

Two related lithium calixarene complexes, [*p*-*tert*-butylcalix[4]arene(OMe)(OH)₂(OLi)]₂·4MeCN and {*p*-*tert*-butylcalix[4]arene(OH)₂(OLi)[OLi(NCMe)₂]}₂·8MeCN, determined using synchrotron radiation

Darren S. Lee,^a Mark R. J. Elsegood,^{a*} Carl Redshaw^b and Shuzhong Zhan^b

^aChemistry Department, Loughborough University, Leicestershire LE11 3TU, England, and ^bSchool of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, Norfolk NR4 7TJ, England
Correspondence e-mail: m.r.j.elsegood@lboro.ac.uk

Received 3 June 2009

Accepted 30 June 2009

Online 9 July 2009

The crystal structures of acetonitrile solvates of two related lithium calixarene complexes have been determined by low-temperature single-crystal X-ray diffraction using synchrotron radiation. Bis(μ -5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxy-25-methoxy-27-oxido-calix[4]arene)dilithium(I) acetonitrile tetrasolvate, [Li₂(C₄₅H₅₇O₄)₂]·4C₂H₃N or [*p*-*tert*-butylcalix[4]arene(OMe)(OH)₂(OLi)]₂·4MeCN, (I), crystallizes with the complex across a centre of symmetry and with four molecules of unbound acetonitrile of crystallization per complex. Tetra-acetonitrilebis(μ -5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxy-25,27-dioxido-calix[4]arene)tetralithium(I) acetonitrile octasolvate, [Li₄(C₄₄H₅₄O₄)₂(C₂H₃N)₄]·8C₂H₃N or [*p*-*tert*-butylcalix[4]arene(OH)₂(OLi)[OLi(NCMe)₂]]₂·8MeCN, (II), also crystallizes with the complex lying across a centre of symmetry and contains eight molecules of unbound acetonitrile per complex plus four more directly bound to two of the lithium ions, two on each ion. The cores of both complexes are partially supported by O—H...O hydrogen bonds. The methoxy methyl groups in (I) prevent the binding of any more than two Li⁺ ions, while the corresponding two O-atom sites in (II) bind an extra Li⁺ ion each, making four in total. The calixarene cone adopts an undistorted cone conformation in (I), but an elliptical one in (II).

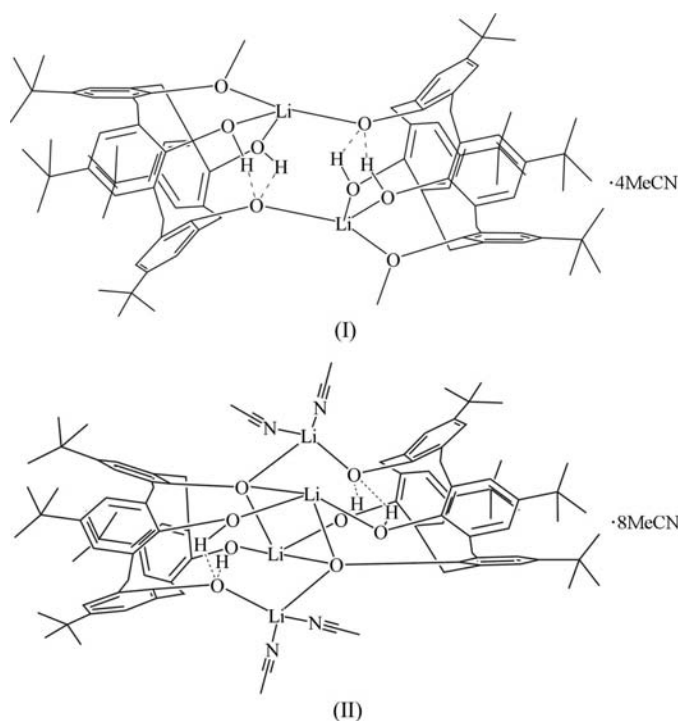
Comment

Lithiated calixarenes are useful synthons and continue to attract interest for a number of reasons, most recently because of their hydrogen storage potential (Venkataramanan *et al.*, 2008). A number of lithium-containing calixarenes have now been structurally characterized and some intriguing structure–

reactivity relationships have been highlighted (Dubberley *et al.*, 1997; Gueneau *et al.*, 2003), most notably the C–H activation in the chromium complex C₉₂H₁₁₁CrLi₂N₂O₈·4CH₃CN (Gibson *et al.*, 1997).

