ware used to prepare material for publication: *CIFTAB* in *SHELXL*93 and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1039). Services for accessing these data are described at the back of the journal.

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Mononuclear Indium and Gallium Tetrachlorocatecholate Complexes

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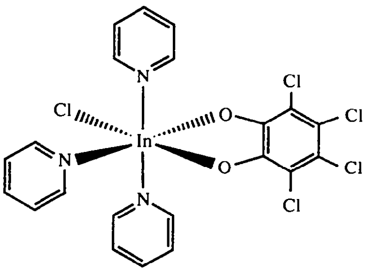
Abstract

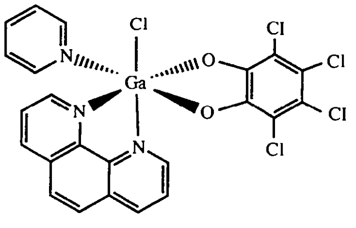
Two mononuclear tetrachlorocatecholate complexes, chlorotri(pyridine-*N*)[3,4,5,6-tetrachloro-1,2-benzenediolato(2−)-*O*,*O*′]indium, $[\mathrm{InCl}(1,2\text{-}\mathrm{O_2C_6Cl_4})(\mathrm{py})_3]$, (1), and chloro(1,10-phenanthroline-*N*,*N*′)(pyridine-*N*)[3,4,5,6-tetrachloro-1,2-benzenediolato(2−)-*O*,*O*′]gallium, $[\mathrm{GaCl}(1,2\text{-}\mathrm{O_2C_6Cl_4})(\mathrm{py})(\mathrm{phen})]$, (2) (py is pyridine, $\mathrm{C_5H_5N}$, and phen is 1,10-phenanthroline, $\mathrm{C_{12}H_8N_2}$), have been structurally characterized as solvates, (1) as its bis(diethyl ether) solvate and (2) as its 3.5-pyridine solvate. Both (1) and (2) contain octahedrally coordinated metals but with the nitrogen donor ligands in a *mer* arrangement in (1) and a *fac* arrangement in (2). Stabilization by intramolecular CH···O and CH···Cl interactions is evident, and, together with steric considerations, is likely to promote the observed configurations. Compound (1) shows an interesting packing arrangement of infinite planar sheets held together by short Cl···Cl contacts.

Comment

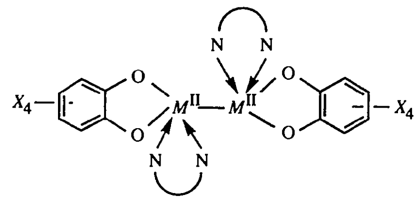
The compounds $[\mathrm{InCl(py)_3(1,2\text{-}O_2C_6Cl_4)}].2\mathrm{Et_2O}$ and $[\mathrm{GaCl(py)(phen)(1,2\text{-}O_2C_6Cl_4)}].3.5\mathrm{py}$ were obtained as minor crystalline products from reactions carried out in order to synthesize M^{II}–M^{II} dimer species $[M_2(\mathrm{O_2C_6Cl_4})_2(\mathrm{phen})_2]$ (M = Ga or In) by procedures related to those of Tuck and co-workers (Annan & Tuck, 1989).



(1)



(2)



Compound (1) (Fig. 1) crystallizes as a 1:2 $\mathrm{Et_2O}$ solvate in the orthorhombic space group *Pnma* with the catecholate, chloride and one pyridine lying on a mirror plane, and exhibits an octahedral coordination about the indium centre [N1—In1—N1$^{\mathrm{i}}$ 173.7 (2)°]. The structural data are consistent with the complex being an indium(III) catecholate species since the In—O bond lengths [2.120 (5) and 2.126 (5) Å] and the O—C distances of the catecholate [1.327 (8) and 1.316 (8) Å] are consistent with the catecholate form as opposed to quinone or semiquinone alternatives. Thus, accurate structure determinations have revealed a marked lengthening in the C—O bond length as the form of the ligand is successively reduced from benzoquinone (1.23 Å), through semiquinone (1.29 Å), to catecholate (1.35 Å; Carugo *et al.*, 1992). The O—In—O angle of 79.2 (2)° is close to that found in other such complexes. The In—N bond length of the pyridine *trans* to oxygen [2.284 (6) Å] is shorter than the In—N bonds of the *trans* pyridines [2.318 (4)°], consistent with chlorine having a weaker *trans* influence than pyridine. The In—Cl bond length of 2.417 (2) Å is similar to those in other In^{III} species for which a range of 2.394–2.538 Å has been reported (Annan & Tuck, 1989). The displacement ellipsoids of the atoms of the pyridine ring (N2, C12–C16) have an elongated form which may be due to unresolved disorder about the mirror plane.

