



Supporting Information

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**Rational Design of Tightly Closed Coordination Tetrahedra Stable  
in the Solid State, in Solution and in the Gas Phase**

Iris M. Müller\*, Daniela Möller, Christoph Schalley

Dr. Iris M. Müller\*, Dipl. Chem. Daniela Möller

Lehrstuhl für Analytische Chemie

NC 4 / 27

Ruhr-Universität Bochum

44780 Bochum (Germany)

Telefax: (+49) 234 321 4420

E-mail: [iris.m.mueller@rub.de](mailto:iris.m.mueller@rub.de)

Priv.-Doz. Dr. Christoph Schalley

Kekulé-Institut für Organische Chemie und Biochemie

Universität Bonn

53121 Bonn (Germany)

Table S1 Hydrogen bridges in **1a** and **1b**

	Proton	Bond to	Distance [Å]	Angle at H
<b>1a</b>	H15	Cl	2.26	165°
	H25	O (H <sub>2</sub> O)	1.82	169°
	H35	Cl	2.35	144°
	H11	N (CH <sub>3</sub> CN)	2.22	159°
	H21	N (CH <sub>3</sub> CN)	2.35	153°
	H31	N (CH <sub>3</sub> CN)	2.15	157°
<b>1b</b>	H115 / H215	Cl	2.55 / 2.34	129° / 152°
	H125 / H225	Cl	2.45 / 2.43	138° / 138°
	H135 / H235	O (acetone / H <sub>2</sub> O)	1.98 / 1.86	177° / 165°
	H111 / H211	O (acetone)	2.24 / 2.15	148° / 145°
	H121 / H221	O (acetone)	2.47 / 2.49	153° / 113°
	H131 / H231	O (acetone)	2.08 / 2.06	157° / 150°

Table S2 Selected bond length and angles in **1a** - **4**.

(\* inside five membered chelate ring, \*\* inside six membered chelate ring, # outside chelate ring, ## in (CdO)<sub>2</sub> ring)

	<b>1a</b>	<b>1b</b>	<b>2</b>	<b>3</b>	<b>4</b>
	(100 K)	(213 K)	(100 K)	(100 K)	(100 K)
C - N [Å]	1.330 (4)	1.32 (2)	1.36 (2)	1.36 (2)	1.36 (1)
N - N [Å]	1.385 (5)	1.39 (1)	1.38 (2)	1.38 (2)	1.38 (1)
N = C [Å]	1.279 (4)	1.27 (1)	1.28 (2)	1.29 (2)	1.29 (1)
C - Br [Å]	1.903 (5)	1.89 (2)	1.92 (2)	1.92 (3)	1.91 (1)
Angle C1	120.0 (6) °	120 (3) °	120 (1) °	120 (2) °	120.0 (6) °
Angle N1	117.1 (9) °	117 (1) °	114.4 (9) °	114 (2) °	114.2 (5) °
			118 (1) °*	118 (2) °*	118.2 (6) °*
			127 (1) °#	127 (2) °#	127.4 (7) °#
Angle N2	114.7 (9) °	115 (2) °	117.1 (9) °	117 (2) °	116.9 (7) °
			117.3 (7) °*	118 (1) °*	117.5 (7) °*
			124.7 (8) °**	125 (2) °**	124 (1) °**
Angle O	-	-	120 (2) °	119 (2) °	119 (2) °
			104.9 (9) °##	105 (1) °##	105.2 (8) °##
deviation from CN <sub>6</sub> -plane [Å]	0.04 (1)	0.02 (2)	0.04 (1)	0.05 (1)	0.05 (1)
Torsion CN <sub>6</sub> vs. phenyl	3.6° - 12.5°	2.9° - 24.9°	16.9° - 36.4°	18.0° - 31.9°	22.0° - 33.7°

Table S3 Bond length and angles at the cadmium centres in **2** - **4**

(100 K, O' oxygen of neighboured ligand)

