THE PREPARATION AND PROPERTIES OF COBALT(II) TELLURATES

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Received January 17th, 1979

Cobalt(II) tellurates with the composition $CoTeO_4$, $CoTeO_4.1/2\,H_2O$ and Co_3TeO_6 were prepared. The first two are cubic with octahedral coordination around the cobalt atom and with TeO_6 octahedra joined at the edges. In Co_3TeO_6, which is isostructural with Ni_3TeO_6, the TeO_6 octahedra are isolated. At least one cobalt atom is tetrahedrally coordinated by oxygen atoms. The high values of the temperature independent paramagnetism, 11 $m^3\,kg^{-1}$, and the Weiss constant, $\Theta = -64$ K, indicate marked magnetic exchange interaction. The thermal decomposition of all three tellurates leads to formation of cobalt tellurates and finally to CoO and TeO_2. At laboratory temperature all three substances are paramagnetic with μ_{eff} values corresponding to divalent cobalt.

Orthotelluric acid is a weak acid and dissociates to only the second step in water. The orthotellurates of the transition metals must thus be prepared either under hydrothermal conditions[1,2]

$$3\,M^{2+} + Te(OH)_6 = M_3TeO_6 + 6\,H^+$$

or through reaction in the solid phase[3,4]

$$6\,MO + 2\,TeO_2 + O_2 = 2\,M_3TeO_6$$

or through thermal decomposition of amporhous tellurates[5].

So far the orthotellurates of most first row transition metals have been prepared, *i.e.* chromium(III), manganese(II and III), iron(III), nickel(II), copper(II) and zinc(II). Only slight attention has been paid to cobalt(II) tellurates. Sokolov and coworkers[6] demonstrated by thermographic study of the CoO–TeO_2 system heated in the air that, in contrast to the similar system NiO–TeO_2, oxidation to tellurate does not occur. Similarly, Kasper[7] obtained only tellurate Co_5TeO_8 on heating CoO with TeO_2 or $Te(OH)_6$. The only mention of the preparation of Co_3TeO_6 is in the work by Sloczynski[8], who identified this substance among the products of thermal decomposition of cobalt(II) tellurate–molybdates. This author also described the preparation from CoO and TeO_2 by heating to 1173 K for 5 hours. The analogous compound Ni_3TeO_6 has the corrundum structural type with Te and Ni atoms octahedrally coordinated by oxygen atoms. Zupan, Kolar and Urbanc[9] measured the

magnetic properties and give a crystal field strength of $10Dq = 10700\ cm^{-1}$. The TeO_6 octahedra are trigonally deformed, as was confirmed by Blasse and Hordijk[10] from the vibrational spectra.

EXPERIMENTAL

Chemicals and Instruments

Orthotelluric acid was prepared from powdered tellurium (Pramet, Šumperk, Czechoslovakia) by oxidizing with hydrogen peroxide according to the method of Křepelka and Kubík[11]. The remaining chemicals were the products of Lachema, Brno, Czechoslovakia and were of *p.a.* purity. The titre of the 0·05M solution of EDTA was found using metallic bismuth (Merck, Darmstadt, GRF) by titration with xylenol orange indicator.

Densities were found pycnometrically by the Gay-Lussac method; the pycnometer was filled with xylene with density $\varrho = 0{\cdot}8549\ g\ cm^{-3}$. The X-ray powder patterns were obtained by the Debye–Scherrer method on a Mikrometa II instrument (Chirana, Czechoslovakia) using the Co K_α radiation with a wavelength of $\lambda = 179{\cdot}02$ pm filtered through Fe at a potential of 30 kV and current of 12 mA. The diffraction patterns were evaluated visually. Thermal analyses were carried out on a Derivatograph instrument[12] with a temperature program of $5\ K\ min^{-1}$. The reflectance spectra were measured in the visible and UV regions after dilution with MgO on a VSU-1 instrument (Zeiss, Jena, GDR) and in the near infrared region in nujol mull[13] on a Unicam SP-700 instrument. The IR spectra were measured in tripene on an UR-20 instrument, (Zeiss, Jena, GDR) over the range $400-4000\ cm^{-1}$ and in KBr pellets on a Perkin–Elmer 325 instrument over the range $200-4000\ cm^{-1}$. The magnetic susceptibility was measured by the Guoy method after dilution with NaCl over the range 77—298 K. The intrument was calibrated with $Co[Hg(SCN)_4]$.

