

CRYSTAL STRUCTURE OF A NEW BISMUTH PERRHENATE $\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ CARLOS MUJICA^a, JAIME LLANOS^a, VÍCTOR SÁNCHEZ^{a,*}, PAOLA BOCAZ^a
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ABSTRACT

Monoaquatris(tetraoxorhenate (VII)) bismuth(III), $\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ was prepared by reaction of $(\text{BiO})_2\text{CO}_3/\text{Bi}_2(\text{CO}_3)_3$ with concentrated HReO_4 at room temperature. The pale yellow compound crystallize triclinic in the space group $P1\bar{1}$, (No. 2); with two formula units per unit cell ($a = 746.0(1)$ pm, $b = 777.1(2)$ pm, $c = 990.5(2)$ pm, $\alpha = 100.99(3)^\circ$, $\beta = 99.88(3)^\circ$, $\gamma = 100.17(3)^\circ$). The main feature of the crystal structure is a distorted bicapped trigonal prism of $\text{Bi}[(\text{ReO}_4)_{3/2}(\text{ReO}_4)_{2/2}(\text{ReO}_4)_{2/2}(\text{H}_2\text{O})]$, which are connected each other through $[\text{ReO}_4]$ -tetrahedra to form a three-dimensional network. In the titled compound, the cation Bi^{3+} is eightfold coordinated which agree with the tendency observed in other compounds of the family.

Keywords: crystal structure, perrhenate anions, X-ray diffraction, coordination number

INTRODUCTION

In previous publications we reported the synthesis and crystal structure of tetraoxorhenates (VII) of some rare earth metals like Gd, Sm, Eu, Yb, La¹⁻⁵. In these perrhenates, the coordination number of the central cation depends mainly on the size of the 3+ ion. This dependence is also observed for many others compounds based on perrhenate as a ligand, including alkalines-earth metals, transition metals and rare-earth ions as central cation⁶⁻¹⁸. All of them with oxidation states 2+ or 3+. According to this, we hypothesized that the coordination number of bismuth 3+ should be also in agreement with the dependence mentioned above. On the other hand, the distance between the central cation and oxygen for all of the perrhenate compounds reveals the presence of ionic interaction, considering the sum of the ionic radii. In this sense we also expected an interaction with ionic character between the ReO_4 ligands and the central Bi atom.

EXPERIMENTAL

Synthesis:

$\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ was synthesized dissolving stepwise $(\text{BiO})_2\text{CO}_3/\text{Bi}_2(\text{CO}_3)_3$ in perrhenic acid and keeping the solution below pH = 3. HReO_4 was prepared according to the well known method by reacting H_2O_2 (Merck, 30%) with solid rhenium powder (Aldrich 99.9%). $(\text{BiO})_2\text{CO}_3/\text{Bi}_2(\text{CO}_3)_3$ was prepared mixing BiCl_3 and a saturated aqueous solution of Na_2CO_3 with permanent stirring during 24h. Subsequently, the product was washed several times, centrifuged and dried at 60°C. Well shaped, colorless crystals of $\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ were grown by slow concentration of the acid mother solution.

Structure determination:

A single crystal with approximate dimensions of 0.14×0.13×0.11 mm was isolated in a glove box under Argon atmosphere ($\text{O}_2 < 1.0$ ppm; $\text{H}_2\text{O} < 1.0$ ppm) and fixed in a sealed glass capillary for x-ray single crystal analysis. Intensity data were collected on a STOE-IPDS diffractometer. The unit cell was determined from a setting of 1679 reflections in the range $4.32^\circ \leq 2\theta \leq 45.0^\circ$; Numerical absorption correction was performed with optimized shape of the crystal¹⁹. The structure was solved by direct methods (SHELXS-97) in the space group $P1\bar{1}$, (No. 2) and subsequently refined by least-squares methods using SHELXL-97⁷. Crystallographic details are given in Table 1.

