The Isomorphous Structures of Ammonium *trans*-Diiodobis(ethanedial-dioximato-(1-)-N,N')cobaltate(III) and Ammonium *trans*-Diiodobis(ethanedial-dioximato-(1-)-N,N')rhodate(III): Extended Metaloximate Chains with a Novel $\cdots\text{I}-\text{M}-\text{I}\cdots\text{I}-\text{M}-\text{I}\cdots$ Zigzagged Structure

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The ammonium salts of the complex anions *trans*-diiodobis(ethanedial-dioximato)-cobaltate(III), $[\text{CoI}_2(\text{GH})_2]^-$, and *trans*-diiodobis(ethanedial-dioximato)rhodate(III), $[\text{RhI}_2(\text{GH})_2]^-$ (GH^- = ethanedial dioximate or glyoximate), have been synthesized and their structures determined from single crystal X-ray diffraction data at room temperature. The crystals of the two salts are monoclinic, space group C2/c. $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ (I) crystallizes as dark-brown prisms with a greenish reflectance; its crystal data are: $\text{C}_4\text{H}_{10}\text{CoI}_2\text{N}_5\text{O}_4$, $M_r = 504.90$; $a = 8.910(6)$, $b = 11.700(9)$, $c = 11.691(6)$ Å; $\beta = 93.55(5)^\circ$; $V = 1216.4$ Å³; $Z = 4$; $D_c = 2.78$ Mg m⁻³. $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$ (II) crystallizes as yellow-brown blocks with crystal data: $\text{C}_4\text{H}_{10}\text{I}_2\text{N}_5\text{O}_4\text{Rh}$, $M_r = 548.88$; $a = 9.038(4)$, $b = 11.949(5)$, $c = 11.770(3)$ Å; $\beta = 95.54(3)^\circ$; $V = 1265.16$ Å³; $Z = 4$; $D_c = 2.87$ Mg m⁻³. The two structures were refined to a final $R_w = 0.045$ for 1209 observed independent reflections and 95 parameters for I, and to a final $R_w = 0.040$ for 1922 observed independent reflections and 87 parameters for II. The coordination geometry around Co or Rh in the anionic complexes is a distorted (4 + 2) octahedron of four equatorial chelating N atoms and two apical iodides. The H atoms of the hydroxyl groups are involved, as usual, in intramolecular O–H–O bridges with uniform O $\cdots$ O separations of 2.582 Å for I, and 2.713 Å for II. The rectilinear I–Co–I or I–Rh–I triads form “infinite” zigzag chains extending parallel to the *ab* plane, with a weak I $\cdots$ I contact of 3.988 Å for I, and 4.010 Å for II.

Introduction

We are currently involved in a research program that aims at developing a large class of “cobaloximate” salts typified by tetraethylammonium *trans*-diiodobis(ethanedial-dioximato)cobaltate(III), $\text{N}(\text{C}_2\text{H}_5)_4[\text{CoI}_2(\text{GH})_2]$ [1–3]. Detailed X-ray structural investigation has revealed that this material crystallizes in two different forms.

In the one form, namely $\alpha\text{-N}(\text{C}_2\text{H}_5)_4[\text{CoI}_2(\text{GH})_2]$, the anionic complexes, $[\text{CoI}_2(\text{GH})_2]^-$, are disposed in a head-on-tail alignment such that the rectilinear I–Co–I triads form extended zigzagged heteroatomic chains involving vanishingly small intermolecular iodine–iodine interactions. This is the *brown modification*. In the

other crystalline form or $\beta\text{-N}(\text{C}_2\text{H}_5)_4[\text{CoI}_2(\text{GH})_2]$, the I–Co–I triads are, by contrast, disposed in straight linear “infinite” chains brought about by *quasi*-covalent bonding forces acting between the iodine atoms of adjacent complexes. This is the *green modification*, the crystals of which are characterized by a magnificent, markedly dichroic emerald-green reflectance (“Cameroon Green”) [2, 3].

The fundamental scientific and technological potential of this type of material ought to be associated mainly with this macroscopic anisotropy which obviously reflects low-dimensional solid state magnetic and optoelectronic phenomena taking place on the microscopic scale. It is well understood that such phenomena are of crucial relevance in the development of novel advanced materials for innovations in emerging technologies. Furthermore, these salts generally dissolve fairly well in water and in most polar organic solvents.

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Their prospective applicability with respect to catalysis, biological and electrochemical processes, therefore, should not be overlooked.

In an effort to expand the range of this class of interesting salts, we now have prepared the isomorphous salts, $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ and $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$, and we report their X-ray structures in the following.

