

$M(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($M = \text{Co}, \text{Zn}$): Preparation and Crystal Structure Determination

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Single crystals of cobalt perrhenate tetrahydrate and zinc perrhenate tetrahydrate were characterized by X-ray single-crystal structure analysis (299 K; MoK α radiation, 71.069 pm). Crystals of $\text{Co}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ are triclinic, with space group $P\bar{1}$. $\text{Co}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ has the following parameters: $a = 654.4(9)$ pm, $b = 687.9(8)$ pm, $c = 727.6(2)$ pm, $\alpha = 64.61(1)^\circ$, $\beta = 70.52(2)^\circ$, $\gamma = 71.76(1)^\circ$, and $D_x = 3.84$ g cm⁻³. $\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ has the following parameters: $a = 651.0(3)$ pm, $b = 697.2(3)$ pm, $c = 721.0(3)$ pm, $\alpha = 64.53(1)^\circ$, $\beta = 70.31(1)^\circ$, $\gamma = 72.10(1)^\circ$, and $D_x = 3.85$ g cm⁻³. The structure consists of almost tetrahedral ReO_4^- units, octahedrally coordinated cations M^{2+} ($M = \text{Co}, \text{Zn}$), and water molecules. Each M^{2+} cation is surrounded by six oxygen atoms belonging to two different ReO_4^- anions and four water molecules forming a slightly distorted octahedron. The octahedra and tetrahedra are linked to each other parallel to [101]. © 1995 Academic Press, Inc.

INTRODUCTION

The salts of the perrhenic acid, the perrhenates, contain the tetrahedral ReO_4^- ion (1). In contrast to deep purple colored MnO_4^- , the ReO_4^- is colorless and a very weak oxidizing agent.

Although a considerable number of perrhenates of alkaline, alkaline-earth, and transition metal cations have been reported in the literature, only a few crystal structures were described.

In 1978 Zaitseva *et al.* prepared cobalt perrhenate tetrahydrate by reaction of cobalt carbonate with aqueous perrhenic acid (2). Despite DTA/TG, infrared spectroscopy, and powder diffraction, no crystal structure was determined.

The synthesis of zinc perrhenate hydrate was first reported by Wilke-Dörfurt and Gunzert in 1933 (3). Smith and Maxwell described a reaction of zinc oxide, hydroxide, or carbonate with perrhenic acid (4). The product obtained was the tetrahydrate and they determined its solubility and density. Zaitseva *et al.* reported on the

preparation of zinc perrhenate tetrahydrate, thermo-analytical measurements, and X-ray powder diffraction measurements (5).

EXPERIMENTAL

The preparation of the perrhenates was carried out in two steps:

1. A colorless solution of perrhenic acid, HReO_4 , was prepared by solving 500 mg high-purity rhenium powder (99.995%, Aldrich) in 20 ml 30% hydrogen peroxide (Aldrich) (6).

2. A 20% excess of CoCO_3 (99.999%, Aldrich) (ZnCO_3 , 99.99%, Aldrich) was brought into the solution of the acid. At a temperature of 50–60°C the reaction took place under release of CO_2 bubbles. At the end of the reaction the excess carbonate was filtered off and the solution was kept in a water bath (56°C) until a crystalline surface was built. Then the solution was removed from the water bath and kept at room temperature. After a period of 5–7 days crystals large enough for a single-crystal X-ray measurement had grown.

CRYSTAL STRUCTURE DETERMINATION

$\text{Co}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$

Intensities for the structure determination of the $0.2 \times 0.1 \times 0.2$ mm³ sized pink crystal of cobalt perrhenate tetrahydrate were recorded on an Enraf Nonius CAD 4 diffractometer with graphite monochromatized MoK α radiation and a scintillation counter. Lattice parameters of the triclinic cell and the orientation matrix were obtained from a least-squares refinement of 22 reflections in the range $4.1^\circ \leq 2\theta \leq 48.2^\circ$. The X-ray intensity data of 1699 reflections were collected at 299 K in the range $2^\circ \leq 2\theta \leq 60^\circ$ using the $\omega/2\theta$ scanning mode and the collection range was $h = \bar{9}, 9$; $k = \bar{9}, 9$; and $l = 0, 10$. The standard reflections 222, 445, and $1\bar{1}\bar{2}$ were monitored every 3 hr and showed consistency throughout the measurement. The data collection time was 20.9 hr. An absorption cor-