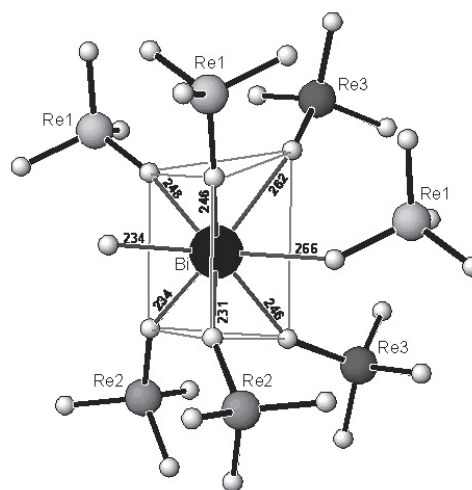
RESULTS AND DISCUSSION

$\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ crystallizes in a new structure type in the centrosymmetric space group $P1\bar{1}$, (No. 2), with two formula units in the unit cell. The Bi(III) ion shows a 8-fold coordination where the H_2O molecule and one ReO_4 anion are in capped position over rectangular faces and the other six ReO_4 anions form the distorted trigonal prism (Fig.1).

Three crystallographic independent positions for the Re atoms are found in the crystal structure. They bridge the Bi-polyhedra in different way and directions building up a three dimensional network: Re(1)-tetrahedra bonds three Bi atoms bridging them along [100] (Fig.2a), two Re(2)-tetrahedra bonds two Bi atoms along [001] (Fig.2b) and two Re(3)-tetrahedra bonds two Bi atoms along [011] (Fig.2c).

Table 1: Crystallographic data and detail of the structure analysis

Formula; molar mass	$\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$; 976.59 amu	
Crystal	Colorless prism; 0.14 x 0.13 x 0.11 mm	
Space group; formula units	$P1\bar{1}$, (No. 2); Z = 2	
Lattice parameter (294 K)	$a = 746.0(1)$ pm $b = 777.1(2)$ pm $c = 990.5(2)$ pm	$\alpha = 100.99(3)^\circ$ $\beta = 99.88(3)^\circ$ $\gamma = 100.17(3)^\circ$
Volume; density	$542.2(2) \times 10^6 \text{ pm}^3$; 5.982 g cm ⁻³	
Data collection	STOE-IPDS; Ag K α radiation ($\lambda = 56.086$ pm, graphite monochromator; 200 exposures, $\Delta\phi = 1.0^\circ$)	
Structure refinement	SHELXS-97, SHELXL-97 [20] Full-matrix least-squares on F^2 (155 parameter)	
Measured/unique reflections	6973/2744	
R_{int}	0.0650	
Measured Range	$4.32^\circ \leq 2\theta \leq 45.0^\circ$; $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$	
Observed reflections ($F_o > 4.0\sigma(F_o)$)	2004	
$R(F)$; wR2	0.0313/0.0529 Goof = S = 0.906 $\Delta\rho_{\text{max}} = 2.42 \text{ e } \text{Å}^{-3}$; $\Delta\rho_{\text{min}} = -2.63 \text{ e } \text{Å}^{-3}$	

Figure 1: Coordination polyhedron of Bismuth in $\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$.

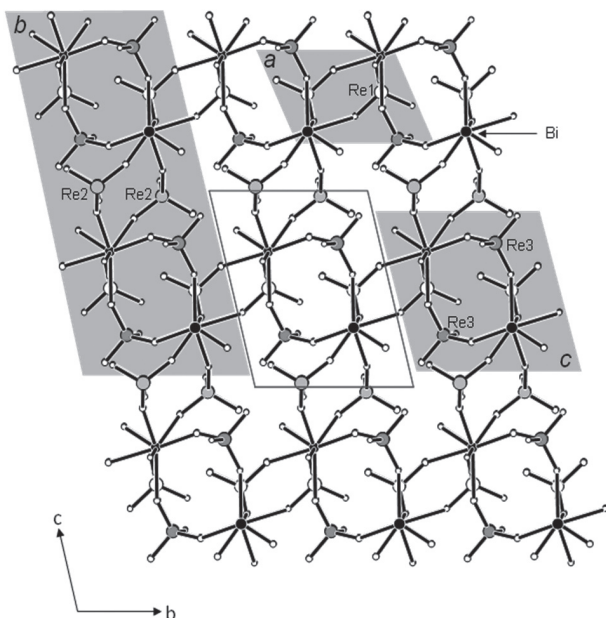


Figure 2: Projection of the crystal structure of $\text{Bi}(\text{ReO}_4)_3 \cdot \text{H}_2\text{O}$ along $[100]$. (For the labeled gray zones a, b and c, see text).