Experimental

$\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ was obtained following a procedure used to prepare $\text{N}(\text{C}_2\text{H}_5)_4[\text{CoI}_2(\text{GH})_2]$ [1]. Freshly recrystallized NH_4I and commercial I_2 (doubly sublimed) were, however, introduced in required stoichiometric amounts into the reaction mixture. The microcrystalline product which was isolated in good yield, was recrystallized from high purity methanol (>99.9%) to afford brown-black prisms with a greenish, faintly dichroic reflectance.

Analysis for $\text{C}_4\text{H}_{10}\text{CoI}_2\text{N}_5\text{O}_4$

Calcd C 9.52 H 2.00 N 13.87 I 50.77,
Found C 9.72 H 2.01 N 13.96 I 50.22.

$\text{NH}_4[\text{RhI}_2(\text{GH})_2]$ was prepared as follows: Commercial (BDH) $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ (230 mg) was dissolved in 50 ml of 60 °C warm aqueous solution of freshly recrystallized NH_4I (600 mg). The red solution was filtered and stirred for 45 min at same temperature. A solution of analytically pure ethanedial dioxime (190 mg) in H_2O (40 ml) was added with stirring (which was continued for about 2 h). The resulting red solution was filtered and left (loosely covered) to concentrate by slow evaporation on a gently warmed (*ca.* 50 °C) electric plate. Some 10 days later, orange-red crystals had appeared, which were separated by filtration,

washed with little acetone, and dried in air between filter papers (transparent flat or opaque block-like crystals).

Suitable crystals of these materials (see Table I) were utilized for X-ray diffraction at room temperature. Data were collected on a four-circle, automatic diffractometer (Siemens AED 2) equipped with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Lattice parameters were derived from the setting angles, for the Co-based salt, of 27 reflections in the range $6 < 2\theta < 24^\circ$ and, for the Rh-based salt, of 24 reflections in the range $27 < 2\theta < 33^\circ$. Table I summarizes further experimental and computational details.

The structures were solved by Patterson methods and completed by Fourier syntheses. They were refined by full matrix least-squares, based on F with weights $w = 1/\sigma^2(F)$. The H positions of the complex anions were taken from a difference Fourier map, and refined with individual isotropic temperature factors. The H atoms of the ammonium ions were refined as rigid groups with calculated positions. Calculations were carried out on an Eclipse S140 computer with the SHELXTL program [4] which uses scattering factors from "International Tables" [5] and takes anomalous dispersion into account. Plots were drawn on a Tektronix plotter with SHELXTL*. The final re-

* Lists of observed and calculated structure factors, along with anisotropic and isotropic thermal parameters for $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ and $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$ may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry No. CSD 54592, the names of the authors and the journal citation.

Table I. Experimental and computational details.

	$\text{NH}_4[\text{CoI}_2(\text{GH})_2]$	$\text{NH}_4[\text{RhI}_2(\text{GH})_2]$
Crystal shape	prismatic	platelet
Crystal size	$0.15 \times 0.15 \times 0.23 \text{ mm}$	$0.21 \times 0.26 \times 0.38 \text{ mm}$
Possible independent reflections	<i>ca.</i> 1750	2393
Reflections observed $I > 2.5\sigma(I)$	1209	1922
Reflections for ψ -scans	7	7
2θ range	$3-60^\circ$	$3-65^\circ$
$\mu(\text{MoK}\alpha)$	6.440 mm^{-1}	6.17 mm^{-1}
R_{int} (from merging)	0.024	0.06
Parameters for least-squares	95	87
$R_w(R)$	0.045 (0.049)	0.040 (0.044)
Goodness-of-fit	2.63	6.01
Max. shift/error	1.46	0.30
Extremes in diff. Fourier	$-1.8, +1.4 \text{ e\AA}^{-3}$	$-1.58, +1.08 \text{ e\AA}^{-3}$
Min. transmission (max. = 1)	0.60	0.64
Scan type	$\omega-2\theta$	$\omega-2\theta$

finements with anisotropic thermal parameters for non-hydrogen atoms, and isotropic parameters for hydrogen atoms yielded, for the Co-based salt: $R(R_w) = 0.049(0.045)$, and for the Rh-based salt: $R(R_w) = 0.044(0.040)$.

Results and Discussion

Atomic coordinates and equivalent isotropic thermal parameters for $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ and $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$ with their esd's are listed in Table II; bond lengths and angles are given in Table III. The values tabulated here for the complex unit $[\text{CoI}_2(\text{GH})_2]^-$, match very closely those observed earlier on the two crystalline forms of $\text{N}(\text{C}_2\text{H}_5)_4[\text{CoI}_2(\text{GH})_2]$ [1]. Similar to the latter system, Co^{III} finds itself in a distorted $(4 + 2)$ octahedral ligand field of four chelating N atoms lying

in the equatorial molecular plane, and two iodide ligands occupying the apical positions. Thus, the I–Co–I triads are linked together in straight lines oriented perpendicularly to the equatorial planes. The “rhodoximate” ion, $[\text{RhI}_2(\text{GH})_2]^-$, is isostructural to the “cobaloximate” ion. It is worth noting that this geometry appears to be a general feature also encountered in closely related systems such as $[\text{CoBr}_2(\text{GH})_2]^-$ [6] and $[\text{RhCl}_2(\text{GH})_2]^-$ [7]. In each of these cases, all the atoms of the complex anion, except the two halides, lie well within the molecular equatorial plane.