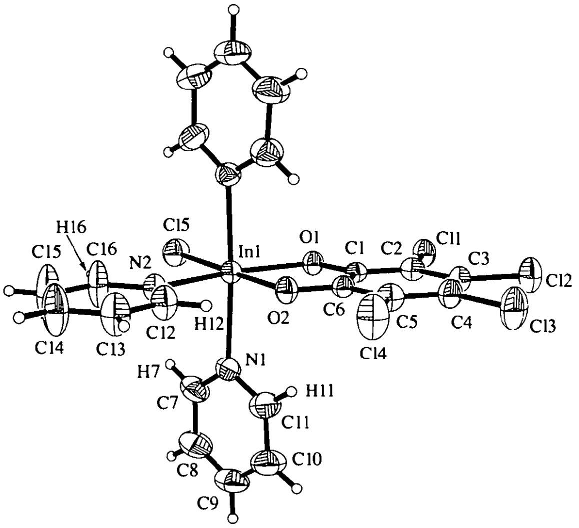


Fig. 1. The molecular structure of (1) with atom labels and 50% probability ellipsoids for non-H atoms.

The packing arrangement of (1) reveals relatively short intermolecular Cl···Cl interactions [Cl3···Cl1 3.275 (3) Å]. These are comparable in length with other Cl···Cl contacts, the shortest reported being 3.21 Å for triphenylchloromethane (Desiraju, 1989). The C4—Cl3···Cl1 unit is essentially linear [177.9 (3)°], whilst the C2—Cl1···Cl3 angle is 150.3 (3)°. The Cl···Cl interactions create infinite planar sheets throughout the whole structure, parallel sheets lying at $y = \frac{1}{4}$ and $\frac{3}{4}$. The interlayer distances are 7.378 Å, with the Et_2O solvate molecules lying between layers. In addition, axial pyridine groups in adjacent layers participate in π–π interactions with 3.703 Å interplanar separations. These interactions can be viewed in Fig. 2. The role of Cl···Cl interactions in crystal engineering has been discussed (Desiraju, 1989), although explanations for the existence of these short non-bonded contacts vary widely (Desiraju, 1989; Price *et al.*, 1994).

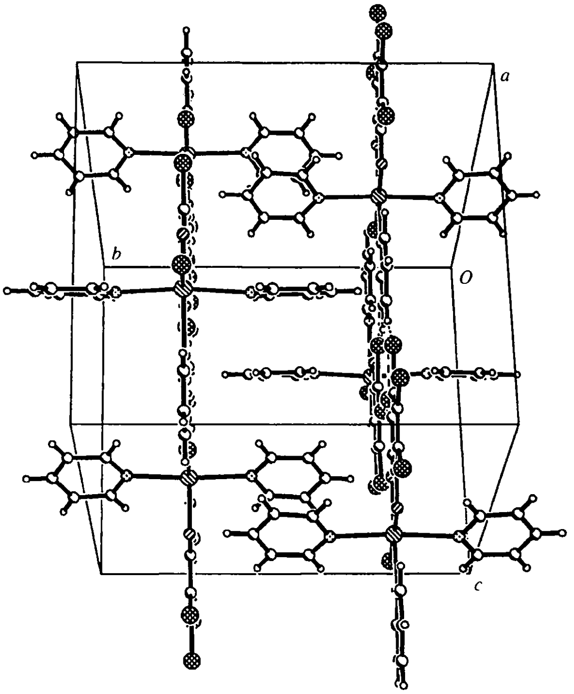


Fig. 2. Packing diagram of (1).Et_2O viewed down the *a* axis. Et_2O molecules have been omitted for clarity.

