Crystal structure of potassium indium (monophosphate-hydrogenmonoborate-monophosphate), $\text{KIn}[\text{BP}_2\text{O}_8(\text{OH})]$

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Received September 14, 2001; accepted November 26, 2001; CSD-No. 409583

Abstract

$\text{BHInKO}_9\text{P}_2$, triclinic, $P\bar{1}$ (No. 2), $a = 5.2638(4)$ Å, $b = 8.4791(5)$ Å, $c = 8.1469(9)$ Å, $\alpha = 91.741(7)^\circ$, $\beta = 93.061(7)^\circ$, $\gamma = 79.823(5)^\circ$, $V = 357.3$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.052$, $wR_{\text{ref}}(F^2) = 0.113$, $T = 293$ K.

Source of material

$\text{KIn}[\text{BP}_2\text{O}_8(\text{OH})]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of In metal (0.057 g) dissolved in 1 ml of HCl (18%), H_3BO_3 (0.062 g) and K_2HPO_4 (0.522 g) (molar ratio of In:P:B = 1:2:3) in aqueous solution. The mixtures were sealed in glass tubes (after adding 1 ml H_2O to achieve a degree of filling of 30%) with subsequent heating at 418 K for 14 days. The starting materials were all of analytical purity grade.

Discussion

With the increasing interest in microporous materials, the syntheses of compounds like borophosphates with open framework structures have drawn much attention during the past few years and show a rich crystal chemistry [1]. Systems including a p-block metal have not been widely explored up to now besides two compounds with Al and Ga [2,3] reported only recently and two phases with In in the present issue [4,5].

The structure of the title compound is isotypic to the K-Fe [6] and ammonium-In analogues [5]. The structure is characterized by isolated $\text{InO}_5(\text{OH})$ octahedra sharing common O-corners with phosphate and common $\text{O}(\text{OH})$ -corner with hydrogenborate groups from the trinuclear oligomeric units $[\text{B}_2\text{P}_4\text{O}_{16}(\text{OH})_2]^{8-}$. The condensation of the borophosphate oligomers with In-coordination octahedra via common corners results in a three-dimensional framework which contains elliptical channels running along the a axis. The cross section of the channels is defined by eight-membered octahedral/tetrahedral rings (two In coordination octahedra, four phosphate- and two borate-groups). Potassium ions are distributed within the open channels. The In—O and In—OH bond distances range from 2.110 Å to 2.179 Å. Both the oligomeric borophosphate and the coordination octahedron of In are similar to its K-Fe- and NH_4 -In-analogues [5,6] by considering the bond distances In—O, P—O and B—O and bond angles.

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.2 \times 0.25 \times 0.3$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	44.09 cm ⁻¹
Diffractionmeter, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	68.04°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3081, 2910
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2126
$N(\text{param})_{\text{refined}}$:	131
Program:	SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	2i	0.68(2)	0.51(1)	0.64(1)	0.05