Analytical Methods

The tellurium and cobalt contents were determined in a single sample. The sample was dissolved in HCl (insoluble $CoTeO_4$ after alkaline fusion) and reduced by boiling to Te(IV). After addition of a known excess of 0·05M-EDTA the pH was adjusted to 4·5—5·0 (methyl red) using NH_3 and acetic acid. The TeO_2 precipitate was filtered off and weighed after washing and drying. The EDTA was back-titrated with 0·1M-$MgSO_4$ using Eriochrome black T at pH 10.

Preparation

1) Amorphous cobalt tellurates. 200 ml of a 1M solution of $Co(NO_3)_2.6\ H_2O$ were mixed with 200 ml of a 0·5M solution of $Te(OH)_6$ and 200 ml of a 2M solution of NH_4OH were added dropwise with constant stirring. The grey-red precipitate formed was decanted several times with water and filtered off. After washing with water it was dried at 373 K in the air. Analysis of the amorphous product corresponds to the formula $CoH_4TeO_6.Co(OH)_2$. When the precipitate was cooled with ice in the aqueous suspension and immediately oxidized with 10% H_2O_2, a brown amorphous product with composition corresponding to the formula $CoH_3TeO_6.Co(OH)_3$ was obtained.

2) $CoTeO_4.1/2\ H_2O$. In a thick-walled glass ampoule with a volume of 50 ml were mixed 20 ml of a 0·01M solution of $Te(OH)_6$ and 20 ml of a 0·03M solution of $Co(NO_3)_2.6\ H_2O$ and the ampoule was heated in an autoclave at 523 K for 24 hours. The red-brown crystalline substance obtained was filtered off, washed with H_2O and dried at 373 K in the air.

3) $CoTeO_4$. Amorphous $CoH_4TeO_6.Co(OH)_2$ was heated to 700 K in a stream of oxygen for 24 hours. The brown powder obtained was boiled in HCl. After dissolving the other decomposition products, *i.e.* CoO or TeO_2, the remaining yellow-brown product was decanted several times with water, filtered off and dried in the air at 373 K.

4) Co_3TeO_6. Amorphous $CoH_4TeO_6.Co(OH)_2$ was heated in the air to 900 K for 24 hours. The blue product obtained was washed with dilute HCl, then with water, filtered off and dried at 373 K in the air.

Analyses of all the crystalline substances obtained are listed in Table I.

RESULTS

Thermal Analysis

It can be seen from Fig. 1 that the tellurate $CoTeO_4.1/2\ H_2O$ decomposes to the anhydrous salt at 470 K. Further thermal decomposition is the same as for $CoTeO_4$ – see Fig. 2. The oxidation state of tellurium is retained up to 930 K in both these tellurates which have a Co : Te ratio of 1 : 1; at this temperature reduction and decomposition to tellurite occur:

$$2\ CoTeO_4 \quad = \quad 2\ CoTeO_3 \ + \ O_2\ .$$

This substance decomposes further at 980 K and the TeO_2 freed sublimes:

$$CoTeO_3 \quad = \quad CoO \ + \ TeO_2\ .$$

Both reductions appear as marked endothermal effects on the DTA curve.

TABLE I
Analysis of the Compounds Prepared

Sample		Co, %	Te, %
Co_3TeO_6	calculated	44·2	31·9
m.w. = 400·4	found	44·5	31·6
	ratio	3·05	1·00
$CoTeO_4$	calculated	23·5	50·9
m.w. = 250·5	found	23·2	50·7
	ratio	0·99	1·00
$CoTeO_4.1/2\ H_2O$	calculated	22·7	49·2
m.w. = 259·5	found	23·0	49·1
	ratio	1·01	1·00

As can be seen in Fig. 3, Co_3TeO_6 is stable on heating in the air up to a temperature of 1070 K (the decrease recorded, 0·25%, apparently corresponds to impurities or to interaction with the crucible material). At 1230 K decomposition occurs,

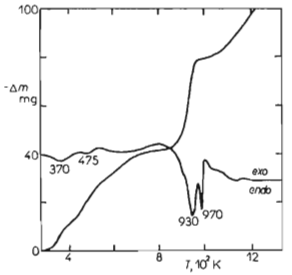

FIG. 1
GTA-DTA Curves of $CoTeO_4.1/2\ H_2O$
Sample weight of 786·2 mg.

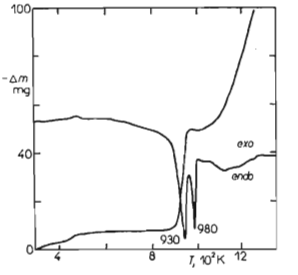

FIG. 2
GTA-DTA Curves of $CoTeO_4$
Sample weight of 797·8 mg.