A Cambridge Structural Database (CSD; Version 5.30 of November 2008 plus two updates; Allen, 2002) search yielded only a few results for lithium-containing calixarenes, some of which have lithium present as a secondary metal cation while the rest contain lithium as the primary metal of the complex.

We report here the structures of two new lithiated calixarenes, (I) and (II), which were isolated as by-products of attempted syntheses of boron- or manganese-containing calixarene complexes. In each case, the lithium originates from the butyl lithium reagent (see *Experimental*).



The new lithium calixarene dimer (I) is located across a centre of symmetry (Fig. 1). The molecule consists of two *p*-*tert*-butylcalix[4]arene(OMe) ligands, each of which adopts a cone conformation with negligible distortion ($\Delta = 0.045$ Å; Δ is the sum difference in length between vectors linking centroids of opposite rings). The molecule contains two lithium ions, both with four-coordinate tetrahedral geometry. The lithium ions are bound to four O atoms, three from one calixarene and one from the other, forming a bridge between the ligands. One of the O atoms (O2) of each calixarene retains its methyl group, having only lost one from the *p*-*tert*-butyl-calix[4]arene(OMe)₂ starting material during the course of the reaction. As a result, these methyl groups are positioned pointing 'up' and 'down' when viewed from a side-on perspective. It is highly likely that the presence of these methyl groups is preventing further lithium ions from binding. A comparison can be made with compound (II), which has no methoxy groups in its starting calixarene but forms a very

similar dimer, except with four lithium ions present. In the dimeric structure, (I), two of the four acetonitrile molecules of crystallization present reside inside the cavities of the calixarenes, one in each, and two are *exo* to the cavities.

An interesting feature of (I) is that there are four intramolecular hydrogen bonds supporting the metal–oxygen core of the molecule. Two O atoms (O1 and O3) of each calixarene

remain protonated. Each of their H atoms forms a hydrogen bond to the same neighbouring O atom (O4) of the same calixarene ligand (see Table 2).

Compound (II) also lies across a centre of symmetry. In this case, the calixarene adopts a distorted cone, or elliptical, conformation ($\Delta = 0.671$ Å; Fig. 2). The molecule contains a total of four lithium ions, each of which is four-coordinate and

