Supplementary Materials for

$Cs[H_2NB_2(C_6F_5)_6]$, Featuring an Unequivocal 16-Coordinate Cation

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This PDF file includes: Page

Isolation of $Cs[H_2NB_2(C_6F_5)_6]$ (1) from water

(a) Neat water

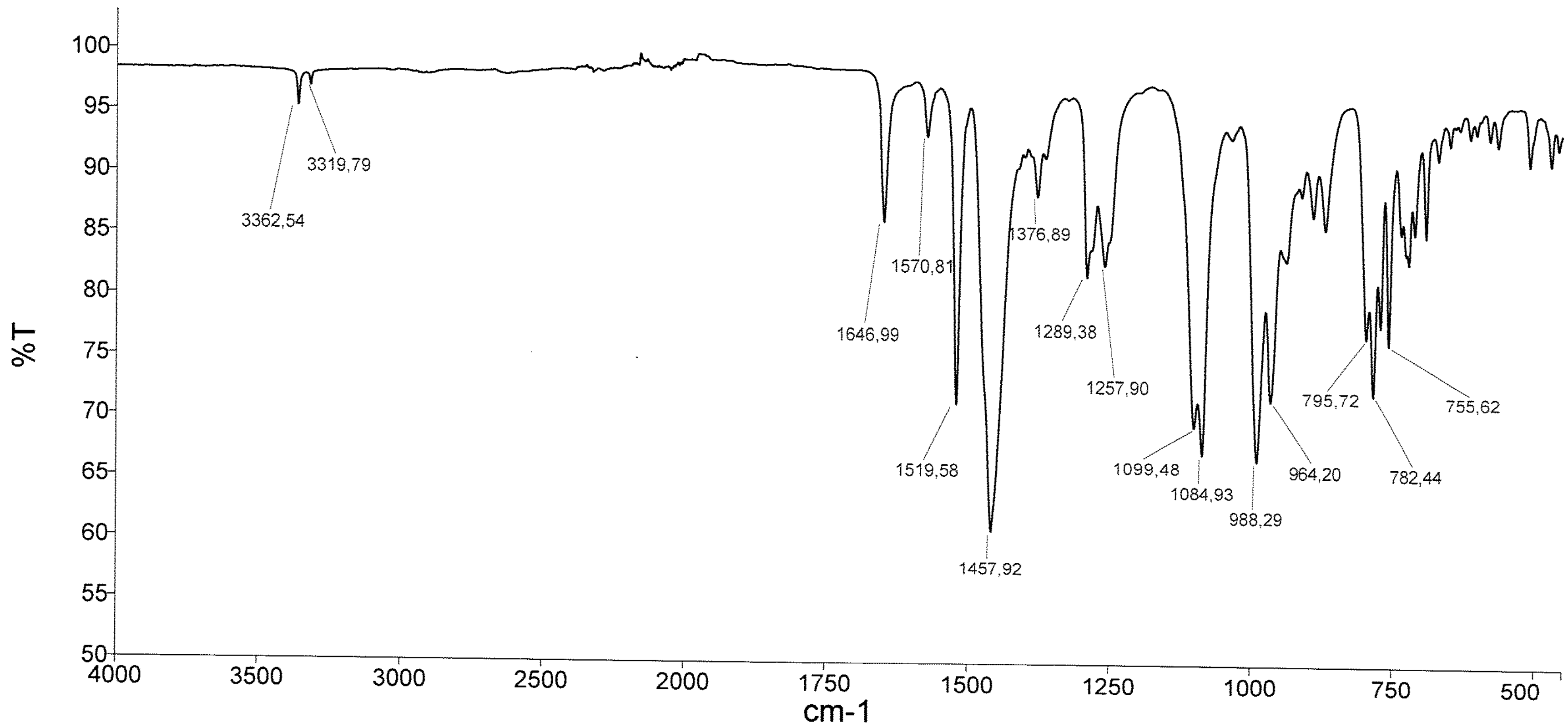
$[Na(OEt_2)_3][H_2NB_2(C_6F_5)_6]$ (69.6 mg, 0.0541 mmol; *FW* = 1285.4; $c \approx 0.9\ 10^{-4}$ M) was dissolved in 570 mL of water. CsCl (9.5 mg, 0.0564 mmol; *FW* = 168.4) was added and after brief mixing the clear solution was left unstirred. Soon colorless crystals began to separate. The mixture was left overnight and the precipitate was isolated by filtration; yield of **1** 42.1 mg (0.0359 mmol, 66%; *FW* = 1172.9). The aqueous mother liquor was extracted once with 20 mL of CH_2Cl_2. Evaporation of the solvent gave an additional crop of 20 mg (0.0170 mmol, 32%). Total isolated yield was 62.1 mg (0.053 mmol; 98%). The IR spectra of the isolated solids were identical with that of pure $Cs[H_2NB_2(C_6F_5)_6]$ (**1**).