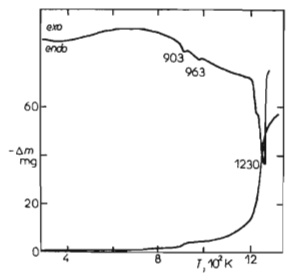

FIG. 3
GTA-DTA Curves of Co_3TeO_6
Sample weight of 784·0 mg.

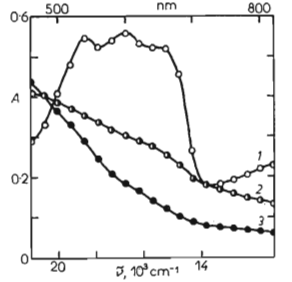

FIG. 4
Reflectance Spectra of Cobalt Tellurates: *1* Co_3TeO_6; *2* $CoTeO_4.1/2\ H_2O$; *3* $CoTeO_4$.

accompanied by a marked endothermal effect:

$$2\,Co_3TeO_6 \;=\; 6\,CoO \;+\; 2\,TeO_2 \;+\; O_2\,.$$

X-Ray Powder Patterns

The photographic recordings are evaluated in Tables II and III. The h, k, l indexes for the individual diffraction lines were assigned using nomograms[14]. The lattice

TABLE II

X-Ray Powder Patterns of $CoTeO_4$ and $CoTeO_4.1/2\ H_2O$

$CoTeO_4$				$CoTeO_4.1/2\ H_2O$			
I	d_0, pm	$h\ k\ l$	d_{calc}, pm	I	d_0, pm	$h\ k\ l$	d_{calc}, pm
8	325	0 1 2	325	9	329	0 1 2	327
8	256	0 2 2	257	8	258	2 2 0	258
1	230	1 3 0	230	1	232	1 3 0	231
10	172	1 4 1 }	171	10	173	1 4 1 }	172
		0 3 3 }				3 3 0 }	
5	163	2 4 0	163	3	165	0 2 4	163
3	154	3 3 2	155	2	155	3 3 2	156
2	147	2 4 2	148	2	148	2 4 2	149
2	146	1 5 0 }	143	4	140	1 5 1 }	141
		1 3 4 }				3 3 3 }	
3	140	1 5 1 }	143	1	129	4 4 0	129
		3 3 3 }		2	119	1 6 1 }	119
2	138	—				3 5 2 }	
2	137	—		2	113	4 5 1	113
3	128	4 0 4	128	1	110	3 6 0 }	109
5	119	1 6 1	118			4 5 2 }	
1	117	—		5	106	1 6 3	108
1	115	2 6 0	115	1	104	0 7 0 }	104
4	112	4 5 1	112			3 6 2 }	
2	109	3 6 0 }	108	2	101	6 4 0	101
		4 5 2 }		4	93	7 3 2	93
6	106	3 6 1	107				
2	105	4 4 4	105				
1	104	0 7 0 }	104				
		3 6 2 }					
1	103	1 7 0	103				
3	101	6 4 0	101				
6	92	7 3 2	92				

parameters were calculated according to our own programs on an EM-666 calculator (Hungary). The precision of the determination is given by the standard deviation $a = [\sum_{i=1}^{n}(a_i - a)^2/n - 1]^{1/2}$. Both tellurates with ratios Co : Te = 1 : 1 are cubic and their X-ray powder patterns are almost identical. The diffraction lines of $Co_3.TeO_6$ can be assigned the same system of *h*, *k*, *l* indexes as the diffraction lines of Ni_3TeO_6 and thus also the same space group R 3. Considering the differences in the lattice parameters of Co_3TeO_6 and Ni_3TeO_6, the two substances are not isomorphous but only isostructural.

Electronic Spectra

The reflectance spectra were recorded in the visible and UV regions. The UV region does not yield any valuable information, only broad overlapping bands. Similarly, the visible region (Fig. 4) for tellurates $CoTeO_4$ and $CoTeO_4.1/2\,H_2O$ does not yield decisive information on the coordination of the cobalt atoms, as the absorption maxima which may be present are overlapped by the Co ↔ O charge transfer bands. It is possible only to exclude tetrahedral coordination around the cobalt atoms. In the near infrared region, an absorption maximum was recorded at 8200 cm^{-1}, which can be assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition in octahedral cobalt coordination. The spectrum of Co_3TeO_6 has marked bands at 12530, 15310 and 18420 cm^{-1},