Fig. 1 shows the *quasi*-one-dimensional zigzag linear chain of the “cobaloximate” ions, with the atom numbering adopted. Broken lines represent relatively weak intermolecular I...I contacts of 3.988 Å. (The “rhodoximate” ions adopt the same chain ordering with a slightly weaker intermolecu-

Atom	For $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$			U_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
I	46535(8)	20341(6)	136(6)	314(2)
Co	75000(0)	25000(0)	00000(0)	211(5)
N1	72301(89)	37588(71)	10055(62)	252(26)
N2	79392(88)	13395(73)	11258(63)	257(26)
O1	79549(121)	15063(92)	22685(76)	390(35)
O2	74021(83)	36695(60)	21294(52)	330(25)
C1	82297(113)	3498(93)	7424(85)	279(33)
C2	68631(119)	47050(90)	5104(84)	267(33)
NH	00000(0)	50593(143)	25000(0)	346(57)
H1	83668(943)	−3173(779)	11193(708)	
H2	65880(885)	52856(695)	8681(638)	
HN1	99543(1197)	53032(869)	19761(769)	
HN2	108778(1118)	47103(766)	25652(776)	
HO	81564(1272)	19638(875)	23556(946)	

Atom	For $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$			U_{eq}
	<i>x</i>	<i>y</i>	<i>z</i>	
I	3720(6)	70232(5)	49906(6)	3500(20)
Rh	25000(0)	75000(0)	00000(0)	2187(25)
N1	−30130(76)	63235(60)	38151(59)	2813(223)
N2	27773(76)	61442(58)	−9809(64)	2880(223)
O1	−30630(72)	65470(54)	26621(52)	3980(221)
O2	25378(69)	62359(48)	−21023(53)	3497(209)
C1	−32685(95)	53475(74)	41862(84)	3055(277)
C2	−18747(94)	97565(75)	45728(80)	3031(271)
N3	00000(0)	50915(101)	25000(0)	3889(407)
H1	34649(1111)	48187(957)	14470(987)	
H2	31226(1092)	44136(929)	−7725(953)	
H13	9233(1149)	47586(937)	22525(1045)	
H23	−2206(1321)	54197(937)	17976(968)	

Table II. Atomic coordinates ($\times 10^5$) and equivalent isotropic thermal parameters* (defined as $1/3$ of the trace of the orthogonalized U_{ij} tensor).

* U_{eq} values are multiplied by 10^4 for the Co-based and by 10^5 for the Rh-based salt.

Table III. Bond lengths (Å) and angles (°).