(b) Water, containing other metal salts

To a water solution (450 mL), containing the inorganic salts listed below, was added $[Na(OEt_2)_3][H_2NB_2(C_6F_5)_6]$ (27.5 mg, 0.0214 mmol; *FW* = 1285.4; $c \approx 4.75\ 10^{-5}$ M) and the suspension was stirred overnight. A brown precipitate resulted (color presumably arising from $Fe(OH)_3$) which was filtered off and was washed with dichloromethane to extract **1**. The solvent of the extract was evaporated to dryness to leave a colorless residue: yield 19.2 mg of **1** (0.0163 mmol, 76%; *FW* = 1172.9), identified by comparison of the IR spectrum with that of pure **1**. The experiment showed that **1** can be isolated selectively and in relatively high yield from a dilute aqueous solution containing a variety of other cations.

List of added inorganic salts

Salt	FW	mass [mg]	mass [mmol]	concentration [mol/L]
CsCl	168.4	3.8	0.0226	$5\cdot10^{-5}$
KCl	74.6	138.1	1.85	$4.1\cdot10^{-3}$
$PbCl_2$	278.1	121.3	0.436	$1.0\cdot10^{-3}$
$CrCl_3\cdot6H_2O$	266.4	66.3	0.249	$0.55\cdot10^{-3}$
$CaCl_2$	111	92.4	0.832	$1.85\cdot10^{-3}$
$FeCl_3\cdot6H_2O$	270.3	109.0	0.403	$0.9\cdot10^{-3}$



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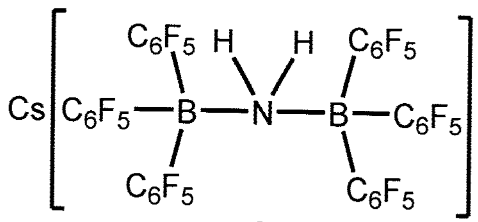

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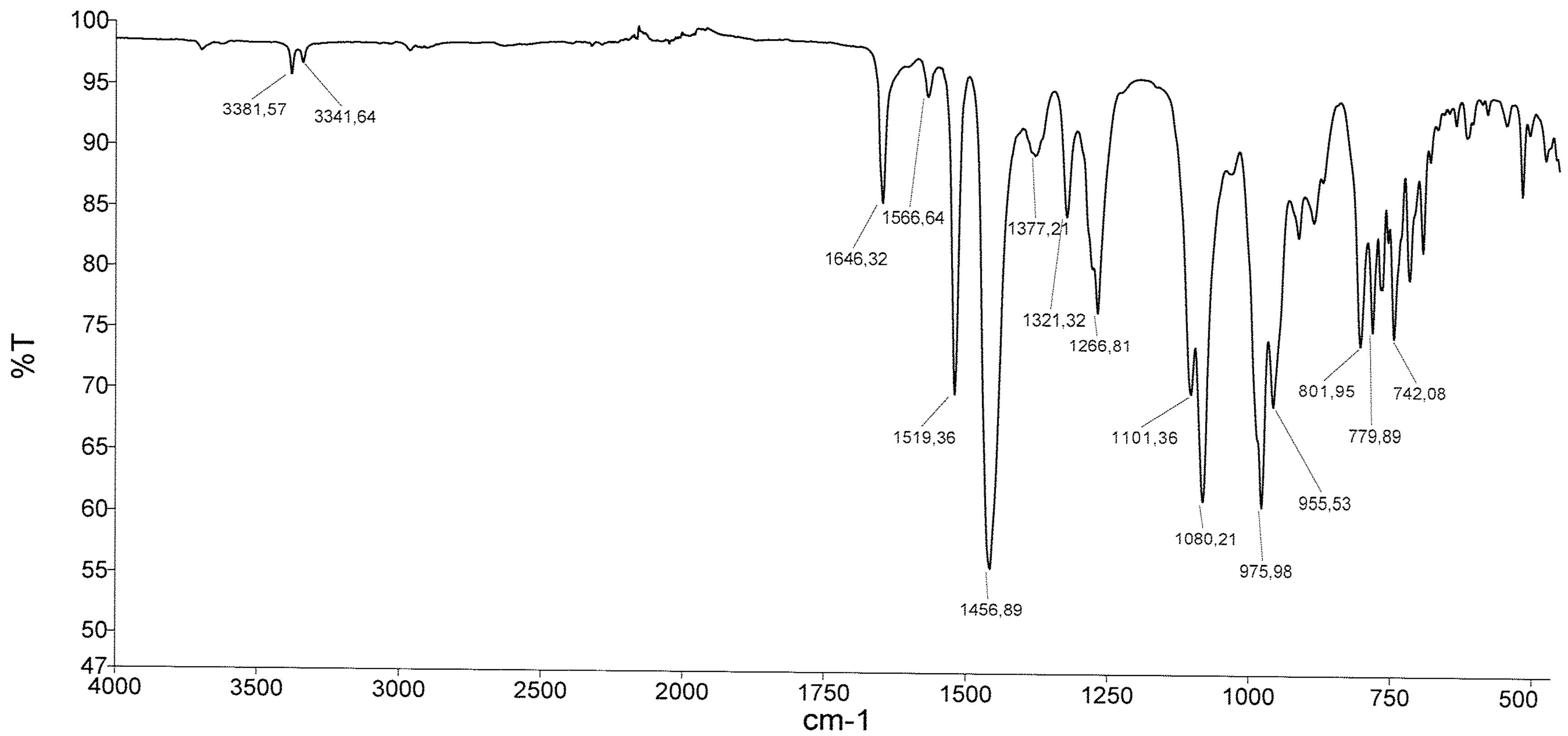

