

Poly[aqua(μ 3-2-hydroxy-5-nitrobenzoato- κ 3O1:O1':O2)rubidium]

Author

Smith, Graham, Wermuth, Urs D, Williams, Michael L

Published

2011

Journal Title

Acta Crystallographica. Section E: Structure Reports Online

DOI

[10.1107/S1600536811037561](https://doi.org/10.1107/S1600536811037561)

Rights statement

© The Author(s) 2011. For information about this journal please refer to the journal's website. All articles published in Acta Crystallographica Section E are open access and distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. See <http://creativecommons.org/licenses/by/2.0/uk/legalcode>

Downloaded from

<http://hdl.handle.net/10072/42921>

Griffith Research Online

<https://research-repository.griffith.edu.au>

Poly[aqua(μ_3 -2-hydroxy-5-nitrobenzoato- κ^3 O¹:O^{1'}:O²)rubidium]

Graham Smith,^{a*} Urs D. Wermuth^a and Michael L. Williams^b

^aFaculty of Science and Technology, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia, and ^bSchool of Biomolecular and Physical Sciences, Griffith University, Nathan, Queensland 4111, Australia
Correspondence e-mail: g.smith@qut.edu.au

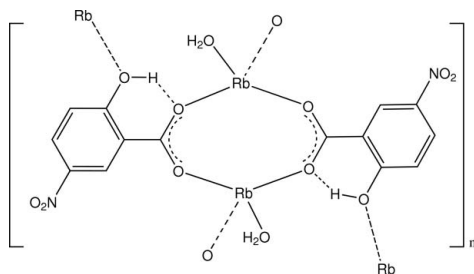
Received 5 September 2011; accepted 14 September 2011

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.054; wR factor = 0.181; data-to-parameter ratio = 13.9.

In the structure of title compound, $[\text{Rb}(\text{C}_7\text{H}_4\text{NO}_5)(\text{H}_2\text{O})]_n$, the centrosymmetric cyclic dimeric repeating unit comprises two irregular RbO_4 complex centres bridged by the carboxylate groups of the 5-nitrosalicylate ligands. The coordination about each Rb atom is completed by a monodentate water molecule and a phenolic O-atom donor which gives a bridging extension $[\text{Rb}-\text{O}$ range = 3.116 (7)–3.135 (5) Å]. The polymeric structure is stabilized by intermolecular water $\text{O}-\text{H}\cdots\text{O}_{\text{carboxylate}}$ hydrogen bonds and weak inter-ring $\pi-\pi$ interactions [minimum ring centroid separation = 3.620 (4) Å]. An intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond between phenol and carboxylate groups is also present.

Related literature

For the structures of some Rb complexes with aromatic carboxylic acids, see: Dinnebier *et al.* (2002); Wiesbrock & Schmidbaur (2003); Smith *et al.* (2007). For the structure of 5-nitrosalicylic acid and some Lewis base salts and metal complexes of this acid, see: Kumar *et al.* (2003); Smith *et al.* (2005); Morgant *et al.* (2006).



Experimental

Crystal data

$[\text{Rb}(\text{C}_7\text{H}_4\text{NO}_5)(\text{H}_2\text{O})]$
 $M_r = 285.6$

Monoclinic, $P2_1/c$
 $a = 11.9738$ (5) Å

$b = 12.0230$ (4) Å
 $c = 6.9571$ (3) Å
 $\beta = 105.401$ (4)°
 $V = 965.59$ (7) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 5.14$ mm⁻¹
 $T = 200$ K
 $0.50 \times 0.20 \times 0.10$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2010)
 $T_{\min} = 0.572$, $T_{\max} = 0.980$

6051 measured reflections
1893 independent reflections
1651 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.181$
 $S = 1.17$
1893 reflections

136 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.81$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.11$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}2-\text{H}2\cdots\text{O}12$	0.97	1.61	2.468 (8)	145
$\text{O}1\text{W}-\text{H}11\text{W}\cdots\text{O}11^i$	0.89	1.90	2.794 (9)	179
$\text{O}1\text{W}-\text{H}12\text{W}\cdots\text{O}12^{ii}$	0.90	1.96	2.861 (9)	180

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the Australian Research Committee, the Faculty of Science and Technology and the University Library, Queensland University of Technology and Griffith University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NK2111).