The molecular structure of the gallium complex, (2), which crystallizes as a pyridine solvate (1:3.5), is shown in Fig. 3. The octahedral coordination geometry around the gallium centre is distorted as a result of the chelating catecholate and *o*-phenanthroline groups [O1—Ga1—N3 170.9 (2), N1—Ga1—N2 85.9 (2) and N2—Ga1—O1 93.6 (2), N2—Ga1—N3 77.8 (2)°] although the Ga1-O1-O2-N1-N3 system is essentially planar (the average atomic deviation from the mean plane is 0.001 Å). The O—Ga—O angle [85.74 (14)°] is significantly larger than that found in (1) due to the smaller radius of gallium and shorter Ga—O bond lengths [1.929 (3) and 1.952 (4) Å]. The O—C bond lengths are 1.321 (6) and 1.325 (6) Å, which compare well with those in (1) [1.327 (8) and 1.316 (8) Å], confirming the presence of a catecholate ligand and hence a Ga^{III} complex. Interestingly, the three nitrogen donor sites in (2) adopt a *fac* configuration, whereas in (1) they are *mer*. The arrangement in (1) is the less sterically demanding and is favoured by several intramolecular CH···ligand contacts [Cl5···H7 2.71 (1), O2···H11 2.47 (1), O2···H12 2.23 (1) and Cl5···H16 2.90 (1) Å]. The stereochemistry of (2) rules out some of these interactions but one is still present [O1···H45*A* 2.46 (1) Å]. Furthermore, in (2), Cl5 can be seen bending towards the *o*-phenanthroline ligand [Cl5—Ga1—N3 92.50 (12)° *cf.* Cl5—Ga1—O1 96.25 (12)°] and makes a contact of 2.65 (1) Å with H32*A*. To obtain a *mer* arrangement in (2), eclipsing of the pyridine and an *ortho*-CH of the *o*-phenanthroline ligand would be required and therefore the *fac* configuration is favoured and promoted further by the intramolecular contacts noted above. The Ga—N bond lengths in (2) are 2.113 (4) and 2.155 (4) Å for the *o*-phenanthroline, the longer being the nitrogen *trans* to Cl5, and 2.096 (4) Å for the pyridine. The Ga—Cl bond length is 2.329 (2) Å. These distances are consistent with other crystallographically determined structures of gallium(III) complexes.

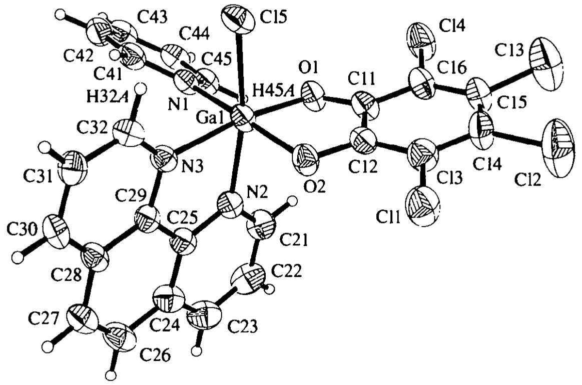


Fig. 3. The molecular structure of (2) with atom labels and 50% probability ellipsoids for non-H atoms.

Experimental

For [InCl(py)$_3$(1,2-O$_2$C$_6$Cl$_4$)].2Et$_2$O [(1).2Et$_2$O], indium powder (0.161 g, 1.42 mmol) was added to a solution of tetrachloro-1,2-benzoquinone (0.35 g, 1.42 mmol) in toluene (25 ml) according to the procedure of Annan & Tuck (1989) and heated to reflux for 24 h, resulting in a colour change from red to dark blue–green. The solution was filtered yielding a dark green filtrate to which excess pyridine (0.15 ml, 2.0 mmol) was then added slowly, resulting in an immediate change from a dark green solution to an off-white suspension. This was allowed to stir for 18 h affording a deep yellow mixture which was then allowed to settle forming a clear yellow solution and a pale solid; the solution was transfered *via* syringe to a separate flask and Et$_2$O added as an overlayer. Colourless needle-like X-ray quality crystals of (1).2Et$_2$O were obtained *via* solvent diffusion at 248 K. For [GaCl(py)(phen)(1,2-O$_2$C$_6$Cl$_4$)].3.5py [(2).3.5py], gallium foil (0.5 g, 0.67 mmol) was added to a solution of tetrachloro-1,2-benzoquinone (0.151 g, 0.61 mmol) in toluene (25 ml) and heated to reflux for 24 h, resulting in a colour change from red to a brown–black solution, according to the procedure of Annan & Tuck (1989). The resultant solution was transfered *via* cannula into a separate flask leaving excess Ga metal as a residue. To this solution, 1,10-phenanthroline (0.11 g, 0.61 mmol) in toluene (5 ml) was added slowly affording a light brown precipitate. The reaction mixture was allowed to stir for 2 h, after which the toluene was removed *in vacuo* affording an orange–brown solid which was redissolved in pyridine (4 ml) and hexane added as an overlayer. Orange rectangular X-ray quality crystals of (2).3.5py were obtained *via* solvent diffusion at 248 K over a period of days. Crystals coated with a hydrocarbon oil were mounted on a glass fibre with silicone grease under an argon atmosphere.