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TABLE 1
Final Cell Parameters and Agreement Factors

	Co(ReO ₄) ₂ · 4H ₂ O	Zn(ReO ₄) ₂ · 4H ₂ O
<i>a</i> (pm)	654.4(9)	651.0(3)
<i>b</i> (pm)	687.9(8)	697.2(3)
<i>c</i> (pm)	727.6(2)	728.3(3)
α (°)	64.61(1)	64.53(1)
β (°)	70.52(2)	70.31(1)
γ (°)	71.76(1)	72.10(1)
<i>V</i> (pm ³)	273.35 × 10 ⁶	275.79 × 10 ⁶
<i>R</i> _{eq}	0.0619	0.0570
<i>R</i>	0.0651	0.0495
<i>R</i> _w	0.0689	0.0483

rection was performed by psiscan with the reflection $\bar{1}13$, $\bar{2}13$, $\bar{2}25$, $\bar{4}26$, and $\bar{3}15$; $t_{\min} = 55.37\%$ and $t_{\max} = 99.86\%$. Data consisting of 1586 unique reflections with $R_{\text{int}} = 0.063$ were obtained. For structure determination and refinement, 1488 reflections with $F < 2\sigma(F)$ were used. The structure was solved using the program SHELXS-86 (7). The positions of the cobalt, rhenium, and oxygen atoms could be deduced from a Patterson synthesis. The hydrogen atoms could not be located, even with a difference Fourier map. For the refinement the program package SHELX-76 (8) was used. Atomic parameters and anisotropic temperature coefficients (Table 2) were refined for Co, Re, and O with a full-matrix least-squares method using 71 parameters. Table 3 shows interatomic bond distances and bond angles.

Zn(ReO₄)₂ · 4H₂O

A colorless crystal with approximate dimensions $0.2 \times 0.4 \times 0.7 \text{ mm}^3$ was mounted on a STOE-STADI-4 automatic four-circle diffractometer with MoK α radiation, graphite monochromator, and scintillation counter. Cell dimensions and crystal orientation were obtained by least-squares refinement based on the setting of 22 reflections with 2θ ranging from 55.4° to 59.4° . At 298 K X-ray intensity data were collected in the range $3^\circ \leq 2\theta \leq 60^\circ$ using the $\omega/2\theta$ scanning mode. The collection range was $h = \bar{9}, 2$; $k = \bar{9}, 9$; and $l = \bar{10}, 10$. Three standard reflections chosen to lie in different regions of reciprocal space were measured every 3 hr and showed no significant variation of their intensities.

A numerical absorption correction was carried out using the crystal faces $(0\bar{1}1)$, $(1\bar{1}0)$, (011) , $(\bar{1}10)$, $(\bar{1}\bar{1}0)$, $(\bar{1}\bar{1}1)$, and (110) with SHELX-76. Measuring 2619 reflections, 1598 unique reflections with $R_{\text{int}} = 0.034$ were obtained. For structure determination and refinement, 1585 reflections with $F > 2\sigma(F)$ were used. The structure was solved with SHELXS-86. A Patterson map showed

the positions of the Zn, Re, and O atoms. A difference Fourier map did not allow the location of the hydrogen atoms. The structure was refined by least-squares methods (SHELX-76) including anisotropic temperature coefficients for Zn, Re, and O atoms (Table 2). Seventy-one