References

- Altomare, A., Casciarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Dinnebier, R. E., Jelonek, S., Sieler, J. & Stephens, P. W. (2002). *Z. Anorg. Allg. Chem.* **628**, 363–368.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kumar, V. S. S., Nangia, A., Kirchner, M. T. & Boese, R. (2003). *New J. Chem.* **27**, 224–226.
Morgant, G., Bouhmaida, N., Balde, L., Ghermani, N. E. & d'Angelo, J. (2006). *Polyhedron*, **25**, 2229–2235.
Oxford Diffraction (2010). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Smith, G., Hortono, A. W., Wermuth, U. D., Healy, P. C., White, J. M. & Rae, A. D. (2005). *Aust. J. Chem.* **58**, 47–52.
Smith, G., Wermuth, U. D., Young, D. J. & White, J. M. (2007). *Polyhedron*, **26**, 3645–3652.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Wiesbrock, F. & Schmidbaur, H. (2003). *Inorg. Chem.* **42**, 7283–7289.

supplementary materials

Acta Cryst. (2011). E67, m1400 [doi:10.1107/S1600536811037561]

Poly[aqua(μ_3 -2-hydroxy-5-nitrobenzoato- $\kappa^3 O^1:O^1':O^2$)rubidium]_n

G. Smith, U. D. Wermuth and M. L. Williams

Comment

The structures of the alkali metal complexes with aromatic carboxylic acids are of interest, particularly with the heavier metals Rb and Cs, because of their expanded coordination spheres and their ability to form polymeric systems. Although the structures of a series of metal^{II} complex adducts with 5-nitrosalicylic acid (5-NSA), of the type $[M(5\text{-NSA}^-(\text{H}_2\text{O})_5)]$. (5-NSA). H₂O ($M = \text{Mg, Co, Ni, Zn}$) have been reported (Morgant *et al.*, 2006), no alkali metal complexes with 5-NSA are known. We obtained crystals of the title compound $[\text{Rb}_2(\text{C}_7\text{H}_4\text{NO}_2)_2(\text{H}_2\text{O})_2]_n$ from the reaction of 5-NSA with rubidium hydroxide and the structure is reported here.

In the structure of this complex, the cyclic centrosymmetric dimeric repeating unit (Fig. 1) comprises two irregular RbO_4 complex centres bridged by the carboxylate groups of the 5-NSA ligands. The coordination about each Rb is completed by a monodentate water molecule and a phenolic O donor which gives a bridging extension [Rb—O range 3.116 (7)–3.135 (5) Å]. The nitro O atoms (O51, O52) also give a weak symmetric bidentate association with inversion-related Rb centres [Rb—O, 3.290 (7), 3.261 (8) Å], a little too long to be considered formal Rb—O bonds. The coordination about Rb in this structure is therefore simpler than is found in other polymeric rubidium carboxylate complexes, *e.g.* and in rubidium salicylate (RbO_7) (Dinnebier *et al.*, 2002) and rubidium anthranilate monohydrate (RbO_8) (Wiesbrock & Schmidbaur, 2003) and rubidium sulfosalicylate 1.33 hydrate (RbO_7) (Smith *et al.*, 2007).

The two-dimensional polymeric structure of the title compound (Fig. 2) is stabilized by intermolecular water $O\cdots O_{\text{carboxyl}}$ hydrogen bonds (Table 1) and weak inter-ring $\pi\text{-}\pi$ interactions [minimum ring centroid separation, 3.620 (4) Å]. The 5-NSA anion has the short intramolecular phenolic $O\cdots O_{\text{carboxyl}}$ hydrogen bond and the essentially planar conformation commonly found in this ligand (Kumar *et al.*, 2003; Smith *et al.*, 2005) [torsion angles: C2—C1—C11—O11, -177.1 (7)°; C4—C5—N5—O52, 172.0 (7)°].

Experimental

The title compound was synthesized by heating together under reflux for 15 minutes, 1 mmol quantities of 5-nitrosalicylic acid and rubidium hydroxide in 50 ml of 1:9 ethanol–water. After concentration to *ca* 30 ml, partial room temperature evaporation of the solution gave pale yellow needle prisms from which a suitable specimen was cleaved for the X-ray analysis.

Refinement

The water and hydroxyl H atoms were located in a difference-Fourier synthesis and their positional and isotropic displacement parameters were allowed to ride together with the ring hydrogen atoms which were included in calculated positions with C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{O})$.