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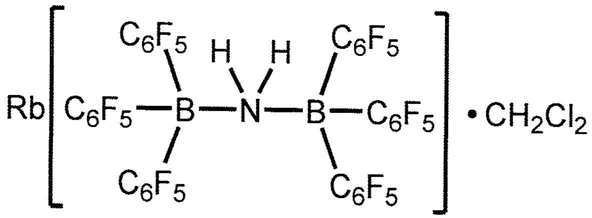

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Lattice potential energy U_{POT}

U_{POT} was calculated by the Jenkins-Passmore equation, given in Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609 (eq 3).

$Cs[H_2NB_2(C_6F_5)_6]$ (1)

$$U_{POT} = |z_+|\,|z_-|\,\nu\left(\frac{\alpha}{\sqrt[3]{Vm}} + \beta\right)$$

$|z_+| = 1$ (charge of cation)

$|z_-| = 1$ (charge of anion)

$\nu = 2$ (number of ions)

$\alpha = 117.3$ kJ mol^{-1} nm (empirical constant)

$\beta = 51.9$ kJ mol^{-1} (empirical constant)

V_m molecular volume of **1**, obtained from the structure data

$V_m = V/Z = 0.8879$ nm^3 ; $\sqrt[3]{Vm} = \sqrt[3]{0.8879}$ nm = 0.961 nm

$$U_{POT} = 2\left(\frac{117.3}{0.961} + 51.9\right) \text{ kJ mol}^{-1} = 348 \text{ kJ mol}^{-1}$$

$Tl[B(C_6F_5)_4]$

$$U_{POT} = |z_+|\,|z_-|\,\nu\left(\frac{\alpha}{\sqrt[3]{Vm}} + \beta\right)$$

$V_m = V/Z = 0.5802$ nm^3 ; $\sqrt[3]{Vm} = \sqrt[3]{0.5802}$ nm = 0.834051 nm $\approx$ 0.834 nm

$$U_{POT} = 2\left(\frac{117.3}{0.834} + 51.9\right) \text{ kJ mol}^{-1} = 385 \text{ kJ mol}^{-1}$$