TABLE 2
Final Atomic Parameters and Anisotropic Temperature Coefficients

Atomic parameters for Co(ReO ₄) ₂ · 4H ₂ O						
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>			
Re	0.0857(1)	0.3213(1)	0.2921(1)			
Co	0.5	0	0			
O1	0.8031(3)	0.3239(3)	0.3809(2)			
O2	0.4848(3)	0.6954(2)	0.2299(2)			
O3	0.1242(4)	0.5785(4)	0.0927(2)			
O4	0.2107(3)	0.1155(3)	0.1909(3)			
O5	0.6841(4)	0.0751(3)	0.1281(4)			
O6	0.1958(5)	0.2776(4)	0.4886(3)			
Atomic parameters for Zn(ReO ₄) ₂ · 4H ₂ O						
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>			
Re	0.0853(1)	0.3205(1)	0.2929(1)			
Zn	0.5	0	0			
O1	0.8005(2)	0.3297(1)	0.3794(1)			
O2	0.5162(2)	0.2995(2)	0.7672(2)			
O3	0.1352(3)	0.5612(2)	0.1029(3)			
O4	0.2033(2)	0.1202(1)	0.1918(2)			
O5	0.6818(3)	0.0664(2)	0.1392(1)			
O6	0.1980(2)	0.2684(2)	0.4945(1)			
Anisotropic temperature coefficients for Co(ReO ₄) ₂ · 4H ₂ O						
Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Re	0.029(1)	0.024(1)	0.019(1)	-0.003(2)	-0.006(2)	-0.003(2)
Co	0.025(2)	0.019(2)	0.018(2)	-0.003(2)	-0.007(2)	-0.001(2)
O1	0.034(7)	0.051(7)	0.028(8)	-0.009(7)	0.008(8)	0.009(7)
O2	0.038(7)	0.024(7)	0.027(7)	0.006(7)	-0.008(8)	0.002(6)
O3	0.094(8)	0.053(8)	0.024(7)	0.005(8)	-0.028(8)	-0.045(8)
O4	0.033(7)	0.038(8)	0.043(8)	0.015(7)	-0.008(6)	-0.015(6)
O5	0.074(8)	0.039(8)	0.102(9)	-0.024(9)	-0.072(9)	0.013(9)
O6	0.119(8)	0.046(9)	0.039(8)	0.110(8)	-0.042(9)	-0.024(9)
Anisotropic temperature coefficients for Zn(ReO ₄) ₂ · 4H ₂ O						
Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Re	0.031(1)	0.028(2)	0.019(2)	0.004(2)	-0.007(2)	-0.004(2)
Zn	0.033(1)	0.031(1)	0.027(1)	-0.008(1)	-0.010(1)	-0.003(1)
O1	0.035(6)	0.055(7)	0.037(5)	-0.015(6)	-0.000(6)	-0.004(5)
O2	0.039(6)	0.033(5)	0.028(4)	-0.004(5)	-0.009(4)	-0.003(4)
O3	0.097(9)	0.058(6)	0.047(7)	0.011(5)	-0.040(6)	0.040(6)
O4	0.049(8)	0.061(8)	0.041(8)	0.024(6)	0.000(8)	0.008(5)
O5	0.057(8)	0.056(7)	0.066(6)	-0.020(7)	-0.028(7)	-0.015(6)
O6	0.051(7)	0.087(9)	0.046(6)	-0.026(6)	-0.026(6)	-0.001(6)

TABLE 3
Final Interatomic Distances (pm) and Bond Angles ($^\circ$)

	$\text{Co}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$
Re-O1	174(2)	174(1)
Re-O3	177(2)	170(1)
Re-O4	173(2)	174(1)
Re-O6	169(2)	171(1)
<i>M</i> -O2	205(2)	205(1)
<i>M</i> -O4	210(1)	214(1)
<i>M</i> -O5	204(2)	205(1)
<i>M</i> -Re	363(3)	365(2)
Re-Re	434(2)	437(2)
O1-Re-O3	108.3(10)	109.2(6)
O1-Re-O4	108.6(9)	108.5(6)
O1-Re-O6	110.7(10)	110.8(5)
O3-Re-O4	109.6(9)	109.3(6)
O3-Re-O6	109.7(9)	109.5(6)
O4-Re-O6	110.0(9)	109.5(6)
O2- <i>M</i> -O4	86.2(6), 93.8(8)	91.1(5), 93.1(4)
O2- <i>M</i> -O5	86.2(6), 93.8(8)	91.1(5), 93.1(4)
O4- <i>M</i> -O5	89.8(9),	91.2(4),

parameters were refined. Final cell parameters and agreement factors are listed in Table 1. Table 3 shows interatomic bond distances and bond angles.