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
In(1)	2i	0.72710(8)	0.19798(5)	0.69319(5)	0.0071(2)	0.0078(2)	0.0084(2)	−0.0014(1)	0.0006(1)	−0.0002(1)
P(1)	2i	0.7814(3)	−0.1870(2)	0.5678(2)	0.0060(6)	0.0049(6)	0.0086(6)	−0.0004(5)	−0.0004(5)	0.0005(5)
P(2)	2i	1.1961(3)	0.3039(2)	0.9245(2)	0.0066(6)	0.0067(6)	0.0067(6)	0.0006(5)	0.0002(5)	0.0000(5)
B(1)	2i	0.889(1)	−0.4448(7)	0.7639(8)	0.009(3)	0.004(2)	0.010(3)	−0.001(2)	−0.001(2)	−0.001(2)
K(1)	2i	0.7200(3)	0.1142(2)	1.1733(2)	0.0131(6)	0.0223(7)	0.0157(6)	−0.0016(5)	0.0006(5)	0.0022(5)
O(1)	2i	0.7483(9)	−0.0535(5)	0.6979(5)	0.016(2)	0.005(2)	0.013(2)	0.001(2)	0.004(2)	−0.003(2)
O(2)	2i	0.717(1)	0.4523(5)	0.6825(6)	0.016(2)	0.007(2)	0.019(2)	−0.003(2)	−0.006(2)	0.001(2)
O(3)	2i	0.9728(8)	0.2126(5)	0.9151(5)	0.009(2)	0.014(2)	0.009(2)	−0.007(2)	−0.003(2)	0.002(2)
O(4)	2i	0.4439(8)	0.2029(5)	0.8692(5)	0.008(2)	0.011(2)	0.010(2)	0.000(2)	−0.000(2)	−0.001(2)
O(5)	2i	1.0872(8)	0.1446(5)	0.5799(5)	0.012(2)	0.012(2)	0.011(2)	−0.003(2)	0.004(2)	0.001(2)
O(6)	2i	1.1311(8)	0.4576(5)	0.8202(5)	0.011(2)	0.011(2)	0.013(2)	0.001(2)	−0.001(2)	0.007(2)
O(7)	2i	0.9608(8)	−0.3334(5)	0.6487(5)	0.008(2)	0.011(2)	0.010(2)	0.003(2)	0.000(2)	0.003(2)
O(8)	2i	1.2568(8)	0.3545(5)	1.1037(5)	0.013(2)	0.016(2)	0.007(2)	0.000(2)	−0.001(2)	−0.004(2)
O(9)	2i	0.5177(8)	−0.2345(5)	0.5210(5)	0.009(2)	0.019(2)	0.009(2)	−0.005(2)	−0.002(2)	0.006(2)

Acknowledgments. This project was supported by the Fund for Distinguished Young Scholars from the NNSF of China, the Fund for University Key Teachers from MOE of China, the NSF of Fujian province and the Fund from the State Key Laboratory for Materials Synthesis and Processing at Wuhan University of Technology. JTZ is indebted to the financial support from the Max-Planck-Gesellschaft.

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Crystal structure of ammonium indium (monophosphate-hydrogenmonoborate-monophosphate), $(\text{NH}_4)\text{In}[\text{BP}_2\text{O}_8(\text{OH})]$

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Received September 14, 2001; accepted November 26, 2001; CSD-No. 409584

Abstract

$\text{BH}_5\text{InNO}_9\text{P}_2$, triclinic, $P\bar{1}$ (No. 2), $a = 5.2980(4)$ Å, $b = 8.4880(4)$ Å, $c = 8.3901(5)$ Å, $\alpha = 93.077(5)^\circ$, $\beta = 93.331(6)^\circ$, $\gamma = 80.634(5)^\circ$, $V = 371.3$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.091$, $T = 293$ K.

Source of material

$(\text{NH}_4)\text{In}[\text{BP}_2\text{O}_8(\text{OH})]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of In metal (0.057g) dissolved in 1ml of HCl (18%), $(\text{NH}_4)_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (2.088g) and H_3BO_3 (0.310g) (molar ratio of In:B:P = 1:10:12) in aqueous solution. The mixtures were sealed in glass tubes (after adding 1ml H_2O to achieve a degree of filling of 30%) with subsequent heating at 403 K for 14 days. The starting materials were all of analytical grade.

Discussion

With the increasing interest in microporous materials the syntheses of compounds like borophosphates with open framework structures have drawn much attention during the past few years and show a rich crystal chemistry [1]. Systems including a p-block metal have not been widely explored up to now besides two compounds with Al and Ga [2,3] reported only recently and two phases with In in the present Issue [4,5]. The structure of the

title compound is isotypic to the K-In and K-Fe analogues [5,6] and is characterized by isolated $\text{InO}_5(\text{OH})$ octahedra sharing common O-corners with phosphate and common $\text{O}(\text{OH})$ -corner with hydrogenborate groups from the trinuclear oligomeric units $[\text{B}_2\text{P}_4\text{O}_{16}(\text{OH})_2]^{8-}$. The condensation of the borophosphate oligomers with In-coordination octahedra via common corners results in an overall three-dimensional framework which contains elliptical channels running along the a axis. The cross section of the channels is defined by eight-membered octahedral/tetrahedral rings (two In coordination octahedra, four phosphate- and two borate-groups). Ammonium ions are distributed within the open channels. The In—O and In—OH bond distances range from 2.104 Å to 2.171 Å. Both the oligomeric borophosphate and the coordination octahedron of In are similar to its K-In-analogue [5] and the Na-In compound [4] by considering the bond distances In—O, P—O and B—O and bond angles.