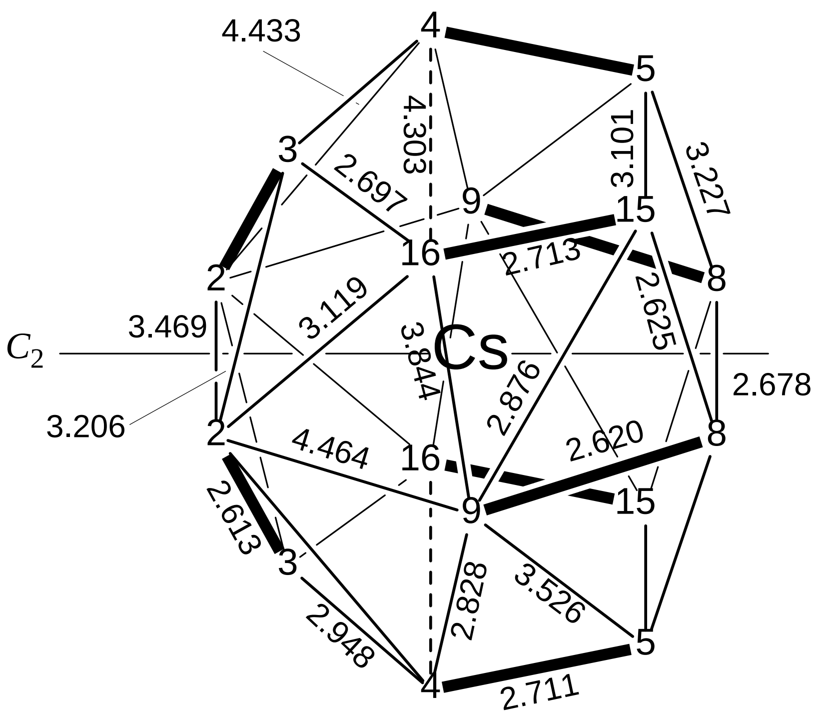

Figure S1. Summary of geometrical features of the 24-hedron in **1**. Length of edges in Å.

Bond distances (Å)		Bite angles of chelate	
Cs–F2	3.569(2)	F2–Cs–F3	45.5(1)°
Cs–F3	3.099(3)		
Cs–F4	3.799(1)	F4–Cs–F5	42.9(1)°
Cs–F5	3.591(3)		
Cs–F8	3.200(2)	F8–Cs–F9	47.5(1)°
Cs–F9	3.303(3)		
Cs–F15	3.629(5)	F15–Cs–F16	46.3(1)°
Cs–F16	3.196(5)		

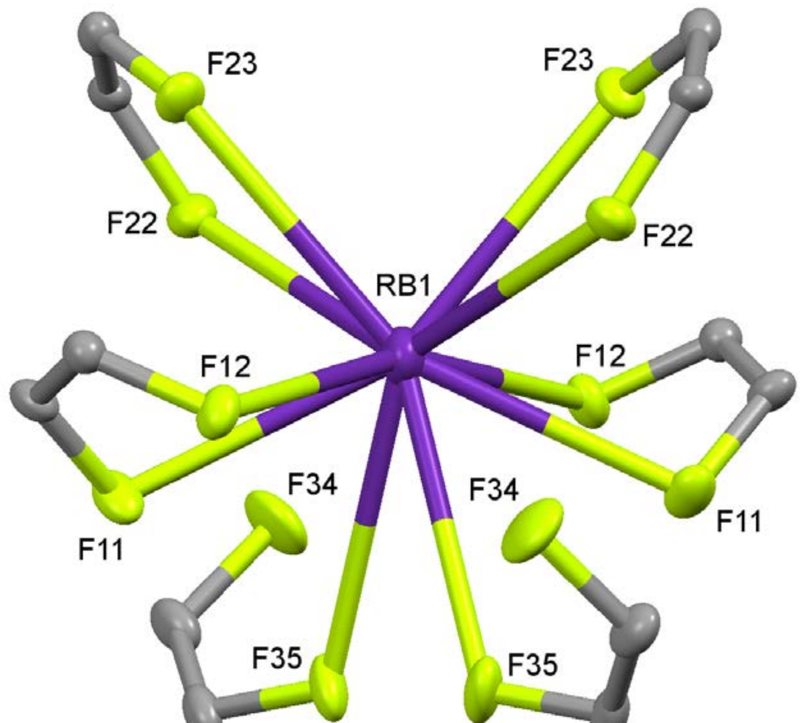

Figure S2. Coordination sphere of Rb1 in the structure of $Rb[H_2NB_2(C_6F_5)_6]\cdot CH_2Cl_2$ (**2**).