The mean bond length $d(\text{Re}-\text{O}) = 172$ pm in ReO_4 ; tetrahedra is approximately the same observed for rare-earth perhenates, transition metal perhenates and earth alkaline perhenates¹⁻¹⁸

The dependence of coordination number upon the Pauling's ionic radii²¹ observed for the central cation in this case, agrees with the relationship for other related compounds. Namely, when the ionic radius of the metal lays in the range 0.6Å to 0.8Å the coordination number is 6 and when the ionic radii lays in the range 1.00Å to 1.20Å the coordination number is 9. In this work, the ionic radii of $\text{Bi}(\text{III})$ is comparable with those of $\text{Yb}(\text{III})$ and $\text{Ca}(\text{II})$ and the three of them are eightfold coordinated ($\text{CN} = 8$), confirming the behavior observed for other compounds of the family (Fig.3).

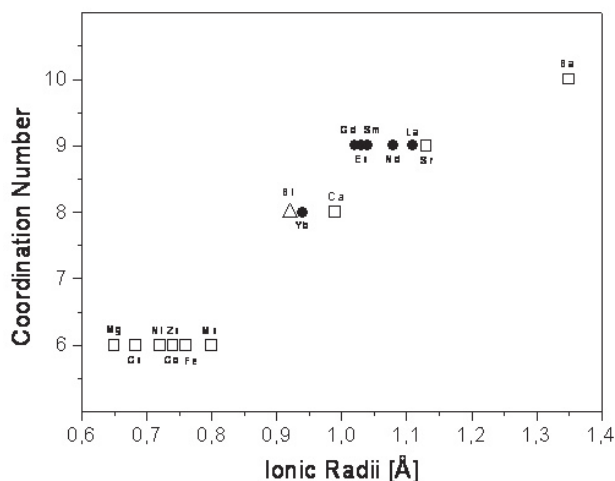


Figure 3: Correlation between coordination number and ionic radii observed for some metal cations in perhenates, with oxidation state (\square , M^{2+} ; \bullet , M^{3+} ; \triangle , Bi^{3+})

Taking that into account, we can infer that when the ionic radii lays approximately between 0.9 to 1.0Å the coordination number of central cation should be 8. Coordination number 7 could be observed when the ionic radii are approximately in the range 0.8 to 0.9Å , leading to different structures, but those are not observed due to the relatively instability of this coordination number.

Table 2: Atomic coordinates and equivalent displacement parameter U_{eq} (in pm^2). Standard deviations are given in parentheses. *

Atom	<i>X</i>	<i>y</i>	<i>z</i>	U_{eq}
Re1	0.27227(6)	0.23305(7)	0.50558(5)	116(1)
Re2	0.77964(6)	0.69835(6)	0.97496(5)	99(1)
Re3	0.75648(7)	0.27061(7)	0.26456(6)	143(1)
Bi	0.83294(6)	0.28758(6)	0.69263(5)	119(1)
O1	0.2419(12)	0.4106(12)	0.4330(10)	230(20)
O2	0.1621(12)	0.2391(14)	0.6432(10)	270(30)
O3	0.1783(12)	0.0358(11)	0.3819(9)	180(20)
O4	0.5061(12)	0.2464(14)	0.5654(10)	270(20)
O5	0.5926(13)	0.7060(12)	0.0496(10)	200(20)
O6	0.8092(12)	0.8632(12)	0.8855(10)	240(20)
O7	0.9799(12)	0.7391(13)	1.1039(10)	240(20)
O8	0.7415(13)	0.4868(12)	0.8626(11)	250(20)
O9	0.7113(18)	0.0897(15)	0.1283(12)	500(40)
O10	0.5556(13)	0.3489(18)	0.2700(11)	420(30)
O11	0.9241(13)	0.4350(13)	0.2322(12)	300(30)
O12	0.8345(13)	0.2149(15)	0.4240(11)	330(30)
O13	0.6320(12)	0.1174(13)	0.7984(10)	210(20)