Compound (1)

Crystal data

[InCl(C$_6$Cl$_4$O$_2$)(C$_5$H$_5$N)$_3$].-2C$_4$H$_{10}$O
M_r = 781.67
Orthorhombic
Pnma
a = 16.876 (3) Å
b = 14.756 (2) Å
c = 13.541 (2) Å
V = 3372.2 (8) Å^3
Z = 4
D_x = 1.540 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 192 reflections
θ = 5–50°
μ = 1.134 mm^{-1}
T = 173 (2) K
Plate
0.4 × 0.2 × 0.2 mm
Clear

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: empirical, pseudo-azimuthal scan (*SHELXTL*; Sheldrick, 1995)
$T_{\min}$ = 0.295, $T_{\max}$ = 0.354

15 255 measured reflections
3095 independent reflections
2459 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.064
$\theta_{\max}$ = 25.03°
$h = -19 \rightarrow 19$
$k = -17 \rightarrow 16$
$l = -16 \rightarrow 7$

Refinement

Refinement on F^2
$R(F)$ = 0.046
$wR(F^2)$ = 0.106
S = 1.167
3092 reflections
214 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 8.18P]$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.72 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
In1	0.55929 (3)	1/4	0.10468 (4)	0.0282 (2)
O1	0.5669 (3)	1/4	−0.0521 (3)	0.0293 (10)
O2	0.6839 (3)	1/4	0.0847 (3)	0.0315 (11)
N1	0.5631 (3)	0.0931 (3)	0.1127 (3)	0.0348 (9)
N2	0.5906 (4)	1/4	0.2688 (4)	0.0341 (14)
Cl1	0.58883 (10)	1/4	−0.26827 (13)	0.0364 (4)
Cl2	0.76733 (12)	1/4	−0.33359 (14)	0.0477 (5)
Cl3	0.90028 (12)	1/4	−0.1745 (2)	0.0579 (6)
Cl4	0.85215 (12)	1/4	0.0511 (2)	0.0581 (6)

Cl5	0.41678 (11)	1/4	0.1223 (2)	0.0441 (5)
C1	0.6417 (4)	1/4	−0.0822 (5)	0.0265 (15)
C2	0.6631 (4)	1/4	−0.1808 (5)	0.030 (2)
C3	0.7425 (4)	1/4	−0.2097 (5)	0.031 (2)
C4	0.8012 (4)	1/4	−0.1394 (6)	0.036 (2)
C5	0.7803 (4)	1/4	−0.0393 (5)	0.035 (2)
C6	0.7028 (4)	1/4	−0.0096 (5)	0.0276 (15)
C7	0.5013 (4)	0.0440 (4)	0.1382 (5)	0.0500 (15)
C8	0.5022 (4)	−0.0499 (4)	0.1370 (5)	0.056 (2)
C9	0.5673 (4)	−0.0930 (4)	0.1072 (4)	0.054 (2)
C10	0.6317 (5)	−0.0436 (4)	0.0790 (5)	0.063 (2)
C11	0.6277 (4)	0.0496 (4)	0.0837 (5)	0.051 (2)
C12	0.6662 (5)	1/4	0.2969 (6)	0.045 (2)
C13	0.6893 (5)	1/4	0.3945 (6)	0.054 (2)
C14	0.6327 (6)	1/4	0.4659 (7)	0.072 (3)
C15	0.5548 (6)	1/4	0.4379 (7)	0.091 (4)
C16	0.5356 (5)	1/4	0.3392 (6)	0.061 (3)
O3	0.8189 (5)	−0.0039 (6)	−0.0373 (7)	0.132 (3)
C20	0.8825 (12)	−0.0009 (16)	0.1060 (15)	0.241 (10)
C21	0.9004 (10)	0.0036 (11)	−0.0061 (15)	0.198 (7)
C22	0.8132 (8)	0.0007 (8)	−0.1420 (10)	0.133 (4)
C23	0.7309 (7)	−0.0048 (9)	−0.1828 (12)	0.179 (7)

