

An indium(III)–water chain based on an unusual acyclic water pentamer

Chun-Bo Liu, Guang-Bo Che,* Chuan-Bi Li and Yun-Cheng Cui

Department of Chemistry, Jilin Normal University, Siping 136000, People's Republic of China

Correspondence e-mail: guangbochejl@yahoo.com

Received 9 February 2006

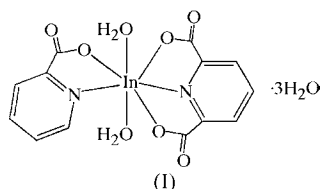
Accepted 27 February 2006

Online 31 March 2006

An *in situ* reaction under hydrothermal conditions leads to the formation of the title compound, diaqua(pyridine-2-carboxylato)(pyridine-2,6-dicarboxylato)indium(II) trihydrate, $[\text{In}(\text{C}_6\text{H}_4\text{NO}_2)(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, in which the central In^{III} atom is seven-coordinated by one pyridine-2,6-dicarboxylate ligand, one pyridine-2-carboxylate ligand and two water molecules in a pentagonal–bipyramidal coordination environment. An indium(III)–water chain based on an unusual water pentamer is observed.

Comment

The study of water clusters is important for an understanding of the structures and characteristics of liquid water and ice (Ludwig, 2001). Thus, the search for the experimental models of small water clusters is important in order to improve our studies of liquid water and ice (Ye *et al.*, 2004). So far, a variety of water clusters, including tetramers, hexamers, octamers and decamers, found in a number of crystalline hosts have been structurally characterized and found to display different configurations (Ghosh & Bharadwaj, 2004). Curiously, odd-membered water clusters are known to occur very rarely (Infantes & Motherwell, 2002), although a few structural characterizations of the cyclic water pentamer have been reported recently. Theoretically, the cyclic water pentamer is much more stable than the acyclic version because of co-operative hydrogen bonding in the cyclic system (Cruzan *et al.*, 1996). To the best of our knowledge, no organic or metal-organic compound is known in which an isolated acyclic water



pentamer has been detected (Infantes & Motherwell, 2002). We report here for the first time the formation and structure of

an acyclic water pentamer in the title compound, $[\text{In}(\text{pc})(\text{pdc})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, (I), where pdc is pyridine-2,6-dicarboxylate and pc is pyridine-2-carboxylate.

Compound (I) was obtained under hydrothermal conditions at 433 K. The compound, once formed, is insoluble in most solvents, including water. The asymmetric unit of (I) is shown in Fig. 1. The central In^{III} atom is seven-coordinated by one pdc ligand, one pc ligand and two water molecules in a pentagonal–bipyramidal coordination environment, in which three carboxylate O atoms (O1, O4 and O5) and two N atoms (N1 and N2) from the pdc and pc anions make up the basal plane, while the axial positions are occupied by two water molecules (O1W and O2W). Selected bond lengths and angles are given in Table 1.

A new *in situ* reaction occurs in the $\text{InCl}_3 \cdot 6\text{H}_2\text{O}/\text{H}_2\text{pdc}$ system under hydrothermal conditions. In the reaction process, some of the pdc ions are transformed into pc ions *via* decarboxylation. A similar reaction process, in which quinolinic acid is transformed into pc *via* decarboxylation, has been observed recently (Yu *et al.*, 2003). In addition, a few novel *in situ* reactions, such as ligand oxidative coupling, hydrolysis and substitution, have been uncovered during the hydrothermal process (Zheng *et al.*, 2004); in these reactions, many factors, including the nature of the metal ion, and the temperature,

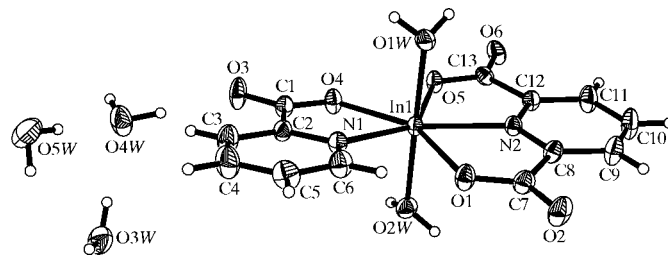


Figure 1
An ORTEP (Burnett & Johnson, 1996) view of the local coordination of the In^{III} atom in (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