Table 3: Anisotropic displacement parameter U_{ij} (pm^2). Standard deviations are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re1	102(2)	130(2)	120(3)	27(2)	23(2)	34(2)
Re2	116(2)	86(2)	114(2)	37(2)	35(2)	43(2)
Re3	143(2)	132(2)	137(3)	21(2)	23(2)	-1(19)
Bi	118(2)	124(2)	113(2)	24(2)	22(2)	27(2)
O1	210(40)	170(50)	310(60)	9(4)	5(4)	-3(4)
O2	180(40)	370(60)	202(50)	-2(5)	10(4)	-1(4)
O3	220(40)	160(50)	90(40)	-4(4)	-1(4)	-1(4)
O4	210(40)	350(60)	330(60)	25(5)	5(4)	10(4)
O5	290(50)	130(40)	250(50)	3(4)	14(4)	15(4)
O6	260(50)	140(50)	280(60)	5(4)	4(4)	-1(4)
O7	220(40)	340(60)	210(50)	17(5)	2(4)	9(4)
O8	340(50)	110(50)	320(60)	2(4)	17(5)	3(4)
O9	710(80)	310(60)	270(70)	-14(5)	15(6)	-22(6)
O10	170(50)	800(90)	250(60)	9(6)	1(4)	6(6)
O11	230(50)	190(50)	450(70)	12(5)	3(5)	-2(4)
O12	270(50)	500(70)	310(70)	15(6)	11(5)	20(5)
O13	210(40)	250(50)	220(50)	10(4)	9(4)	12(4)

The unsuccessful synthesis of $\text{Pt}(\text{II})$ and $\text{Pd}(\text{II})$ perhenates attempted in our laboratories can be explained considering the correlation shown on fig. 3. Thus, the ionic radii of both cations (0.86Å) lay in the middle range ($0.8 - 0.9\text{Å}$) expected for coordination 7, being this CN relatively unstable.

On the other hand, perhenates of alkali metals are not included in this comparison since none of them contain H_2O molecules as ligands and do not fit the correlation showed in Fig.3.

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REFERENCES

- [1] C. Mujica, J. Llanos, K. Peters, E.-M. Peters and G. von Schnering. *Bol. Soc. Chil. Quim.*, **45**, 329, (2000).
- [2] C. Mujica, J. Llanos, V. Sánchez, W. Schnelle and R. Cardoso-Gil. *J. Alloys and Comp.*, **364**, 89, (2004).
- [3] C. Mujica, L. Llanos, K. Peters, E.-M. Peters, H.G. von Schnering. *J. Alloys and Comp.*, **288**, 120, (1999).
- [4] C. Mujica, L. Llanos, V. Sánchez, P. Gomez-Romero and N. Casañ-Pastor. *J. of Solid State Chemistry*, **172**, 200, (2003).
- [5] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **212**, 297, (1997).
- [6] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **212**, 295, (1997).
- [7] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **213**, 229, (1998).
- [8] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **212**, 294, (1997).
- [9] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **213**, 11, (1998).
- [10] C. Mujica, K. Peters, E.-M. Peters and G. von Schnering. *Z. Kristallogr. New Crystal Struct.*, **213**, 10, (1998).
- [11] A. Butz, G. Miehe, H. Paulus, P. Strauss, H. Fuess. *J. of Solid State Chemistry*, **138**, 232, (1998).
- [12] M.B. Varfolomeev, A.N. Zemenkova, V.N. Chrustalev, A.P. Struckov, T. Yu. *J. Alloys and Compounds*, **215**, 339, (1994).
- [13] A. Butz, I. Svodoba, H. Paulus, H. Fuess. *J. of Solid State Chemistry*, **115**, 255, (1995).
- [14] W.H. Baur, D. Kassner. *J. of Solid State Chemistry*, **100**, 166, (1992).
- [15] V.N. Khrustalev, M.B. Varfolomeev, N.B. Shamrai, A.P. Struckov. T. Yu. *Coordination Chemistry (USSR)*, **20**, 362, (1994).
- [16] R.G. Mateeva, M.B. Varfolomeev, N.B. Samraj, H.F. Lunk. *Zeitschrift fuer Anorganische und Allgemeine Chemie*, **532**, 193, (1986).
- [17] M.B. Varfolomeev, N.B. Samraj, J. Fuchs, H.J. Lunk. *J. of Alloys and Comp.*, **261**, 201, (1993).
- [18] T. Todorov, O. Angelova, J. Macicek. *Acta Crystallographica C*, **52**, 1319 (1996).
- [19] X-Shape 1.03, Cristal Optimization for Numerical Absortion Correction, Stoe & Cie GmbH, Darmstadt, Germany, 1998.
- [20] G.M. Sheldrick, SHELXS-97, SHELXL-97 (1997). A program for refining crystal structures University of Göttingen, Göttingen.
- [21] N.N. Greenwood, Ionenkristalle Gitterdefekte und Nichtstöchiometrische Verbindungen, Verlag Chemie, 1973.