic anion, trans-diiodobis(ethanedian
dioxidamato(1−)-N,N)cobaltate(III), \((\text{CoI}_2\text{(GH)}\text{)}^2\text{)}_\text{2}^\text{-}\), with atom numbering. Ellipsoids have been drawn at 40% probability.](image-url)
Fig. 2. Projection of the structure along \( b \) onto mirror plane \( y = 1/4 \) (the tetramethylammonium cations and the organic parts of the cobaloximatic anions have been left out for clarity). Van der Waals type intermolecular contacts (3.850–3.908 Å) between \( I \) atoms of adjacent \( I_3^- \) and ICol units (white balls = I, black balls = Co) are represented by broken lines. Also indicated is the numbering of \( I \) atoms within a selected “stripe” of the two-dimensional network of \( I_3^- \) and ICol units extending throughout the structure, parallel to the \( ac \) plane.

176.8°, closely comparable with the above value for the \( I-Co-I \) triads.

The iodine atoms within the \( I_3^- \) ion are numbered 11 for the central, 14 and 15 for the terminal \( I \) atoms, respectively. The \( I \) atoms of the ICol triad are numbered 12 and 13. The two kinds of triatomic units interact (rather weakly) with each other via intermolecular \( I \cdots I \) contacts to form interesting domain-strips which propagate throughout the structure, parallel to the crystallographic \( ac \) plane. On the one hand, the interaction between \( I_3^- \) and ICol units, concretized by an intermolecular 14···13 contact of 3.850 Å, occurs following a head-on-tail relative orientation of the two units. The interaction amongst \( I_3^- \) ions, on the other hand, occurs following an approximated “T” pattern, with an intermolecular 15···11 contact of 3.908 Å. It is seen in Fig. 2 that 12 atoms do not participate in any intermolecular \( I \cdots I \) interactions, nor do ICol triads interact among themselves as this is generally the case in isotypical systems studied earlier [2, 3].

To the best of our knowledge, the present material appears to be the first well-documented case of a double salt involving a “cobaloximate” ion.

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