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.1 \times 0.2 \times 0.3$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	36.48 cm^{-1}
Diffraction, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	67.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6584, 3022
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2743
$N(\text{param})_{\text{refined}}$:	128
Program:	SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	2i	0.4017	0.4683	1.3493	0.05
H(2)	2i	0.8349	0.1606	1.2094	0.05
H(3)	2i	0.8236	0.0224	1.1231	0.05
H(4)	2i	0.6678	0.1431	1.0773	0.05
H(5)	2i	0.6338	0.062	1.2057	0.05

* Correspondence author (e-mail: zhao@cpfs.mpg.de)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
In	2i	0.72294(4)	0.20588(3)	0.68316(3)	0.0093(1)	0.0096(1)	0.0100(1)	-0.00154(7)	0.00029(7)	-0.00047(6)
P(1)	2i	0.2180(2)	0.1890(1)	1.4297(1)	0.0092(3)	0.0089(3)	0.0093(3)	-0.0014(3)	0.0004(2)	0.0004(2)
P(2)	2i	0.1954(2)	0.3102(1)	0.9154(1)	0.0082(3)	0.0101(3)	0.0088(3)	0.0004(3)	0.0001(2)	-0.0001(2)
O(1)	2i	0.0419(5)	0.3223(3)	1.3348(3)	0.011(1)	0.013(1)	0.017(1)	-0.0016(8)	-0.0005(8)	0.0037(8)
O(2)	2i	0.1304(5)	0.4684(3)	0.8259(3)	0.013(1)	0.013(1)	0.019(1)	0.0000(9)	-0.0038(9)	0.0050(9)
O(3)	2i	-0.0258(5)	0.2150(3)	0.8961(3)	0.011(1)	0.016(1)	0.012(1)	-0.0033(8)	0.0015(8)	0.0015(8)
O(4)	2i	0.0723(5)	0.1542(3)	1.5693(3)	0.015(1)	0.017(1)	0.012(1)	-0.0028(9)	0.0042(8)	0.0000(8)
O(5)	2i	0.4684(5)	0.2512(3)	0.4811(3)	0.013(1)	0.020(1)	0.016(1)	-0.0066(9)	-0.0050(9)	0.0031(9)
O(6)	2i	0.2532(5)	0.3505(3)	1.0948(3)	0.015(1)	0.021(1)	0.009(1)	0.0023(9)	-0.0001(8)	-0.0014(9)
O(7)	2i	0.2757(6)	0.0433(3)	1.3132(3)	0.022(1)	0.011(1)	0.015(1)	-0.0026(9)	0.0073(9)	-0.0024(8)
O(8)	2i	0.2811(5)	0.5388(3)	1.3115(3)	0.018(1)	0.009(1)	0.019(1)	-0.0009(9)	-0.007(1)	-0.0003(9)
O(9)	2i	0.4431(5)	0.2164(3)	0.8581(3)	0.010(1)	0.014(1)	0.013(1)	0.0024(8)	0.0023(8)	-0.0008(8)
N	2i	0.7193(6)	0.1148(4)	1.1607(4)	0.015(1)	0.022(2)	0.020(1)	-0.004(1)	0.001(1)	0.004(1)
B	2i	0.1120(7)	0.4369(4)	1.2278(4)	0.010(1)	0.008(1)	0.013(1)	-0.001(1)	0.000(1)	0.000(1)

Acknowledgments. This project was supported by the Fund for Distinguished Young Scholars from the NNSF of China, the Fund for University Key Teachers from MOE of China, the NSF of Fujian province and the Fund from the State Key Laboratories for Materials Synthesis and Processing at Wuhan University of technology. JTZ is indebted to the financial support from the Max-Planck-Gesellschaft.

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- Sheldrick, G. M.: SHELXL-97. Program for refining crystal structures. University of Göttingen, Germany 1997.

Crystal structure of sodium indium (monohydrogenmonophosphate-dihydrogenmonoborate-monophosphate), $\text{NaIn}[\text{BP}_2\text{O}_7(\text{OH})_3]$

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Received September 14, 2001, accepted November 26, 2001; CSD-No. 409585

metal have not been widely explored besides one Al [2] and one Ga [3] compound reported only recently. Two In containing phases are published in this issue [4,5].