DESCRIPTION OF CRYSTAL STRUCTURES AND DISCUSSION

The crystal structure of the perrhenates is displayed in Figs. 1 and 2. $\text{MO}_2(\text{OH}_2)_4$ octahedra and ReO_4 tetrahedra, linked to each other, are the main feature of the two structures (Fig. 1). They form $M(\text{OH}_2)_4(\text{ReO}_4)_2$ units parallel to [101] (Fig. 2). The separate units are fixed to one another by hydrogen bonds between water molecules of one and oxygen atoms of the neighboring units. This can be seen from the infrared spectra of the substances. An unperturbed H-O bond shows a stretching frequency near 3700 cm^{-1} . When the hydroxyl group enters into hydrogen bonding the stretching frequency shifts to lower values. This change progresses with increasing strength of the hydrogen bonds. The observed values of about 3400 cm^{-1} for the stretching frequency of both substances shows the existence of fairly strong hydrogen bonds (9).

The ReO_4 tetrahedra are only slightly distorted with a mean Re-O distance of 173.1(2) pm (cobalt perrhenate tetrahydrate) and 172.7(2) pm (zinc perrhenate tetrahydrate). These values correspond well with the Re-O distances in other perrhenates: NH_4ReO_4 , 172.0(5) pm (10); LiReO_4 , 171.5(3) pm (11); KReO_4 , 172.3(4) pm (12); Ca-

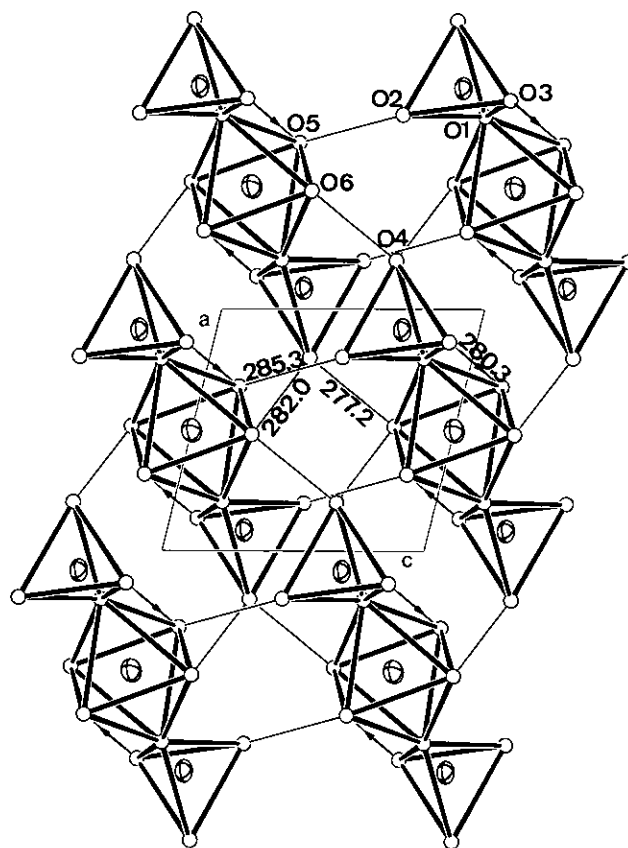


FIG. 1. Ortepe plot of $\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ illustrating hydrogen bonding between the $M(\text{OH}_2)_4(\text{ReO}_4)_2$ units. Lines with arrowheads connect an O(3) with a hidden O(5) of another unit. Values denote interatomic distances (pm).

$(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$, 172.4(13) pm (13); and $\text{HReO}_4 \cdot \text{H}_2\text{O}$, 173.7 pm (14). They show good agreement with the sum of effective ionic radii (15).

Each transition metal atom is surrounded by six oxygen atoms—two from ReO_4 tetrahedra and four water molecules—forming a fairly regular octahedron. The distances between the transition metal atom and the oxygen atom of the water molecules are nearly identical (204–205 pm), whereas the distances between the transition metal atom and the oxygen atoms of the ReO_4 tetrahedra are much longer (210–214 pm). The reason for this is the polarizing effect of the Re^{7+} ion.