TABLE III
X-Ray Powder Pattern of Co_3TeO_6

I	d_0, pm	*h k l*	d_{calc}, pm	*I*	d_0, pm	*h k l*	d_{calc}, pm
7	429	0 1 2	430	8	165	1 2 5	165
3	402	0 0 4	399	1	155	2 0 8	157
5	311	0 1 4	314	1	148	2 2 0	147
5	297	1 1 0	295	1	138	1 3 3	137
3	276	1 1 2	277	2	133	1 3 4	134
3	267	0 0 6	266	1	129	2 2 6	129
10	252	0 2 1	252	1	126	0 4 2	126
1	238	1 1 4	237	1	107	2 3 6	107
1	197	1 1 6	197	1	105	1 4 5	105
1	188	1 2 1	192	3	103	1 4 6	103
2	185	0 2 6	184	1	101	1 5 2	102
1	176	0 0 9	177	1	99	3 3 0	98
2	171	0 3 0	170	1	98	0 5 5	98
				1	97	2 4 1	97

corresponding to splitting of the band at 16670 cm^{-1}, belonging to the transition $^4A_2 \rightarrow {}^4T_1(P)$ in tetrahedral cobalt coordination. The splitting is a result of spin-orbital interaction. The near infrared region contains two bands at 8900 and 7200 cm^{-1} with centre at 8300 cm^{-1}, corresponding to the transition $^4A_2 \rightarrow {}^4T_1(F)$. These values yield the parameter $10Dq = 4500\ cm^{-1}$.

Infrared Spectra

Assignment of the absorption maxima to the individual vibrations (Table IV) is based on the assumption, confirmed by many authors, that the tellurate anion has octahedral shape .For a regular octahedron, only the ν_3 and ν_4 vibrations should be IR-active, while the ν_1, ν_2 and ν_5 vibrations should be active in the Raman spectra. This is true for the spectra of $CoTeO_4$ and $CoTeO_4.1/2\ H_2O$, where the infrared spectrum also contains the ν_1 vibration as a result of interaction with lattice vibrations or tetragonal deformation of the octahedron. The two spectra are very similar and, in contrast to Co_3TeO_6, vibrations corresponding to H_2O, *i.e.* δ(H—O—H) deformation at 1625 cm^{-1} and ν(O—H) valence vibration at 3400 cm^{-1}, are visible. As the latter is also present in the spectrum of Co_3TeO_6 obtained using a KBr pellet but is missing in the spectrum obtained using tripene, it can be assigned to atmospheric moisture. The IR spectrum of this compound also contains the ν_1, ν_2 and ν_5 vibrations, indicating that the tellurate octahedron lies in a field of lower symmetry, probably trigonal. The Co—O vibration is split into two bands at 230 and 310 cm^{-1}, similarly to $CoTeO_4$ at 260 and 325 cm^{-1}. The $CoTeO_4.1/2\ H_2O$ spectrum has only a single band at 290 cm^{-1}.

TABLE IV
Infrared Spectra of Cobalt Tellurates

Co_3TeO_6 $\tilde{\nu}$, cm^{-1}	$CoTeO_4$ $\tilde{\nu}$, cm^{-1}	$CoTeO_4.1/2\ H_2O$ $\tilde{\nu}$, cm^{-1}	Assignment
700 s	740 s	740 s	ν_1
570 m	—	—	ν_2
640 s	700 s	680 s	
535 s	540 m	520m	ν_3
450 s	480 m (sh)	380 m (sh)	
350 m	350 m	340 m	ν_4
400 m	—	—	ν_5
—	1 625 w	1 625 w	δ(H—O—H)
3 400 w	3 400 w	3 400 w	ν(O—H)

Magnetic Properties

In order to determine the type of coordination of the cobalt atoms in Co_3TeO_6, the dependence of the magnetic susceptibility on temperature was measured. The value of the temperature-independent paramagnetism, 11 $m^3\,kg^{-1}$, and the Weiss constant, $\Theta = -64$ K, are unusually large and indicate large magnetic exchange interactions. This interaction obscures finer effects resulting from the differences in the coordination sphere of the cobalt atoms and thus this measurement yielded no information on the type of coordination. The values of the effective magnetic moments of the cobalt atoms at room temperature are listed in Table V. All the values are larger than the pure spin value, 3·87 μ_B.