The structure of the title compound is isotypic to the Fe [6], Al and Ga analogues [2,3] and is characterized by isolated $\text{InO}_4(\text{OH})_2$ octahedra sharing common O-corners with hydrogen phosphate and common $\text{O}(\text{OH})$ -corners with hydrogenborate groups from the oligomeric units $[\text{BP}_2\text{O}_7(\text{OH})_3]^{4-}$. The condensation of the borophosphate oligomers with In-coordination octahedra via common corners results in a three-dimensional framework which contains elliptical channels running along the [001] direction. The cross section of the channels is defined by eight-membered octahedral/tetrahedral rings (four In coordination octahedra, two hydrogen phosphate- and two hydrogen borate-groups). Sodium ions are distributed within the open channels. The In—O bond distances 2.082 Å and 2.110 Å are shorter than the In—OH value (2.189 Å). The bond distances P—O and B—O in the oligomeric borophosphate groups correspond to respective values in the Ga- and Al-analogues [2,3] and other In compounds [4,5].

Abstract

$\text{B}_4\text{H}_{12}\text{In}_4\text{Na}_4\text{O}_{40}\text{P}_8$, monoclinic, $C12/c1$ (No. 15), $a = 10.368(2)$ Å, $b = 8.520(1)$ Å, $c = 9.415(2)$ Å, $\beta = 115.951(5)^\circ$, $V = 747.8$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.076$, $wR_{\text{ref}}(F^2) = 0.202$, $T = 293$ K.

Source of material

$\text{NaIn}[\text{BP}_2\text{O}_7(\text{OH})_3]$ was synthesized under mild hydrothermal conditions. The reactions were carried out with mixtures of In metal (0.230 g) dissolved in 1 ml of HCl (18%), $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (1.074 g) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1.525 g) (molar ratio of In:P:B = 2:3:16) in aqueous solution. The mixtures were sealed in glass tubes (after adding 1 ml H_2O to achieve a degree of filling of 30%) with subsequent heating at 408 K for 90 days. The starting materials were all of analytical purity grade.

Experimental details

The quality of the crystal studied was not good enough, which is reflected in the resulting high R -values.

Discussion

The synthesis of compounds like borophosphates with open framework structures has drawn much attention during the past few years due to their potential applications as microporous materials. The variety of crystal structures known up to now already shows a rich crystal chemistry [1]. Systems including a p-block

Table 1. Data collection and handling.

Crystal:	colorless prism, size $0.15 \times 0.2 \times 0.3$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	36.90 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	67.78°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1586, 1521
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1141
$N(\text{param})_{\text{refined}}$:	69
Program:	SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
B	4e	1/2	0.019(2)	3/4	0.011(2)
H(1)	4c	1/4	3/4	1/2	0.05
H(2)	8f	0.485	0.163	0.591	0.05

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
In	4d	1/4	1/4	1/2	0.0099(4)	0.0125(4)	0.0130(4)	0.0005(3)	0.0039(3)	0.0015(3)
P	8f	0.2176(2)	−0.0715(3)	0.6709(3)	0.0070(8)	0.0136(9)	0.0127(9)	−0.0005(7)	0.0040(7)	0.0002(8)
Na	4e	0	−0.1319(8)	1/4	0.017(3)	0.025(3)	0.027(3)	0	0.004(2)	0
O(1)	8f	0.1694(7)	0.1047(9)	0.2981(8)	0.012(3)	0.021(3)	0.016(3)	0.001(2)	0.006(2)	−0.003(2)
O(2)	8f	0.3850(7)	−0.0836(8)	0.7416(8)	0.007(2)	0.015(3)	0.022(3)	0.002(2)	0.002(2)	0.000(3)
O(3)	8f	0.4498(7)	0.1154(9)	0.6066(8)	0.010(3)	0.020(3)	0.017(3)	−0.001(2)	0.003(2)	0.003(2)
O(4)	8f	0.1587(7)	−0.196(1)	0.5380(9)	0.011(3)	0.026(3)	0.024(3)	0.001(3)	0.004(3)	−0.010(3)
O(5)	8f	0.1662(7)	0.0943(8)	0.6085(9)	0.011(3)	0.016(3)	0.028(3)	0.003(2)	0.009(3)	0.008(3)

Acknowledgments. This project was supported by the Fund for Distinguished Young Scholars from the NNSF of China, the Fund for University Key Teachers from MOE of China, the NSF of Fujian province and the Fund from the State Key Laboratories for Materials Synthesis and Processing at Wuhan University of technology. JTZ is indebted to the financial support from the Max-Planck-Gesellschaft.