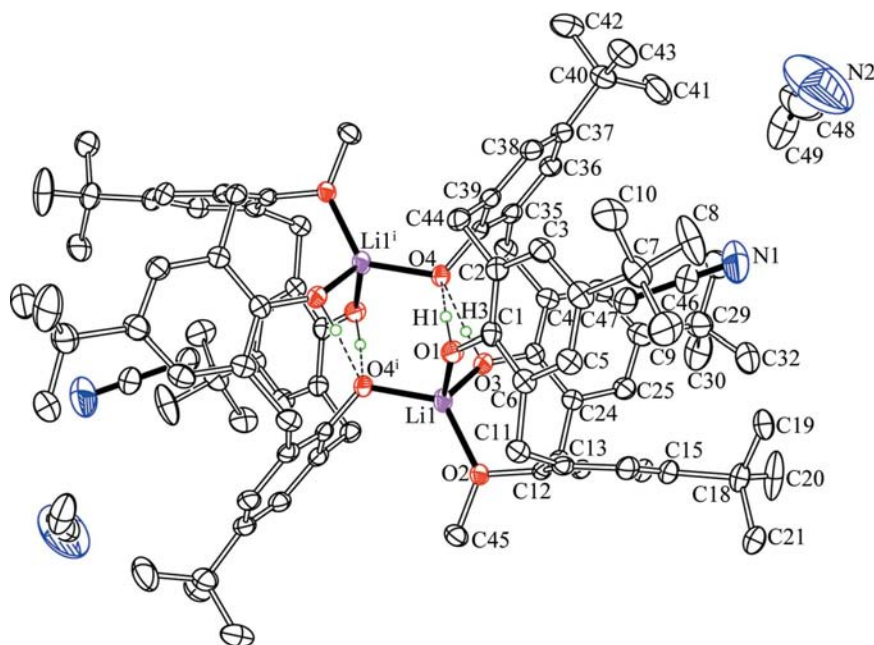


Figure 1

A view of (I), showing part of the atom-labelling scheme. The calixarene numbering scheme starts at the *ipso* C atom, goes around the C₆ ring, then the 'Bu group and finally the bridging CH₂ unit. Displacement ellipsoids are drawn at the 30% probability level. Only those H atoms involved in hydrogen bonding (indicated by dashed lines) are shown. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

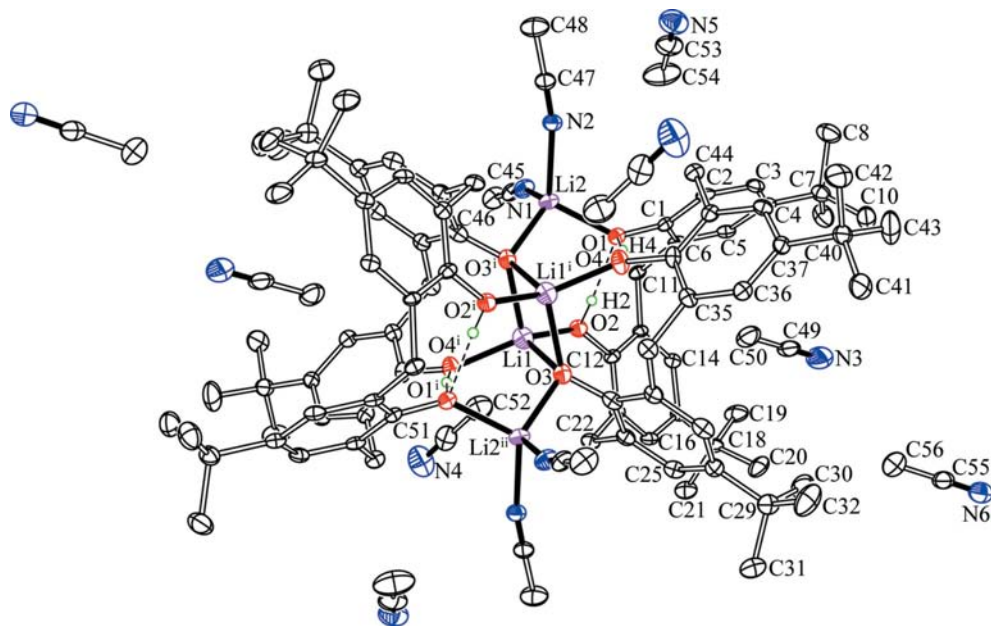


Figure 2

A view of (II), showing part of the atom-labelling scheme. The calixarene numbering scheme starts at the *ipso* C atom, goes around the C₆ ring, then the 'Bu group and finally the bridging CH₂ unit. Displacement ellipsoids are drawn at the 30% probability level. Only those H atoms involved in hydrogen bonding (indicated by dashed lines) are shown. [Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.]