DISCUSSION

The cobalt tellurates prepared in this work are of two kinds. The first type includes $CoTeO_4$ and $CoTeO_4.1/2\,H_2O$, whose electronic spectra indicate octahedral coordination of Co(II). As previous data indicate unambiguously that Te(IV) is also octahedrally coordinated by oxygen, it can be assumed that the structures of these substances will be similar to that of rutile. This structure, however, contains only two formula units per unit cell, while $CoTeO_4$ contains 6 formula units per unit cell. Thus it can be assumed that a certain superstructure is formed, derived from the rutile structure type, similarly as with Fe_2TeO_6 (see[15]), where the stoichiometry indicates a tellurium–transition metal ratio of 1 : 2. This structural arrangement is very compact, reflected in the poor solubility of these substances. However, $CoTeO_4.1/2\,H_2O$, prepared by hydrothermal synthesis, is readily soluble in concentrated hydrochloric acid. Simultaneously, the difference between the experimentally determined density and that calculated on the basis of the lattice parameters is quite

TABLE V
Properties of Cobalt Tellurates

Value	Co_3TeO_6	$CoTeO_4$	$CoTeO_4.1/2\,H_2O$
ϱ_{exp}, g cm^{-3}	5·51	6·49	6·40
ϱ_{calc}, g cm^{-3}	5·53	6·51	6·48
Z	4	6	6
μ_{eff}, μ_B	4·17	4·22	4·22
Coordination of Co	tetr. + oct. (?)	octahedral	octahedral
a, pm	590 ± 6	727 ± 4	730 ± 6
c, pm	1 594 ± 15		

large. It could be suggested that this substance was prepared under conditions where the structural arrangement was incomplete and the product could contain lower amorphous tellurates with Te—O—H bonds, which also contain water of crystallization. The ν(O—H) vibration band is present in both cases in the vibration spectra, which can be explained by pointing out that both substances were washed with water. The two substances differ primarily in their thermal analysis, where the loss of water in $CoTeO_4.1/2\ H_2O$ is apparent.

The second type of tellurate is Co_3TeO_6. This is similar to Ni_3TeO_6, which has rhombohedral structure with space group R3 and unit cell dimensions of $a = 510$ pm, $c = 1376$ pm. Both the Ni and Te atoms are coordinated octahedrally[4]. The same system of h, k, l indexes can be assigned to the diffraction lines of Co_3TeO_6, so that it can be assumed that the two substances are isostructural. It, however, follows from the electron spectrum that at least one of the cobalt atoms is tetrahedrally coordinated by oxygen atoms. Possible absorption bands corresponding to octahedrally coordinated Co(II) would then be overlapped by bands with much greater intensity and would not be visible in the spectrum. Attempts to define the type of coordination through examining the thermal dependence of the paramagnetic susceptibility indicated that the mutual magnetic coupling of the individual cobalt atoms is very marked, masking other finer effects. Antiferromagnetism, if present, apparently appears only at temperatures below 50 K. The value of the parameter $10Dq = 4500\ cm^{-1}$, found from the electronic spectrum, corresponds to tetrahedral coordination of the cobalt atom. If the magnetic moment were influenced by the spin-orbital interaction alone, then the formula

$$\mu_{eff} = \mu_{SO}(1 - 4\lambda/10Dq)$$

yields a value of the spin-orbital interaction constant of $\lambda = -87\ cm^{-1}$. Compared with the value found for the octahedrally coordinated nickel atom, where $10Dq = 10700\ cm^{-1}$, $\lambda = -324\ cm^{-1}$, this value is much lower[9]. The crystal field parameters of $CoTeO_4$ and $CoTeO_4.1/2\ H_2O$ could not be found, as only a single band in the near IR region was available from the measurement.

Comparison of the vibration spectra of Ni_3TeO_6 and Co_3TeO_6 indicates that, in agreement with the slight increase in the ionic character of the Co—O bond compared with the Ni—O bond, the Te—O bond is stronger and thus the valence vibration band appears at somewhat higher wavenumbers. As a result of the trigonal deformation of the TeO_6 octahedra, the ν_1, ν_2 and ν_5 vibrations also become active in the IR spectra. In the $CoTeO_4$ and $CoTeO_4.1/2\ H_2O$ structures, the tellurate octahedra are probably joined in chains by their edges. This is also confirmed by the absence of bands corresponding to ν_2 and ν_5. The remaining oxygen atoms in the axial positions participate in the formation of coordination octahedra around the cobalt atom.

It follows from thermal analysis of cobalt(II) tellurates that they are not thermally stable and decompose spontaneously above 1100 K. This finding is in agreement with those works[6,7] which point out the impossibility of direct synthesis from CoO and TeO_2 by simple heating in the air. Thus cobalt(II) tellurates behave similarly to the tellurates of the alkali metals, as heating results in simultaneous decomposition and reduction of Te(VI) to Te(IV).

The authors thank Miss J. Blažková for carrying out the magnetic susceptibility measurements and Dr J. Podlaha for valuable discussions.

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Translated by M. Štulíková.