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Redetermination of the crystal structure of calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

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Received September 22, 2001; accepted January 23, 2002; CSD-No. 409581

Abstract

$\text{CaH}_4\text{O}_6\text{S}$, monoclinic, $C12/c1$ (No. 15), $a = 6.284(1) \text{ \AA}$, $b = 15.200(1) \text{ \AA}$, $c = 6.523(1) \text{ \AA}$, $\beta = 127.41(1)^\circ$, $V = 494.9 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.079$, $T = 293 \text{ K}$.

Source of material

The crystallising solution was made up from commercial 0.5 M aqueous solutions of A. R. grade.

Discussion

In order to standardize all entries of powder diffraction patterns for gypsum and synthetic calcium sulphate dihydrate, the JCPDS [1,2] uses the reduced cell: $a, b, c = 5.68 \text{ \AA}, 6.29 \text{ \AA}, 8.22 \text{ \AA}$; $\alpha, \beta, \gamma = 67.5^\circ, 81.0^\circ, 65.8^\circ$, and indexing based on the monoclinic cell: $a', b', c' = 6.29 \text{ \AA}, 15.18 \text{ \AA}, 5.68 \text{ \AA}$; $\beta = 114.2^\circ$, and space group $C2/c$. This now seems to be generally accepted as the standard setting, but although it has the correct systematic absences, the symmetry is wrong, and according to International Tables [3] this is cell choice 2 ($A2/n$) in the setting $C2/n$. This incorrect assignment was noticed in the course of the present work, only after data collection according to this cell choice and then transformed to the correct $C2/c$ cell with $a, b, c = 6.28 \text{ \AA}, 15.20 \text{ \AA}, 6.52 \text{ \AA}$; $\beta = 127.4^\circ$, where $ai + bj + ck = -a'i - b'j + (a' + b')k$; with i, j, k being the unit vectors. This choice of unit cell [3] has the correct setting of the space group, but being less eccentric, is now recommended as the standard setting. In the lower figure, a projection along the b axis of the actual unit cell (drawn to scale) is shown together with all previous choices. The unique b axis is common for all cell choices. The space group symmetry for the standard cell is also shown as a guide to the different specifications of the space group. A comparison of the crystal structures of the mineral gypsum with the synthetic material confirmed that there are no differences between the structures. The agreement with the neutron results is particularly striking, with the only significant difference related to the position of H(2), which is clearly wrong in the present work. It is still an improvement over the previous best X-ray study of Cole & Lancucki [4] in which hydrogen position could not be refined against the data. Important issues for discussion are the shape of the sulphate ion and the hydrogen bonding. The known deviation of the sulphate geometry from a symmetrical tetrahedron is convincingly confirmed, while the observed hydrogen-bonding is essentially the same as observed before.

In the final analysis the structure of pure gypsum is now known in sufficient detail from X-ray diffraction to allow an analysis of distortions, introduced by dopants, such as lanthanide ions.

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Table 1. Data collection and handling.

Crystal:	clear prism, size 0.08 × 0.16 × 1.2 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	16.32 cm ⁻¹
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\max}$:	69.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4287, 109
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 971
$N(\text{param})_{\text{refined}}$:	46
Program:	SHELXL-93 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	8 <i>f</i>	0.749(3)	0.162(1)	0.251(4)	0.031(8)
H(2)	8 <i>f</i>	0.584(5)	0.235(2)	0.073(5)	0.057(7)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ca	4 <i>e</i>	1/2	0.07956(1)	3/4	0.0105(1)	0.0124(1)	0.0104(1)	0	0.0057(1)	0
S(2)	4 <i>e</i>	0	0.07724(2)	3/4	0.0084(2)	0.0108(2)	0.0090(1)	0	0.0046(1)	0
O(1)	8 <i>f</i>	0.0372(1)	0.13198(5)	0.5872(1)	0.0163(3)	0.0187(3)	0.0145(3)	0.0006(2)	0.0093(2)	0.0052(2)
O(2)	8 <i>f</i>	0.2424(1)	0.02211(4)	0.9092(1)	0.0115(3)	0.0179(3)	0.0172(3)	0.0052(2)	0.0075(2)	0.0068(2)
OW	8 <i>f</i>	0.6202(2)	0.18197(5)	0.0784(2)	0.0304(4)	0.0182(3)	0.0157(3)	0.0013(3)	0.0099(3)	-0.0028(2)