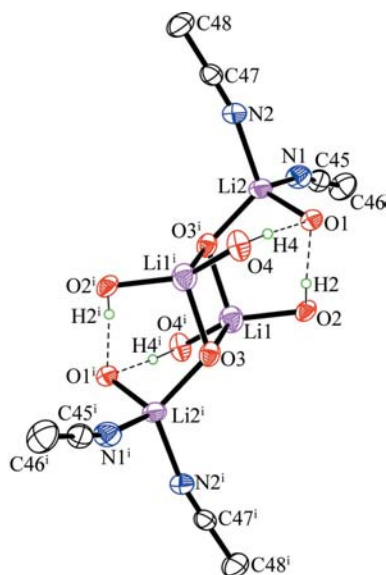


Figure 3

A view of the core for (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms involved in hydrogen bonding are represented by circles of arbitrary radii and hydrogen bonding is indicated by dashed lines. [Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.]

tetrahedral, with two involved in a Li_2O_2 diamond-shaped motif at the core. Two of the lithium ions [Li1 and Li1ⁱ; symmetry code: (i) $-x + 2, -y + 1, -z + 2$] are each bound to four O atoms, two from each calixarene ligand. The other two lithium ions are each only bound to two O atoms, one from each calixarene, but the coordination environment is completed by two molecules of acetonitrile per lithium ion. Lithium calixarenes containing these Li–NMe moieties have been seen before (Liu *et al.*, 2006; Redshaw *et al.*, 2008), with another example being the chromium calix[4]arene complex synthesized by Gibson *et al.* (1997). These acetonitrile ligands sit ‘above’ and ‘below’ the molecule, when viewed from a side-on perspective, and they appear in a ‘wing’ shape relative to each other. The structure also contains eight molecules of unbound acetonitrile per molecule of dimer. One acetonitrile sits in the cavity of each calixarene ligand, one MeCN sits just *exo* to each of the cavities, and the remaining four sit at regular intervals around the ‘waist’ of the molecule. As seen in (I), there are four protonated O atoms, two on each calixarene (O2 and O4). The corresponding H atoms (H2 and H4) form hydrogen bonds with a single neighbouring O atom (O1; see Table 4).

The Li–O bond lengths for (I) and (II) are towards the lower end when compared with the reported calix[4]arene O–Li bond lengths found in the CSD (range 1.83–2.35 Å). The Li–O lengths are shorter for bonds to the deprotonated phenoxy O atoms, as expected. The O–Li–O bond angles seen in (I) are larger, while those in (II) are mostly close to the average when compared to those reported in the CSD; the mean of these being 96.5° (range 86.3–105.4°). The exception is O4ⁱ–Li1–O2, which is much larger than any reported and

in this case bridges the two calixarene molecules, giving rise to a significantly distorted tetrahedral environment at Li1 (see Tables 1 and 3). The Li–N bond lengths are within the range of values reported in the CSD (1.91–2.20 Å). The range of reported angles for O–Li–N is 105.5–168.6°; the angles seen in (II) are rather towards the lower end of those reported. The three hits from the CSD containing a lithium ion bound to two acetonitrile ligands and two O atoms, yielded a range of N–Li–N bond angles of 91.2–119.6°. The corresponding angles in (II) are at the centre of the range.

The major differences in the two structures reported lie in their different core motifs (Fig. 3) and in the significant elliptical distortion of the calixarene ligands for (II), in contrast to the ligands in (I) which exhibit negligible distortion. Other than these major differences, bond lengths and angles are similar and show nothing too unusual. There is a significant link between these structures, and although they were obtained using different synthetic methods, they are quite similar. It would appear that (I) represents a partially reacted version of (II), with one –OMe per calixarene still present, blocking further reaction with lithium.

Experimental

For the synthesis of (I), a solution of calix[4]arene(OMe)₂ (1.00 g, 1.48 mmol) in diethyl ether (30 ml) was cooled to 195 K and then *n*-BuLi was added (2.03 ml, 3.25 mmol, 1.6 M). The resulting solution was allowed to warm to ambient temperature and was stirred for 3 h, after which MnCl_2 (0.18 g, 1.43 mmol) in tetrahydrofuran (10 ml) was added. The solution was stirred for 12 h, the volatiles were removed *in vacuo* and the residue extracted into MeCN (30 ml). On cooling the brown–purple solution to 273 K, small colourless rods of (I) formed (yield 0.39 g, 35%).