	<b>2</b>	<b>3</b>	<b>4</b>
Cd - N(1)	2.25 (1)	2.26 (2)	2.251 (8)
Cd - N(2)	2.32 (2)	2.33 (2)	2.32 (1)
Cd - O	2.28 (2)	2.29 (2)	2.28 (2)
Cd - O'	2.23 (2)	2.24 (2)	2.23 (1)
Cd - Cl	2.43 (1)	2.49 (2)	2.450 (8)
N(1) - Cd - N(2)	69.4 (5) °	69.4 (8) °	69.5 (3) °
N(1) - Cd - O	131 (2) °	131 (3) °	132 (1) °
N(2) - Cd - O	75.4 (9) °	75.4 (8) °	75.7 (6) °
N(1) - Cd - O'	108 (2) °	110 (2) °	110 (2) °
N(2) - Cd - O'	135 (2) °	136 (2) °	135 (2) °
O - Cd - O'	74.5 (6) °	74.5 (9) °	74.2 (7) °
N(1) - Cd - Cl	113 (3) °	111 (3) °	113 (4) °
N(2) - Cd - Cl	113 (2) °	111 (2) °	111 (3) °
O - Cd - Cl	112 (4) °	113 (4) °	111 (4) °
O' - Cd - Cl	109 (2) °	110 (3) °	109 (3) °

## Experimental Section

Triaminoguanidinium chloride was prepared according to literature methods.<sup>[13]</sup>

### **[C<sub>22</sub>H<sub>18</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>3</sub>]Cl (1)**

Triaminoguanidinium chloride (4.681 g, 33.3 mmol) was dissolved in a hot mixture of H<sub>2</sub>O (50 mL) and ethanol (100 mL). A solution of 5-bromosalicylaldehyde (20.0392 g, 99.7 mmol) in ethanol (140 mL) was slowly added. The resulting suspension was allowed to cool to room temperature. **1** was crystallized from acetone (400 mL). Yield: 22.2691 g (32.3 mmol, 97 %). Elemental analysis (calc. + 1 H<sub>2</sub>O) C 37.42 (37.34); H 2.57 (2.85); N 11.77 (11.88). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO, 25°C): 12.12, 10.83, 9.01, 8.37, 7.48, 7.01 ppm. <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO, 25°C): 156.38, 148.79, 145.92, 135.70, 128.70, 121.55, 118.50, 110.95 ppm. Crystals suitable for X-ray crystallography were grown by slow diffusion of HCl gas into a solution of **1** in acetonitrile.

### **[C<sub>22</sub>H<sub>18</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>3</sub>]<sub>2</sub>[CdCl<sub>4</sub>] (1b)**

Tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride (69.3 mg, 0.1 mmol) and cadmium chloride dihydrate (48.2 mg, 0.22 mmol) were mixed in acetone (2 mL) and sealed in a glass tube. The reaction mixture was heated up to 88°C during a period of 40 hours and allowed to cool to room temperature over 80 hours resulting in the formation of pale yellow crystals of **1b**.

### **[(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>5</sub>[(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>3</sub>[{(CdCl)<sub>3</sub>C<sub>22</sub>H<sub>12</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>3</sub>]<sub>4</sub>] (2)**

Cadmium chloride dihydrate (32.8 mg, 0.15 mmol) and tetraethylammonium chloride (16.6 mg, 0.1 mmol) were dissolved in methanol (2 mL) and added to a solution of tris(5-bromo-2-hydroxy-

benzylidene)triaminoguanidinium chloride (34.7 mg, 0.05 mmol) in methanol (2 mL) and triethylamine (0.1 mL). Further triethylamine (1 mL) was slowly diffused into the reaction mixture. After three weeks yellow crystals of **2** were formed. Yield: 56.7 mg (0.0105 mmol, 84 %). Elemental analysis (calc. + 11 H<sub>2</sub>O) C 31.69 (31.75); H 3.90 (3.98); N 8.11 (8.12); Cd 24.5 (24.43).