Acknowledgments. We gratefully acknowledge Quirina Roode for growing the single crystals and Leanne Cook for data collection at the University of the Witwatersrand.

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Crystal structure of rhenium caesium sulfobromide, $\text{CsRe}_6\text{S}_8\text{Br}_3$, the first cluster compound in the Cs-Re-S-Br system exhibiting two types of inter-unit bridges

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Received October 4, 2001, accepted January 20, 2002; CSD-No. 409589

Abstract

$\text{Br}_3\text{CsRe}_6\text{S}_8$, monoclinic, $P12_1/n1$ (No. 14), $a = 6.3481(1)$ Å, $b = 18.5504(3)$ Å, $c = 15.0706(2)$ Å, $\beta = 97.3271(6)^\circ$, $V = 1760.2$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.026$, $wR_{\text{obs}}(F) = 0.030$, $T = 293$ K.

Source of material

The title compound was prepared as a pure sample by solid state synthesis from a stoichiometric mixture of CsBr, Re, S powder and liquid bromine. After being sealed under an argon residual pressure, the silica tube was heated to 1173 K in a vertical furnace during 132 h followed by a cooling to room temperature in 6 h.

Discussion

The octahedral core of the rhenium cluster is slightly distorted: the independent Re—Re bond lengths range from 2.590(1) Å to 2.634(1) Å. The eight inner positions around the cluster are fully occupied by sulfur, while four bromine and two sulfur atoms are fully ordered on the six apical positions. The Re_6 clusters are connected to each other via two different kinds of bridges (Figure). Two of the four bromine apical ligands are shared with two neighbouring clusters via Re—Br^{a-a}—Re bridges. A chain is thereby formed, extending along the [101] direction. In addition, two of the eight sulfur inner ligands participate in trans position in Re—S^{a-i,i-a}—Re bridges towards two neighbouring Re_6 clusters, linking the above mentioned chains to form a layer parallel to the (010) plane. Consequently, the framework is strongly 2-D, as the cohesion along the direction perpendicular to the layers (the [010] one) is obtained only by coulombic interactions involving the caesium ions intercalated between layers. These cations are located inside a complex environment formed by four sulfur atoms (exclusively Sⁱ) and five bromine atoms (four Br^a and one Br^{a-a}). The Cs—ligand distances lie between 3.732(2) Å and 3.929(1) Å. The developed formula is: $\{[\text{Re}_6\text{S}_6^i\text{S}_{2/2}^{i-a}\text{S}_{2/2}^{a-i}\text{Br}_{2/2}^{a-a}\text{Br}_2^a]^-$. $\text{CsRe}_6\text{S}_8\text{Br}_3$ is isostructural with $\text{CsRe}_6\text{Se}_8\text{I}_3$ (although the size of the ligands is significantly different in these two examples), the structure of which has been previously reported [1], but with a limited accuracy ($R = 0.076$). The stacking of the title compound can be compared to that of the neutral, ternary $\text{Re}_6\text{S}_8\text{Br}_2$ one [2] but in the latter the $\text{Br}^a \cdots \text{Cs} \cdots \text{Br}^a$ coulombic interactions are replaced with strong Re—Br^{a-a}—Re bridges, giving rise to a true 3-D structure.

Table 1. Data collection and handling.