For the synthesis of (II), to 1,3-bis(trifluoromethyl)benzene (1.00 g, 4.67 mmol) was added *n*-BuLi (2.91 ml, 4.66 mmol, 1.6 M) in diethyl ether (30 ml) at 195 K. After stirring for 2 h at room temperature, $[\text{CIB}]_2\text{tert-butylcalix[4]arene}$ (1.71 g, 2.32 mmol) was added and stirring was continued for a further 12 h. Volatile components were removed *in vacuo*, and the residue was taken up in MeCN (30 ml). Prolonged standing (2–3 d) at 273 K afforded small colourless tablets of (II) (yield 0.33 g, 16%).

Compound (I)

Crystal data

$[\text{Li}_2(\text{C}_{45}\text{H}_{57}\text{O}_4)_2] \cdot 4\text{C}_2\text{H}_3\text{N}$
 $M_r = 1501.91$
 Monoclinic, $P2_1/n$
 $a = 12.8368$ (11) Å
 $b = 17.8044$ (15) Å
 $c = 19.6735$ (16) Å
 $\beta = 90.2746$ (12)°

$V = 4496.4$ (7) Å³
 $Z = 2$
 Synchrotron radiation
 $\lambda = 0.6911$ Å
 $\mu = 0.07$ mm^{−1}
 $T = 150$ K
 $0.24 \times 0.06 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Version 2004/1; Sheldrick, 2004)
 $T_{\min} = 0.984, T_{\max} = 0.997$

29080 measured reflections
 8536 independent reflections
 5918 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$

Table 1

Selected geometric parameters (Å, °) for (I).

Li1—O1	1.987 (5)	Li1—O3	1.981 (5)
Li1—O2	1.853 (5)	Li1—O4 ⁱ	1.866 (5)
O1—Li1—O2	105.5 (2)	O2—Li1—O3	107.8 (2)
O1—Li1—O3	112.6 (2)	O2—Li1—O4 ⁱ	127.6 (3)
O1—Li1—O4 ⁱ	102.4 (2)	O3—Li1—O4 ⁱ	100.9 (2)

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<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>
O1—H1...O4	1.00 (4)	1.59 (4)	2.568 (3)	165 (3)
O3—H3...O4	0.89 (4)	1.68 (4)	2.541 (3)	162 (3)

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.074$

$wR(F^2) = 0.226$

$S = 1.03$

8536 reflections

561 parameters

172 restraints

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Compound (II)

Crystal data

$[\text{Li}_4(\text{C}_{44}\text{H}_{54}\text{O}_4)_2(\text{C}_2\text{H}_3\text{N})_4] \cdot 8\text{C}_2\text{H}_3\text{N}$

$M_r = 1814.16$

Triclinic, $P\bar{1}$

$a = 12.8190 (12) \text{ \AA}$

$b = 13.5649 (13) \text{ \AA}$

$c = 18.223 (3) \text{ \AA}$

$\alpha = 106.035 (2)^\circ$

$\beta = 94.097 (2)^\circ$

$\gamma = 115.286 (2)^\circ$

$V = 2687.4 (5) \text{ \AA}^3$

$Z = 1$

Synchrotron radiation

$\lambda = 0.8466 \text{ \AA}$

$\mu = 0.07 \text{ mm}^{-1}$

$T = 150 \text{ K}$

$0.15 \times 0.14 \times 0.07 \text{ mm}$

Data collection

Bruker APEXII CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Version 2.10;

Sheldrick, 2003)

$T_{\min} = 0.990$, $T_{\max} = 0.995$

15630 measured reflections

7870 independent reflections

4532 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 28.4^\circ$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.172$

$S = 1.00$

7870 reflections

638 parameters

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Aromatic (C—H = 0.95 Å), methyl (C—H = 0.98 Å) and *tert*-butyl methylene (C—H = 0.99 Å) H atoms were placed in geometrically calculated positions using a riding model. H atoms on acetonitrile were initially located from difference maps. Methyl H atoms, including those of acetonitrile, were refined allowing rotational freedom in all ordered groups. The coordinates of hydroxy H atoms were freely refined. $U_{\text{iso}}(\text{H})$ values were generally set at $1.2U_{\text{eq}}$ of the carrier atom, and at $1.5U_{\text{eq}}$ for OH in (I) and for all methyl H atoms.