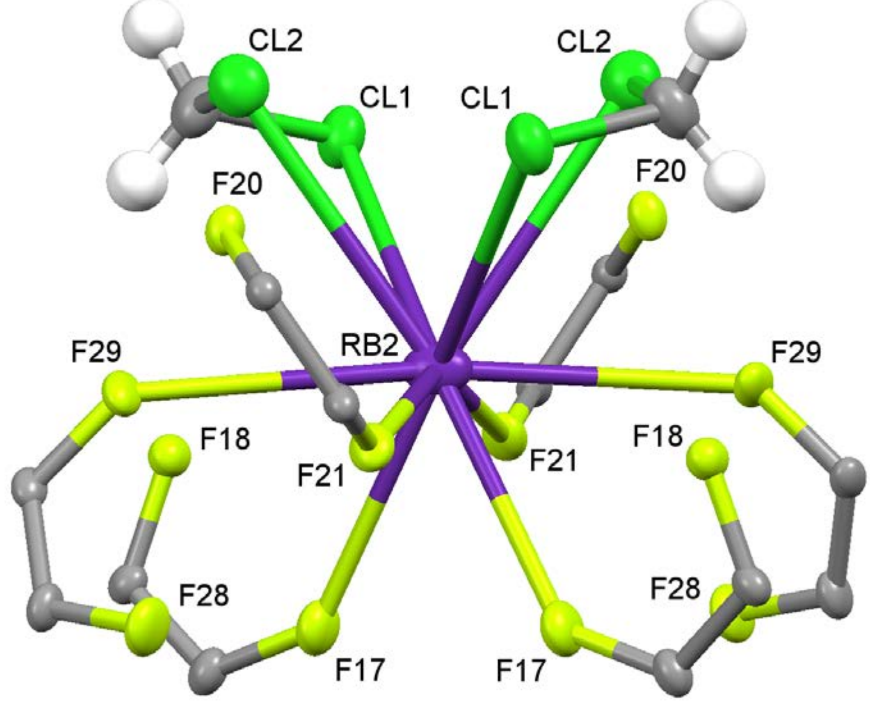

Figure S3. Coordination sphere of Rb2 in the structure of $Rb[H_2NB_2(C_6F_5)_6]\cdot CH_2Cl_2$ (**2**).

Table S1. Prominent Polyhedra having 16 Vertices

Name	Description	Point group	References
Octagonal prism	vertices 16 edges 24 **faces 10** 8 squares 2 octagons	D_{8h}	http://polyhedra.org
Triakis truncated tetrahedron	vertices 16 edges 30 **faces 16** 12 triangles 4 hexagons	T_d	Conway, J. H.; Burgiel, H.; Goodman-Strauss, C. *The Symmetries of Things*, Taylor & Francis, 2008 (ISBN 1-5688-1220-5).
Octagonal antiprism	vertices 16 edges 32 **faces 18** 16 triangles 2 octagons	D_{8d}	http://polyhedra.org
Square orthobicupola	vertices 16 edges 32 **faces 18** 8 triangles 8+2 squares	D_{4h}	http://polyhedra.org Johnson Solid J28 Sironi, D'Alfonso, et al. *JACS* 1990, *112*, 9395.
Square gyrobicupola	vertices 16 edges 32 **faces 18** 8 triangles 8+2 squares	D_{4d}	http://polyhedra.org Johnson Solid J29 Lerner et al. *Chem. Commun.* 2005, 4545. Houser et al. *Dalton Trans.* 2009, 4439.
Disphenocingulum	vertices 16 edges 38 **faces 24** 20 triangles 4 squares	D_{2d}	http://polyhedra.org Johnson Solid J90
Snub square antiprism	vertices 16 edges 40 **faces 26** 8+16 triangles 2 squares	D_{4d}	http://polyhedra.org Johnson Solid J85 Longoni, Manassero, et al. *Inorg. Chem.* 1985, 24, 117.
Capped truncated tetrahedron Friauf polyhedron Franck-Kasper polyhedron	vertices 16 edges 42 **faces 28** all triangles	T_d	Nesper, R. *ACIE* 1991, 30, 789. Bobev, S.; Sevov, S. C. *JACS* 2002, 124, 3359.
Thomson tetrahedron	vertices 16 edges 42 **faces 28** all triangles	T	Thomson, J. J. *Philos. Mag.* 1904, *7*, 237. LaFave Jr., T. *J. Electrostatics* 2013, *71*, 1029.