Crystal:	black needle, size 0.014 × 0.018 × 0.048 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	508.66 cm ⁻¹
Diffractometer, scan mode:	Nonius Kappa-CCD, ϕ
$2\theta_{\text{max}}$:	69.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	40418, 7739
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 3 \sigma(I_{\text{obs}})$, 3700
$N(\text{param})_{\text{refined}}$:	164
Programs:	SIRWARE [3], CRYSTALS [4], NUMABS [5], CAMERON [6]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Re(1)	4e	0.29277(6)	0.26187(2)	-0.04120(2)	0.0081(1)	0.0138(1)	0.0080(1)	0.0001(1)	0.0013(1)	-0.0003(1)
Re(2)	4e	-0.06935(6)	0.20471(2)	-0.10254(2)	0.0085(2)	0.0136(2)	0.0080(1)	-0.0001(1)	0.0009(1)	-0.0013(1)
Re(3)	4e	-0.21537(5)	0.24074(2)	0.04452(2)	0.0079(2)	0.0140(1)	0.0081(1)	-0.0002(1)	0.0013(1)	-0.0003(1)
Re(4)	4e	0.14656(6)	0.29770(2)	0.10591(2)	0.0087(2)	0.0134(2)	0.0080(1)	-0.0002(1)	0.0009(1)	-0.0010(1)
Re(5)	4e	-0.04930(6)	0.33942(2)	-0.04705(2)	0.0094(2)	0.0126(1)	0.0089(1)	0.0004(1)	0.0011(1)	-0.0000(1)
Re(6)	4e	0.12653(6)	0.16315(2)	0.05037(2)	0.0093(2)	0.0127(1)	0.0093(1)	0.0005(1)	0.0009(1)	0.0001(1)
Br(1)	4e	-0.2149(2)	0.13191(5)	-0.24721(7)	0.0259(4)	0.0154(4)	0.0119(3)	0.0007(4)	-0.0039(3)	0.0002(4)
Br(2)	4e	0.2452(2)	0.04286(6)	0.11890(9)	0.0321(6)	0.0177(5)	0.0286(6)	0.0052(4)	0.0017(5)	0.0055(4)
Br(3)	4e	-0.1688(2)	0.45963(6)	-0.11596(8)	0.0305(6)	0.0186(5)	0.0258(6)	0.0061(4)	0.0015(4)	0.0056(4)
S(1)	4e	-0.0173(4)	0.2031(1)	0.1822(2)	0.014(1)	0.022(1)	0.0100(9)	-0.0009(8)	0.0016(8)	0.0024(8)
S(2)	4e	0.6249(4)	0.2810(1)	-0.1073(2)	0.010(1)	0.020(1)	0.0110(9)	0.0001(8)	0.0014(7)	-0.0009(8)
S(3)	4e	0.2947(4)	0.3838(1)	0.0118(2)	0.015(1)	0.016(1)	0.016(1)	-0.0028(8)	0.0020(8)	-0.0011(8)
S(4)	4e	0.0936(4)	0.2995(1)	-0.1790(2)	0.015(1)	0.020(1)	0.011(1)	-0.0010(8)	0.0018(8)	0.0018(8)
S(5)	4e	0.4525(4)	0.2217(1)	0.1104(2)	0.0090(9)	0.017(1)	0.0117(9)	0.0005(7)	0.0018(7)	-0.0001(8)
S(6)	4e	-0.1789(4)	0.3642(1)	0.0932(2)	0.013(1)	0.018(1)	0.014(1)	0.0011(8)	0.0030(8)	-0.0028(8)
S(7)	4e	0.2576(4)	0.1385(1)	-0.0895(2)	0.013(1)	0.019(1)	0.016(1)	0.0034(8)	0.0037(8)	-0.0035(8)
S(8)	4e	-0.2178(4)	0.1188(1)	-0.0083(2)	0.013(1)	0.018(1)	0.015(1)	-0.0020(8)	-0.0010(8)	-0.0019(8)
Cs(1)	4e	0.2135(2)	0.97960(6)	0.74809(9)	0.0406(5)	0.0414(5)	0.0661(7)	0.0038(4)	0.0149(4)	-0.0019(5)

Acknowledgments. This work has been supported in part by a research grant from the French Ministry of Research and Education and by Fondation Langlois. We would like to thank the Centre de Diffractométrie de l'Université de Rennes 1 for the data collection on the Nonius KappaCCD X-ray diffractometer. In particular, the useful advice of Dr. T. Roisnel is gratefully acknowledged.

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