Table 2. *Selected geometric parameters (Å, °) for (1)*

In1—O2	2.120 (5)	In1—Cl5	2.417 (2)
In1—O1	2.126 (5)	O1—C1	1.327 (8)
In1—N2	2.284 (6)	O2—C6	1.316 (8)
In1—N1	2.318 (4)	C1—C6	1.425 (9)
O2—In1—O1	79.2 (2)	N1^{i}—In1—N1	173.7 (2)
O2—In1—N2	83.9 (2)	O2—In1—Cl5	178.32 (13)
O1—In1—N2	163.1 (2)	O1—In1—Cl5	99.12 (13)
O2—In1—N1	88.76 (11)	N2—In1—Cl5	97.7 (2)
O1—In1—N1	92.60 (10)	N1—In1—Cl5	91.33 (11)
N2—In1—N1	87.00 (10)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Compound (2)

Crystal data

[$GaCl(C_6Cl_4O_2)(C_5H_5N)$-
($C_{12}H_8N_2$)]$.3.5C_5H_5N$
$M_r = 887.18$
Monoclinic
$C2/c$
$a = 25.504$ (7) Å
$b = 17.640$ (7) Å
$c = 18.572$ (4) Å
$\beta = 106.99$ (2)°
$V = 7991$ (4) Å^3
$Z = 8$
$D_x = 1.475$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 236 reflections
$\theta = 5$–50°
$\mu = 1.068$ mm^{-1}
$T = 173$ (2) K
Block
0.5 × 0.3 × 0.2 mm
Orange

Data collection

Siemens SMART area-detector diffractometer
ω rotation scans with narrow frames
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{min} = 0.453$, $T_{max} = 0.694$
20 029 measured reflections

6994 independent reflections
4283 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.00°$
$h = -33 \rightarrow 32$
$k = -19 \rightarrow 22$
$l = -24 \rightarrow 13$

Refinement

Refinement on F^2
$R(F) = 0.059$
$wR(F^2) = 0.153$
$S = 1.068$
6992 reflections
497 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1084P)^2]$
where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3} (0.73 Å from Cl3)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Ga1—O1	1.929 (3)	Ga1—Cl5	2.329 (2)
Ga1—O2	1.952 (4)	O1—C11	1.321 (6)
Ga1—N1	2.096 (4)	O2—C12	1.325 (6)
Ga1—N3	2.113 (4)	C11—C12	1.424 (7)
Ga1—N2	2.155 (4)		
O1—Ga1—O2	85.74 (14)	N1—Ga1—N2	85.9 (2)
O1—Ga1—N1	89.8 (2)	N3—Ga1—N2	77.8 (2)
O2—Ga1—N1	173.2 (2)	O1—Ga1—Cl5	96.25 (12)
O1—Ga1—N3	170.9 (2)	O2—Ga1—Cl5	95.04 (12)
O2—Ga1—N3	91.10 (15)	N1—Ga1—Cl5	90.59 (12)
N1—Ga1—N3	92.5 (2)	N3—Ga1—Cl5	92.50 (12)
O1—Ga1—N2	93.6 (2)	N2—Ga1—Cl5	169.49 (12)
O2—Ga1—N2	89.2 (2)		

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 30 s exposure. A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ 0, 88 and 180° with the area detector held at $2\theta = -27°$ for (1).2Et$_2$O and −29° for (2).3.5py, and each frame exposed for 30 s. The crystal-to-detector distance was 4.974 cm for (1).2Et$_2$O and 5.974 cm for (2).3.5py. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their attached C atom for aromatics and 1.5 U_{iso} for all others. In (2).3.5py, one pyridine (C91–C90′) is disordered about a centre of inversion, and the other solvent molecules also exhibit unusually large displacements (*e.g.* for C74 and C83) indicating probable disorder.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We thank the EPSRC for a studentship (MJQ) and Laporte plc and the Royal Society for additional funds.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1155). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1809–1811

Polysulfonylamines. XCIII.† (1,2-Benzenedisulfonylimido-O)(1,4,7,10-tetraoxacyclododecane-κ^4O)lithium