**[ (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P ]<sub>1.33</sub> [ (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH ]<sub>6.67</sub> [ { (CdCl)<sub>3</sub>C<sub>22</sub>H<sub>12</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>3</sub> }<sub>4</sub> ] (3)**

Tetraphenylphosphonium bromide (10.8 mg, 0.026 mmol) and cadmium chloride dihydrate (33.2 mg, 0.151 mmol) were dissolved in methanol (2 mL) and added to a solution of tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride (34.5 mg, 0.05 mmol) in methanol (2 mL) and triethylamine (0.1 mL). Additional triethylamine (1 mL) was then slowly diffused into the reaction mixture. After three weeks yellow crystals of **3** were formed. Yield: 61.8 mg (0.0109 mmol, 87 %). Elemental analysis (calc. + 12 H<sub>2</sub>O) C 33.65 (33.62); H 3.59 (3.62); N 7.69 (7.51).

**[ (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH ]<sub>8</sub> [ { (CdCl)<sub>3</sub>C<sub>22</sub>H<sub>12</sub>N<sub>6</sub>O<sub>3</sub>Br<sub>3</sub> }<sub>4</sub> ] (4)**

Cadmium chloride dihydrate (32.9 mg, 0.15 mmol) was dissolved in methanol (2 mL) and added to a solution of tris(5-bromo-2-hydroxybenzylidene)triaminoguanidinium chloride (34.9 mg, 0.051 mmol) in methanol (2 mL) and triethylamine (0.1 mL). Further triethylamine (1 mL) was slowly diffused into the reaction mixture. After two weeks yellow crystals of **4** were formed. Yield: 65.5 mg (0.0126 mmol, 99 %). Elemental analysis (calc. + 12 H<sub>2</sub>O) C 30.18 (30.25); H 3.60 (3.73); N 8.15 (8.30); Cd 25.1 (24.98). <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]acetone, 25°C): 7.52, 7.23, 6.57, 3.18, 1.27, 0.95.

## **X-ray analysis**

Intensity data were collected for **1a**, **2**, **3** and **4** on a Nonius Kappa CCD (Mo- $K_{\alpha}$  rotating anode) and for **1b** on an AXS Smart / CCD diffractometer (Mo- $K_{\alpha}$  radiation) always employing the  $\omega$  scan method. All data were corrected for Lorentz and polarization effects. **1a** - **4** were solved by using direct methods (SHELXS-97)<sup>[14]</sup> and refined by using a full-matrix least-squares refinement procedure (SHELXL-97)<sup>[15]</sup>. All protons were placed at geometrically estimated positions. Due to the large number of disordered counter cations and solvent molecules outside the cages and the resulting low data to parameter ratio we decided to correct the X-ray data of **2**, **3** and **4** for their influence employing the SQUEEZE routine in PLATON.<sup>[16]</sup> Nevertheless the cations inside the cages were located in the difference syntheses and refined. They were all disordered but could be modelled with bond lengths fixed to literature values.

## **ESI-FT-ICR mass spectrometry**

High resolution ESI mass spectra were recorded on a Bruker APEX IV Fourier-transform ion-cyclotron-resonance (FT-ICR) mass spectrometer with an Apollo electrospray ion source equipped with an off-axis 70° spray needle. Typically, acetone and acetonitrile served as the spray solvent and 100  $\mu$ M solutions of the analytes were used. Analyte solutions were introduced into the ion source with a syringe pump (Cole-Parmer Instruments, Series 74900) at flow rates of ca. 3 - 4  $\mu$ L/min. Ion transfer into the first of three differential pumping stages in the ion source occurred through a glass capillary with 0.5 mm inner diameter and nickel



coatings at both ends. Ionization parameters were adjusted as follows: capillary voltage: 4.7 to 4.9 kV; endplate voltage: 3.8 to 4.1 kV; capexit voltage: -70 to -90 V; skimmer voltages: -10 to -12 V; temperature of drying gas: 30 °C. The flows of the drying and nebulizer gases were kept in a medium range (ca. 10 psi). The ions were accumulated in the instruments hexapole for 0.5 - 1 s, introduced into the FT-ICR cell, which was operated at pressures below  $10^{-10}$  mbar and detected by a standard excitation and detection sequence. For each measurement 128 to 512 scans were averaged to improve the signal-to-noise ratio.

## References

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