Table 3

Selected geometric parameters (Å, °) for (II).

Li1—O2	1.919 (7)	Li2—O1	1.888 (6)
Li1—O3	1.996 (7)	Li2—O3 ⁱ	1.996 (6)
Li1—O3 ⁱ	1.996 (7)	Li2—N1	2.082 (7)
Li1—O4 ⁱ	1.912 (7)	Li2—N2	2.087 (6)
O1—Li2—O3 ⁱ	99.6 (3)	O3 ⁱ —Li1—O4 ⁱ	99.4 (3)
O2—Li1—O3	104.6 (3)	N1—Li2—O1	105.4 (3)
O2—Li1—O3 ⁱ	101.4 (3)	N1—Li2—O3 ⁱ	115.6 (3)
O2—Li1—O4 ⁱ	141.2 (4)	N2—Li2—O1	114.1 (3)
O3—Li1—O3 ⁱ	107.3 (3)	N2—Li2—O3 ⁱ	116.5 (3)
O3—Li1—O4 ⁱ	99.9 (3)	N1—Li2—N2	105.4 (3)

Symmetry code: (i) $-x + 2, -y + 1, -z + 2$.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

<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>
O2—H2...O1	0.82 (3)	1.74 (3)	2.554 (3)	171 (4)
O4—H4...O1	0.93 (4)	1.61 (4)	2.525 (3)	171 (3)

Geometric and displacement parameter restraints were applied to two 'Bu groups, which were modelled as disordered with two sets of positions for the methyl groups [at C7 and C18 in (I)]. The major occupancies were 70.3 (17) and 86.4 (7)%, respectively. The N2/C48/C49 acetonitrile group in (I) has fairly large U values, but these were left unrestrained as applying the restraints had little effect on the displacement parameters and the observed values are a true reflection of reality in the crystal lattice. This behaviour is common for unbound solvent molecules in calixarene complexes (Redshaw *et al.*, 2007).

For both compounds, data collection: *APEX2* (Bruker 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and local programs.

We acknowledge the STFC for beam time at Daresbury Laboratory. We also acknowledge the assistance provided by the station scientists Dr J. E. Warren and Dr T. J. Prior at Daresbury Laboratory SRS. The Big C Cancer appeal (Norwich, UK) is thanked for their financial support (CR).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3021). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruker (2006). *APEX2* (Version 7.06a) and *SAINT* (Version 7.34a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dubberley, S. R., Blake, A. J. & Mountford, P. (1997). *Chem. Commun.* pp. 1603–1604.
- Gibson, V. C., Redshaw, C., Clegg, W. & Elsegood, M. R. J. (1997). *Chem. Commun.* pp. 1605–1606.
- Gueneau, E. D., Fromm, K. M. & Goesmann, H. (2003). *Chem. Eur. J.* **9**, 509–514.

- Liu, L., Zakharov, L. N., Golen, J. A., Rheingold, A. L., Watson, W. H. & Hanna, T. A. (2006). *Inorg. Chem.* **45**, 4247–4260.
- Redshaw, C., Liu, X., Zhan, S., Hughes, D. L., Baillie-Johnson, H., Elsegood, M. R. J. & Dale, S. H. (2008). *Eur. J. Inorg. Chem.* **17**, 2698–2712.
- Redshaw, C., Rowan, M. A., Warford, L., Homden, D. M., Arbaoui, A., Elsegood, M. R. J., Dale, S. H., Yamato, T., Casas, C. P., Matsui, S. & Matsuura, S. (2007). *Chem. Eur. J.* **13**, 1090–1107.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Sheldrick, G. M. (2004). *SADABS*. Version 2004/1. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Venkataramanan, N. S., Sahara, R., Mizuseki, H. & Kawazoe, Y. (2008). *J. Phys. Chem. C*, **112**, 19676–19679.