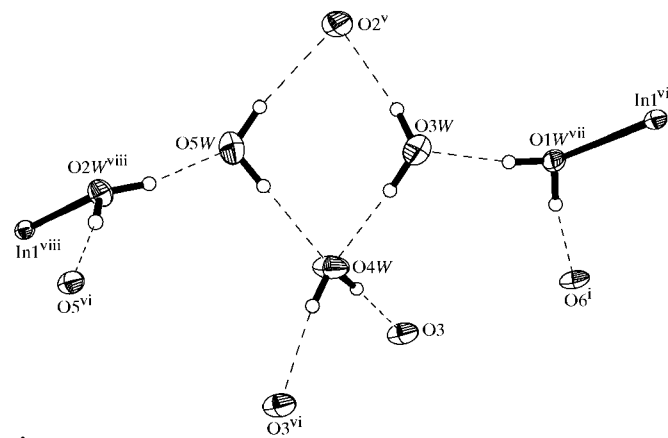


Figure 2
An ORTEP (Burnett & Johnson, 1996) view showing the water pentamer of (I) and its coordination environment. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (v) $-x + 1, -y + 2, -z$; (vi) $-x + 1, -y + 1, -z + 1$; (vii) $x - 1, y, z$; (viii) $x, y - 1, z$.]

pressure and pH, have been found to influence significantly the reaction outcome. As far as our system is concerned, the pH value may play a key role in the decarboxylation of pdc. When the pH value was adjusted to be higher or lower than 5.5, no crystals of (I) were obtained under hydrothermal conditions at 433 K. To the best of our knowledge, the *in situ* transformation from pdc to pc has not been observed before.

An interesting feature of (I) is the presence of an indium(III)–water chain based on an unusual acyclic water pentamer (Figs. 2 and 3; Li *et al.*, 2005). Within the water pentamer, three water molecules (O3W, O4W and O5W) act as both hydrogen-bond donors and acceptors, while the other two water molecules (O1W^{vii} and O2W^{viii}, symmetry codes as in Fig. 2) act only as hydrogen-bond acceptors. The hydrogen-bond parameters are given in Table 2. The average hydrogen-bond distance is 2.73 (5) Å, which is slightly shorter than the average hydrogen-bond distance of the liquid water pentamer (2.78 Å; Naskar *et al.*, 2005). Interestingly, the water molecules of the pentamer are hydrogen bonded to carboxylate O atoms (O2^v, O3, O3^{vi}, O5^{vi} and O6ⁱ) of the pdc and pc ligands. Meanwhile, two water molecules (O1W^{vii} and O2W^{viii}) bind to the In^{III} atoms, resulting in a three-dimensional supramolecular structure. This observation indicates that the water pentamer is stabilized not only by hydrogen bonds but also by

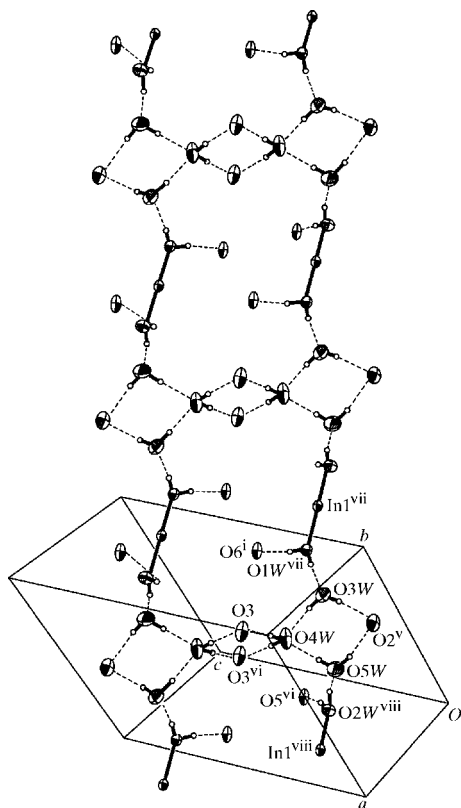


Figure 3
An ORTEP (Burnett & Johnson, 1996) view showing the structure of an indium(III)–water chain based on the unusual acyclic water pentamer. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (v) $-x + 1, -y + 2, -z$; (vi) $-x + 1, -y + 1, -z + 1$; (vii) $x - 1, y, z$; (viii) $x, y - 1, z$.]

coordination interactions. The water molecules, the pdc and pc ligands, and the In^{III} atom each play a crucial role in the formation of the water clusters.

In summary, a new In^{III} compound with a three-dimensional supramolecular structure was synthesized *via* a new *in situ* reaction under hydrothermal conditions at 433 K. In this compound, an indium(III)–water chain based on an unusual acyclic water pentamer was observed.

Experimental

InCl₃·6H₂O (0.38 g, 1.0 mmol) and H₂pdc (0.246 g, 1.5 mmol) were dissolved in distilled water (20 ml) and the pH was adjusted to 5.5 with dilute aqueous NaOH solution. The solution was heated in a 25 ml Teflon-lined reaction vessel at 433 K for 90 h and then cooled to room temperature over a period of 12 h. Colorless crystals of (I) were collected in a yield of 75%.