a) For $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$				b) For $\text{NH}_4[\text{RhI}_2(\text{GH})_2]$			
Bond lengths		Bond angles		Bond lengths		Bond angles	
Co-I	2.595(1)	I-Co-N1	89.9(2)	Rh-I	2.658(1)	I-Rh-N2	90.3(0.2)
Co-N1	1.909(8)	I-Co-N2	90.3(2)	Rh-N1	2.003(7)	I'-Rh-N2	89.7(0.2)
Co-N2	1.914(8)	I-Co-I'	180.0(0)	Rh-N2	2.019(7)	N1-Rh-N2	78.6(0.3)
Co-I'	2.595(1)	I-Co-N1'	90.1(2)	Rh-I'	2.658(1)	N1'-Rh-N2	101.4(0.3)
Co-N1'	1.909(8)	I-Co-N2'	89.7(2)	Rh-N1'	2.003(7)	N2'-Rh-N2	180.0(0.0)
N1-O2	1.318(9)	N1-Co-N2	98.7(3)	Rh-N2'	2.019(7)	I'-Rh-I	180.0(0.0)
N1-C2	1.282(13)	N1-Co-I'	90.1(2)	N1-O1	1.380(9)	N1-Rh-I	90.4(0.2)
N2-O1	1.349(12)	N1-Co-N1'	180.0(0)	N1-C1	1.274(11)	N1'-Rh-I	89.6(0.2)
N2-C1	1.274(14)	N1-Co-N2'	81.3(3)	C1-C2	1.459(14)	N2'-Rh-I	89.7(0.2)
O1-HO	0.572(98)	N2-Co-I'	89.7(2)	C2-N2	1.282(11)	N1-Rh-I'	89.6(0.2)
C1-H1	0.901(89)	N2-Co-N1'	81.3(3)	N2-O2	1.321(10)	N1'-Rh-I'	90.4(0.2)
C1-C2'	1.464(14)	N2-Co-N2'	180.0(0)	C1-H1	0.980(114)	N2'-Rh-I'	90.3(0.2)
C2-H2	0.842(79)	I'-Co-N1'	89.9(2)	C2-H2	1.072(114)	N1'-Rh-N1	180.0(0.0)
C2-C1'	1.464(14)	I'-Co-N2'	90.3(2)	N3-H13	0.993(115)	N2'-Rh-N1	101.4(0.3)
NH-HN1'	0.675(91)	N1'-Co-N2'	98.7(3)	N3-H23	0.919(112)	N2'-Rh-N1'	78.6(0.3)
NH-HN1''	0.674(91)	Co-N1-O2	122.8(6)	N3-H13'	0.993(115)	C1-N1-O1	121.6(0.7)
NH-HN2'	0.881(98)	Co-N1-C2	115.2(6)	N3-H23'	0.919(112)	Rh-N1-O1	122.2(0.5)
NH-HN2''	0.882(98)	O2-N1-C2	122.0(8)			Rh-N1-C1	116.2(0.6)
		Co-N2-O1	124.6(7)			O2-N2-Rh	119.2(0.5)
		Co-N2-C1	116.1(7)			C2-N2-Rh	114.9(0.6)
		O1-N2-C1	119.3(9)			C2-N2-O2	125.9(0.7)
		N2-O1-HO	107.2			N2-C2-C1	115.6(0.8)
		N2-C1-H1	129.8(5.6)			H2-C2-C1	117.1(5.7)
		N2-C1-C2'	113.1(9)			H2-C2-N2	126.4(5.7)
		H1-C1-C2'	116.7(5.6)			H23-N3-H13	91.3(9.9)
		N1-C2-H2	123.1(5.6)			H13'-N3-H13	132.8
		N1-C2-C1'	114.3(9)			H23'-N3-H13	108.6(9.7)
		H2-C2-C1'	122.2(5.5)			H13'-N3-H23	108.6(9.7)
		HN1'-NH-HN1''	130.0			H23'-N3-H23	129.5
		HN1'-NH-HN2'	106.1			H23'-N3-H13'	91.3(9.9)
		HN1'-NH-HN2''	96.5			C2-C1-N1	114.8(0.8)
		HN1''-NH-HN2'	96.6			H1-C1-N1	110.8(6.9)
		HN1''-NH-HN2''	106.1			H1-C1-C2	134.3(6.8)
		HN2'-NH-HN2''	124.8

Fig. 1. View onto the ab -plane showing the zigzagged chain ordering of the cobaloximates, $[\text{CoI}_2(\text{GH})_2]^-$. Atom numbering within one cobaloximate unit as well as along the chain is also indicated. (The picture was drawn after rotation by an angle of 20° about axis 1.)

lar I...I interaction of 4.010 Å.) The Co atoms within a chain lie strictly on a straight line running parallel to the *a*-axis throughout the structure, the shortest distance between them being 8.910 Å. The molecular equatorial planes are disposed parallel to the *bc* plane. Tilting slightly the molecules such as to bring the I–Co–I lines into coincidence with the line joining the Co atoms would put adjacent iodides at a somewhat shorter intermolecular distance of about 3.835 Å, thus nearing the value of 3.721 Å observed on the so-called “Cameroon Green” system [1]. One may suspect even that application of convenient pressure along the chain direction might still cause considerable reduction of this intermolecular I...I separation, possibly leading, therefore, to a dramatic enhancement of electric and optoelectronic one-dimensional solid state phenomena.

The projection of the structure onto the crystallographic *bc* plane is depicted in Fig. 2 for the Co-based salt. All the atoms of the salt are easily recognizable, and so are the usual intramolecular O–H–O bridges with a uniform O–O separation of 2.582 Å (2.713 Å in the case of the Rh-based material). The Co (or the Rh) atoms sit at molecular center of symmetry of the complex anions and occupy crystallographic special positions. The ammonium ions form distorted tetrahedra (C_2 symmetry) and sit also at special positions. The drawing shows in particular that these NH_4^+ ions are

Fig. 2. Projection of the $\text{NH}_4[\text{CoI}_2(\text{GH})_2]$ structure onto the *bc*-plane, showing channel-like rooms in which the NH_4^+ ions are located.

actually located in channel-like rooms delimited by the organic parts of the complex anions. These channels extend throughout the structure, parallel to the *a*-axis which represents the direction of chain propagation. There are no considerable intermolecular effects other than the iodine–iodine interactions in the present structures.

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