MAGNETIC SUSCEPTIBILITY

Using a Lake Shore Cryotronics Model 7000 AC susceptometer, the susceptibilities of the hydrates were measured between 15 and 200 K. While the zinc compound shows diamagnetic behavior (in accordance with the $3d^{10}$ ground state), for the cobalt compound a paramagnetic Curie-Weiss law was observed with $\Theta = 4\text{ K}$ and $\mu = 4.4\ \mu_B$. The difference to the spin-only value of

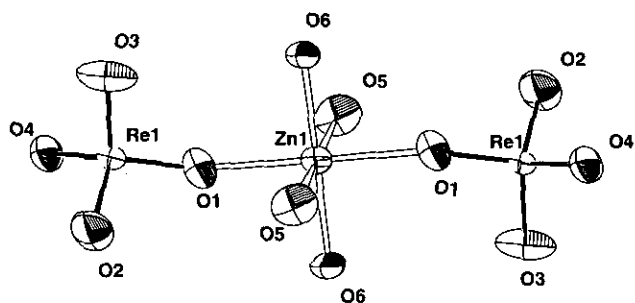


FIG. 2. $M(\text{OH}_2)_4(\text{ReO}_4)_2$ unit of zinc perrhenate tetrahydrate ($\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$). Thermal ellipsoids are based on a 90% probability.

TABLE 4
Results of Thermal Studies

	Temperature (°C)	Note
$\text{Co}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$	120–130	Loss of two H_2O molecules
	165–175	Loss of two H_2O molecules
	840–930	Decomposition
$\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$	130–145	Loss of two H_2O molecules
	175–185	Loss of two H_2O molecules
	748	Melting point
	740–1130	Decomposition

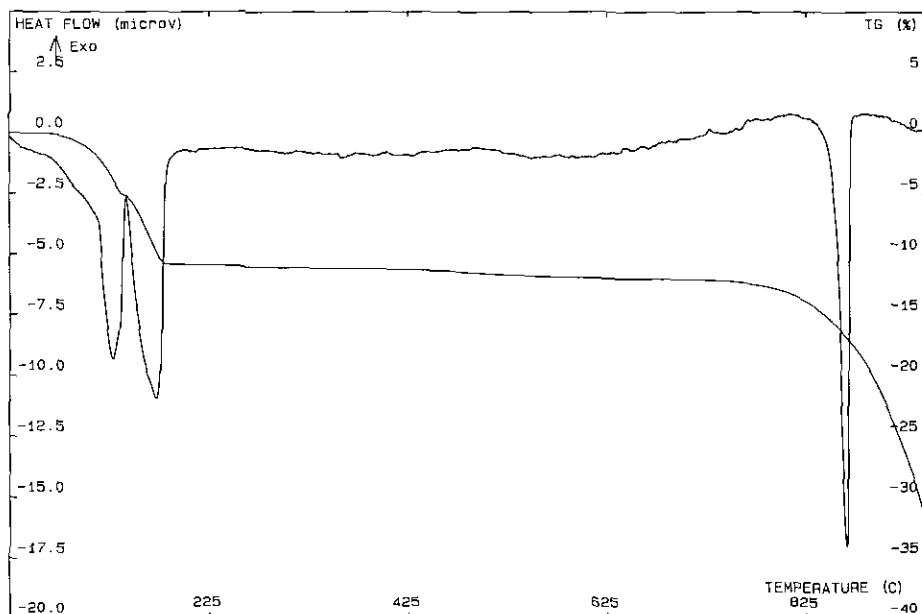


FIG. 3. DTA/TG curve of $\text{Zn}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ showing the two steps of dehydration.

$3.87 \mu_B$ arises from contribution of the angular momentum which is not quenched completely.

THERMAL DEHYDRATION

Thermoanalytical studies were carried out with a Setaram DTG 92.16.18 DTA/TG system. Additionally temperature-dependent X-ray measurements were made using the high-temperature attachment of the STOE diffractometer. At 34 different temperatures between room temperature and 800°C , powder patterns were recorded in the range $5^\circ \leq 2\theta \leq 50^\circ$. The number of steps of the dehydration was obtained by comparing the powder patterns.

Both perrhenates show identical thermal behavior. Two dehydration steps are observed below 200°C . No phase transition is detected between the temperatures of dehydration and decomposition.

The decomposition takes place in different steps under release of Re_2O_7 with the oxides of the divalent cations as residues. Table 4 and Fig. 3 summarize the results of the thermal studies.

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