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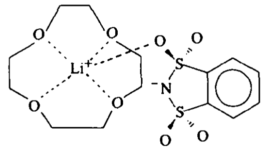
Abstract

In the title complex, $[Li(C_6H_4NO_4S_2)(C_8H_{16}O_4)]$, a square-pyramidal coordination sphere around Li^+ is formed by the four mutually coplanar O atoms of 12-crown-4 at the basal positions and by one O atom of the anionic ligand, 1,3,2-benzodithiazole 1,1,3,3-tetraoxide(1−), at the apical position. The macrocycle adopts the frequently observed [3333] conformation, approximating to C_4 symmetry.

Comment

In 1:1 complexes between lithium salts Li*X* and 1,4,7,10-tetraoxacyclododecane (12-crown-4), the macrocycle commonly displays a [3333] (C_4) conformation and the metal cation is pentacoordinated by the crown O atoms at the basal positions and one donor atom of the anion X^- at the apical position of a square pyramid (Bajaj & Poonia, 1988; Power, 1988; Olsher *et al.*, 1991; for a conformational analysis of free and metal-complexed 12-crown-4, see Raithby, Shields & Allen, 1997). In contrast to the general pattern, the disulfonylamide complex $[(12\text{-crown-4})Li\{N(SO_2CH_3)_2\}]$, (1), exhibits a unique structure. It contains two coordination isomers, in which 12-crown-4 respectively adopts the [3333] (C_4) and the less common [48] (C_s) conformation; moreover, both Li atoms are hexacoordinated by the four ether O atoms and two geminal sulfonyl O atoms of the anion (Blaschette, Nagel & Jones, 1994). The structure determination of the title compound, (2), was prompted by these findings. Unlike (1), it surprisingly shows no new or unusual features when compared with the majority of (12-crown-4)Li*X* structures.



(2)

The asymmetric unit of (2) is shown in Fig. 1 (selected bond lengths and angles are presented in Table 1). The Li atom is coordinated by the four ether O atoms and the O1 atom of the anion in a slightly distorted square-pyramidal arrangement; the Li···O2 distance of 3.556 (4) Å is well beyond bonding distance. The O atoms of the macrocycle are coplanar within ±0.001 (1) Å, the Li atom lying 0.821 (4) Å out of this plane. The apical Li—O1 distance, 1.893 (4) Å, is 0.15–0.20 Å shorter than the basal Li—O bond lengths [average 2.087 (4) Å]. As expected, most Li—O bonds at the six-coordinate Li atoms of (1) are appreciably longer than the chemically corresponding distances in the present structure [overall averages for (1): Li—O(anion) 2.085 and Li—O(crown) 2.175 Å].

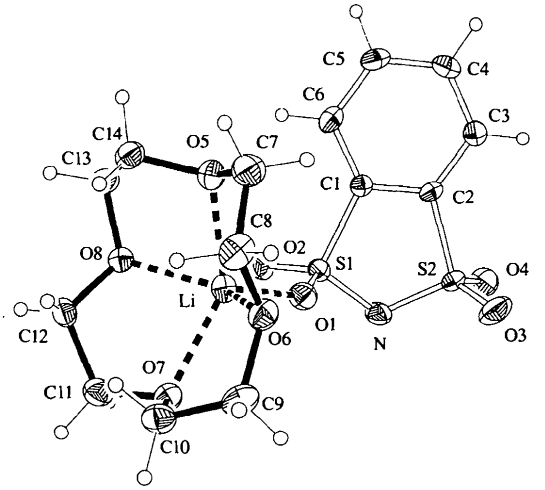


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

The macrocycle in (2) shows the almost ideal C_4 symmetric [3333] conformation that is predominant in metal complexes of 12-crown-4. The C—O [average 1.437 (4) Å] and C—C distances [average 1.503 (2) Å], and the C—O—C angles [average 114.1 (2)°] are normal. The C—C—O angles are systematically larger [average 110.5 (2)°] at the C atoms C7, C9, C11 and C13 (which lie in a plane nearer to the O_4 plane) than those at the other four C atoms [average 106.2 (4)°]. Further characteristics of the [3333] conformation (Raithby, Shields & Allen, 1997) are the *gauche* O—C—C—

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† Part XCII: Henschel, Moers, Blaschette & Jones (1997).

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