Figures

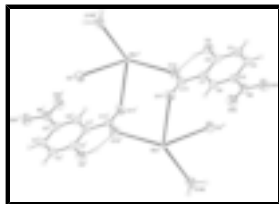


Fig. 1. The molecular configuration and atom-numbering scheme for the dimeric repeat unit of the title complex, with non-H atoms drawn as 40% probability ellipsoids. For symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z$; (v) $-x, y - 1/2, -z + 3/2$.

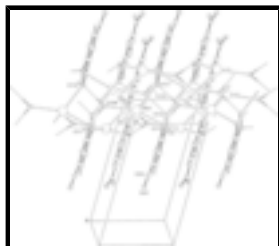


Fig. 2. A perspective view of the polymeric structure with hydrogen bonds shown as dashed lines. For symmetry codes, see Fig. 1 and Table 1.

Poly[aqua(μ -2-hydroxy-5-nitrobenzoato- $\kappa^3 O^1:O^1:O^2$)rubidium]

Crystal data

[Rb(C₇H₄NO₅)(H₂O)]

$M_r = 285.60$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 11.9738\ (5)\ \text{\AA}$

$b = 12.0230\ (4)\ \text{\AA}$

$c = 6.9571\ (3)\ \text{\AA}$

$\beta = 105.401\ (4)^\circ$

$V = 965.59\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 560$

$D_x = 1.965\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4363 reflections

$\theta = 3.4\text{--}28.8^\circ$

$\mu = 5.14\ \text{mm}^{-1}$

$T = 200\ \text{K}$

Needle, yellow

$0.50 \times 0.20 \times 0.10\ \text{mm}$

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer

Radiation source: Enhance (Mo) X-ray source graphite

Detector resolution: $16.077\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan (*Crys.Alis PRO*; Oxford Diffraction, 2010)

$T_{\min} = 0.572, T_{\max} = 0.980$

6051 measured reflections

1893 independent reflections

1651 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 26.0^\circ, \theta_{\min} = 3.4^\circ$

$h = -14 \rightarrow 14$

$k = -14 \rightarrow 14$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.181$	H-atom parameters constrained
$S = 1.17$	$w = 1/[\sigma^2(F_o^2) + (0.1295P)^2 + 0.7347P]$
1893 reflections	where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.81 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -1.11 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Rb1	0.11224 (4)	-0.11709 (4)	0.23072 (7)	0.0208 (2)
O1W	0.0713 (6)	-0.1033 (5)	-0.2300 (10)	0.068 (2)
O2	0.1661 (5)	0.3786 (4)	0.5968 (10)	0.056 (2)
O11	0.2015 (5)	0.0401 (5)	0.5983 (9)	0.063 (2)
O12	0.0880 (4)	0.1881 (5)	0.5829 (8)	0.0583 (19)
O51	0.6650 (5)	0.2709 (6)	0.5398 (9)	0.070 (2)
O52	0.6074 (6)	0.1054 (5)	0.5877 (13)	0.068 (3)
N5	0.5896 (5)	0.2061 (6)	0.5701 (9)	0.049 (2)
C1	0.2840 (6)	0.2186 (6)	0.5897 (9)	0.041 (2)
C2	0.2690 (6)	0.3339 (6)	0.5920 (10)	0.043 (2)
C3	0.3609 (7)	0.4063 (7)	0.5906 (11)	0.049 (3)
C4	0.4652 (7)	0.3660 (6)	0.5873 (12)	0.046 (2)
C5	0.4801 (6)	0.2488 (6)	0.5818 (9)	0.043 (2)
C6	0.3918 (6)	0.1769 (6)	0.5851 (10)	0.042 (2)
C11	0.1863 (7)	0.1422 (6)	0.5922 (11)	0.043 (2)
H2	0.10940	0.32000	0.58910	0.0670*
H3	0.34960	0.48270	0.59180	0.0580*
H4	0.52640	0.41390	0.58870	0.0560*
H6	0.40380	0.10050	0.58420	0.0500*