Crystal data

[In(C₆H₄NO₂)(C₇H₃NO₄)(H₂O)₂]₃·3H₂O
M_r = 492.11
 Triclinic, *P* $\bar{1}$
a = 8.0818 (16) Å
b = 11.129 (2) Å
c = 11.626 (2) Å
 α = 67.56 (3)°
 β = 74.48 (3)°
 γ = 69.55 (3)°
V = 894.6 (4) Å³
Z = 2
D_x = 1.827 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 8707 reflections
 θ = 3.1–27.5°
 μ = 1.38 mm⁻¹
T = 292 (2) K
 Block, colorless
 0.39 × 0.33 × 0.28 mm

Data collection

Rigaku R-Axis RAPID
 diffractometer
 ω scan
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.528, *T_{max}* = 0.670
 8707 measured reflections
 4000 independent reflections
 3457 reflections with *I* > 2 σ (*I*)
R_{int} = 0.035
 θ_{max} = 27.5°
h = -10 → 10
k = -14 → 14
l = -15 → 15

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.028
wR(*F*²) = 0.057
S = 1.01
 4000 reflections
 280 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0254P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.44 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

N1–In1	2.328 (2)	O5–In1	2.3093 (17)
N2–In1	2.277 (2)	O1W–In1	2.147 (2)
O1–In1	2.2734 (19)	O2W–In1	2.1484 (19)
O4–In1	2.1897 (17)		
O1W–In1–O2W	179.22 (7)	O2W–In1–O5	91.26 (8)
O1W–In1–O4	92.87 (8)	O4–In1–O5	72.02 (6)
O2W–In1–O4	87.73 (8)	O1–In1–O5	139.66 (6)
O1W–In1–O1	92.62 (8)	N2–In1–O5	69.61 (7)
O2W–In1–O1	87.13 (8)	O1W–In1–N1	84.52 (7)
O4–In1–O1	147.99 (7)	O2W–In1–N1	96.14 (8)
O1W–In1–N2	88.48 (7)	O4–In1–N1	72.27 (7)
O2W–In1–N2	90.74 (8)	O1–In1–N1	76.91 (7)
O4–In1–N2	141.55 (7)	N2–In1–N1	145.90 (7)
O1–In1–N2	70.10 (7)	O5–In1–N1	143.15 (6)
O1W–In1–O5	88.45 (8)		

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—HW12...O6 ⁱ	0.86 (2)	1.76 (2)	2.601 (2)	166 (3)
O1W—HW11...O3W ⁱⁱ	0.86 (2)	1.75 (2)	2.596 (3)	171 (3)
O2W—HW22...O5 ⁱⁱⁱ	0.86 (2)	1.89 (2)	2.740 (3)	173 (4)
O2W—HW21...O5W ^{iv}	0.86 (2)	1.85 (2)	2.667 (3)	159 (3)
O3W—HW32...O2 ^v	0.90 (2)	1.88 (2)	2.750 (3)	160 (4)
O3W—HW31...O4W	0.89 (4)	1.90 (2)	2.788 (4)	174 (5)
O4W—HW42...O3	0.92 (4)	1.84 (4)	2.758 (3)	177 (3)
O4W—HW41...O3 ^{vi}	0.88 (2)	1.85 (3)	2.701 (3)	162 (4)
O5W—HW52...O2 ^v	0.90 (4)	2.03 (3)	2.902 (3)	162 (5)
O5W—HW51...O4W	0.89 (5)	1.88 (4)	2.766 (4)	177 (5)

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

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms of water molecules were located in a difference Fourier map and refined with a DFIX restraint of O—H = 0.90 Å.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXTL-Plus*.

The authors thank Jilin Normal University for supporting this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3002). Services for accessing these data are described at the back of the journal.

References

- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Cruzan, J. D., Braly, L. B., Liu, K., Brown, M. G., Loeser, J. G. & Saykally, R. J. (1996). *Science*, **271**, 59–62.
- Ghosh, S. K. & Bharadwaj, P. K. (2004). *Angew. Chem. Int. Ed.* **43**, 3577–3580.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Infantes, L. & Motherwell, S. (2002). *CrystEngComm*, **4**, 454–461.
- Li, F.-F., Ma, J.-F., Song, S.-Y., Yang, J., Liu, Y.-Y. & Su, Z.-M. (2005). *Inorg. Chem.* **44**, 9374–9383.
- Ludwig, R. (2001). *Angew. Chem. Int. Ed.* **40**, 1808–1827.
- Naskar, J. P., Drew, M. G. B., Hulme, A., Tocher, D. A. & Datta, D. (2005). *CrystEngComm*, **7**, 67–70.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Ye, B.-H., Ding, B.-B., Weng, Y.-Q. & Chen, X.-M. (2004). *Inorg. Chem.* **43**, 6866–6868.
- Yu, Z.-T., Li, G.-H., Jiang, Y.-S., Xu, J.-J. & Chen, J.-S. (2003). *Dalton Trans.* pp. 4219–4220.
- Zheng, Y.-Z., Tong, M.-L. & Chen, X.-M. (2004). *New J. Chem.* **28**, 1412–1415.