supplementary materials

H11W	0.11310	-0.05780	-0.28540	0.0810*
H12W	0.02110	-0.12980	-0.34140	0.0810*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rb1	0.0199 (4)	0.0188 (4)	0.0234 (4)	-0.0022 (2)	0.0050 (2)	0.0002 (2)
O1W	0.069 (4)	0.071 (4)	0.058 (4)	-0.022 (3)	0.009 (3)	0.002 (3)
O2	0.045 (3)	0.058 (4)	0.065 (4)	0.005 (2)	0.014 (3)	-0.003 (2)
O11	0.072 (4)	0.048 (4)	0.074 (4)	-0.007 (3)	0.027 (3)	-0.008 (3)
O12	0.045 (3)	0.071 (4)	0.059 (3)	-0.002 (3)	0.014 (2)	-0.005 (3)
O51	0.053 (3)	0.071 (4)	0.090 (4)	-0.007 (3)	0.026 (3)	0.003 (4)
O52	0.057 (4)	0.050 (4)	0.099 (5)	0.012 (3)	0.024 (4)	0.007 (3)
N5	0.043 (3)	0.047 (4)	0.056 (4)	-0.002 (3)	0.012 (3)	0.004 (3)
C1	0.045 (4)	0.042 (4)	0.035 (3)	0.000 (3)	0.010 (3)	-0.005 (3)
C2	0.043 (4)	0.046 (4)	0.040 (4)	0.005 (3)	0.013 (3)	0.003 (3)
C3	0.058 (5)	0.042 (4)	0.047 (4)	0.005 (3)	0.015 (4)	0.002 (3)
C4	0.050 (4)	0.044 (4)	0.047 (4)	-0.009 (3)	0.016 (3)	0.002 (3)
C5	0.044 (4)	0.044 (4)	0.039 (3)	0.004 (3)	0.009 (3)	0.000 (3)
C6	0.048 (4)	0.039 (4)	0.038 (3)	0.000 (3)	0.011 (3)	0.002 (3)
C11	0.046 (4)	0.044 (4)	0.039 (4)	-0.003 (3)	0.010 (3)	-0.009 (3)

Geometric parameters (\AA , $^\circ$)

Rb1—O1W	3.116 (7)	N5—C5	1.430 (10)
Rb1—O11	3.131 (6)	C1—C11	1.491 (11)
Rb1—O12 ⁱ	3.132 (5)	C1—C2	1.399 (10)
Rb1—O2 ⁱⁱ	3.135 (5)	C1—C6	1.393 (10)
O2—C2	1.353 (10)	C2—C3	1.405 (11)
O11—C11	1.240 (9)	C3—C4	1.345 (12)
O12—C11	1.286 (10)	C4—C5	1.422 (10)
O51—N5	1.252 (9)	C5—C6	1.371 (10)
O52—N5	1.230 (9)	C3—H3	0.9300
O1W—H11W	0.8900	C4—H4	0.9300
O1W—H12W	0.9000	C6—H6	0.9300
O2—H2	0.9700		
O1W—Rb1—O11	137.27 (16)	C6—C1—C11	120.9 (7)
O1W—Rb1—O12 ⁱ	120.79 (17)	C1—C2—C3	120.7 (7)
O1W—Rb1—O2 ⁱⁱ	68.54 (16)	O2—C2—C3	118.3 (7)
O11—Rb1—O12 ⁱ	87.66 (15)	O2—C2—C1	121.0 (6)
O2 ⁱⁱ —Rb1—O11	68.78 (16)	C2—C3—C4	120.6 (7)
O2 ⁱⁱ —Rb1—O12 ⁱ	127.80 (16)	C3—C4—C5	118.8 (7)
Rb1—O2 ⁱⁱ —C2 ⁱⁱ	129.2 (4)	N5—C5—C6	119.8 (7)
Rb1—O11—C11	123.7 (5)	C4—C5—C6	121.4 (7)
Rb1 ⁱ —O12—C11	130.8 (5)	N5—C5—C4	118.7 (7)
Rb1—O1W—H11W	121.00	C1—C6—C5	119.8 (7)
Rb1—O1W—H12W	139.00	O11—C11—C1	120.1 (7)

H11W—O1W—H12W	100.00	O12—C11—C1	116.5 (6)
Rb1 ⁱⁱⁱ —O2—H2	119.00	O11—C11—O12	123.4 (8)
C2—O2—H2	110.00	C2—C3—H3	120.00
O51—N5—C5	119.9 (7)	C4—C3—H3	120.00
O52—N5—C5	119.0 (7)	C3—C4—H4	121.00
O51—N5—O52	121.1 (7)	C5—C4—H4	121.00
C2—C1—C6	118.7 (7)	C1—C6—H6	120.00
C2—C1—C11	120.5 (7)	C5—C6—H6	120.00
O1W—Rb1—O11—C11	32.4 (7)	C2—C1—C6—C5	-0.4 (9)
O12 ⁱ —Rb1—O11—C11	-102.9 (6)	C11—C1—C6—C5	179.7 (6)
O2 ⁱⁱ —Rb1—O11—C11	29.5 (6)	C2—C1—C11—O11	-177.1 (7)
O1W—Rb1—O12 ⁱ —C11 ⁱ	-62.5 (6)	C2—C1—C11—O12	4.5 (10)
O11—Rb1—O12 ⁱ —C11 ⁱ	83.8 (6)	C6—C1—C11—O11	2.9 (10)
O1W—Rb1—O2 ⁱⁱ —C2 ⁱⁱ	-96.4 (6)	C6—C1—C11—O12	-175.5 (6)
O11—Rb1—O2 ⁱⁱ —C2 ⁱⁱ	81.5 (6)	C11—C1—C2—O2	0.1 (10)
Rb1—O2 ⁱⁱ —C2 ⁱⁱ —C1 ⁱⁱ	-159.4 (5)	C11—C1—C2—C3	179.7 (6)
Rb1—O2 ⁱⁱ —C2 ⁱⁱ —C3 ⁱⁱ	20.2 (9)	C6—C1—C2—O2	-179.9 (6)
Rb1—O11—C11—O12	73.6 (9)	C6—C1—C2—C3	-0.3 (10)
Rb1—O11—C11—C1	-104.7 (7)	O2—C2—C3—C4	179.5 (7)
Rb1 ⁱ —O12—C11—O11	34.3 (11)	C1—C2—C3—C4	-0.1 (11)
Rb1 ⁱ —O12—C11—C1	-147.4 (5)	C2—C3—C4—C5	1.1 (11)
O51—N5—C5—C4	-8.9 (9)	C3—C4—C5—N5	177.5 (7)
O52—N5—C5—C4	172.0 (7)	C3—C4—C5—C6	-1.7 (11)
O51—N5—C5—C6	170.3 (6)	N5—C5—C6—C1	-177.8 (6)
O52—N5—C5—C6	-8.8 (10)	C4—C5—C6—C1	1.4 (10)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $x, -y+1/2, z-1/2$; (iii) $x, -y+1/2, z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O12	0.97	1.61	2.468 (8)	145
O1W—H11W \cdots O11 ^{iv}	0.89	1.90	2.794 (9)	179
O1W—H12W \cdots O12 ^v	0.90	1.96	2.861 (9)	180

Symmetry codes: (iv) $x, y, z-1$; (v) $-x, -y, -z$.

Fig. 1

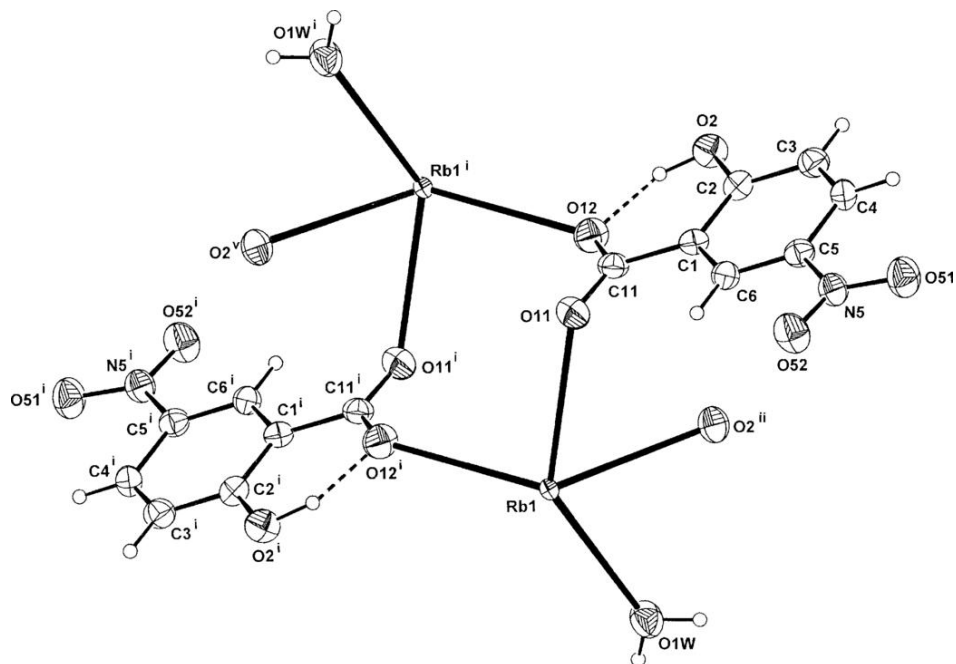


Fig. 2

