Moers, O., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 845–848.
Olsher, U., Izatt, R. M., Bradshaw, J. S. & Dalley, N. K. (1991). *Chem. Rev.* **91**, 137–164.
Power, P. P. (1988). *Acc. Chem. Res.* **21**, 147–153.
Raithby, P. R., Shields, G. P. & Allen, F. H. (1997). *Acta Cryst.* B**53**, 241–251.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C**53**, 1811–1813

Polysulfonylamines. XCV.† (1,2-Benzenedisulfonylimido-*N*,*O*)(1,4,7,10,13-pentaoxacyclopentadecane-$\kappa^5 O$)sodium

Peter G. Jones,* Oliver Moers and Armand Blaschette

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

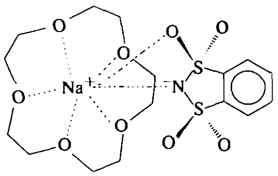
(*Received 16 June 1997; accepted 11 August 1997*)

Abstract

In the title complex, $[\mathrm{Na}(\mathrm{C_6H_4NO_4S_2})(\mathrm{C_{10}H_{20}O_5})]$, an irregular coordination sphere around $\mathrm{Na^+}$ is formed by the five O atoms of 15-crown-5 and the N and one O atom of the disulfonylimide 1,3,2-benzodithiazole 1,1,3,3-tetraoxide(1−). In one C—C—O segment of the polyether ring, two successive *gauche* torsion angles of the same sign constitute a conformational corner.

Comment

The synthesis and structure determination of the title compound, (1), form part of our studies on the coordination behaviour of metal cations of Groups 1 and 2 towards di(organosulfonyl)amide anions, *e.g.* di(methanesulfonyl)amide, $(\mathrm{CH_3SO_2})_2\mathrm{N}^-$ (A^-), or 1,2-benzenedisulfonylimide(1−), $\mathrm{C_6H_4(SO_2)_2N^-}$ (Z^-). In earlier work, we reported the structures of [(15-crown-5)Na(A)], (2) (Blaschette, Nagel & Jones, 1993), [(12-crown-4)Li(A)], (3) (Blaschette, Nagel & Jones, 1994), and [(12-crown-4)Li(Z)], (4) (Jones, Moers & Blaschette, 1997), where 15-crown-5 is 1,4,7,10,13-pentaoxacyclopentadecane and 12-crown-4 is 1,4,7,10-tetraoxacyclododecane. Apart from the appropriate number of crown-ether O atoms, the metal is coordinated by two geminal O atoms of A^- in (3), by only one O atom of Z^- in (4), and by one O and the N atom of A^- in (2), thus attaining an overall coordination number of five in (4), six in (3) and seven in (2). The present result shows that the (15-crown-5)$\mathrm{Na^+}$ fragment, in contrast to (12-crown-4)$\mathrm{Li^+}$, displays essentially the same coordination behaviour towards both A^- and the bicyclic analogue Z^-.



(1)

The asymmetric unit of (1) is shown in Fig. 1 (selected geometric data are presented in Table 1). The $\mathrm{Na^+}$ ion is coordinated by the five ether O atoms and the N and O1 atoms of the anion in an irregular arrangement. A major difference between structures (1) and (2) is furnished by the Na—X(anion) interactions. Although the bite angles O—Na—N of the anions are identical, the Na—O1 and Na—N distances in (1) are quite similar, whereas in (2), the Na—O(anion) bond length is *ca* 0.4 Å shorter than Na—N [(1): Na—O1 2.627 (3), Na—N 2.610 (3) Å and O1—Na—N 55.71 (8)°; (2): Na—O(anion) 2.349 (2), Na—N 2.758 (2) Å and O(anion)—Na—N 55.7 (1)°]. It is conceivable that the divergent coordination behaviour of A^- and Z^- in (1) and (2) and, more markedly, in (3) and (4), results from different steric demands of their respective $\mathrm{N(SO_2C)_2}$ moiety, which approximates to C_2 symmetry in A^- and to C_s symmetry in Z^-.

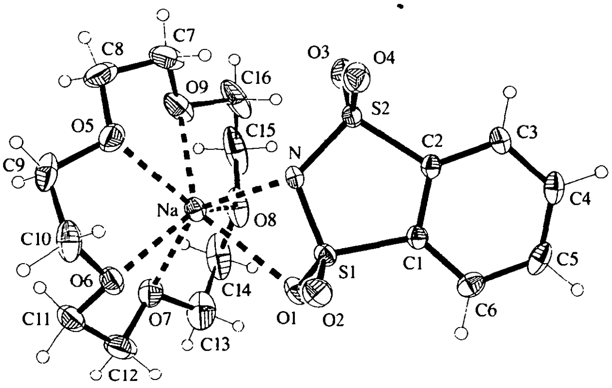


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 30% probability levels and H-atom radii are arbitrary.

---

† Part XCIV: Hamann, Blaschette & Jones (1997).

The (15-crown-5)Na^+ fragment of (1) is very similar to that in (2). The Na—O(crown) distances and the O—Na—O angles between adjacent Na—O(crown) bonds average 2.427 Å and 68.3°, respectively [for (2): 2.433 Å and 69.3°]. The crown O atoms are far from being coplanar; their mean distance from the least-squares plane is 0.338 Å, and the greatest deviations of −0.489 (2) and 0.439 (2) Å are observed for O7 and O8, respectively. The Na cation lies 0.846 (2) Å out of the mean plane of the crown O atoms [in (2): 0.78 Å]. The C—O (average 1.426 Å) and C—C distances (average 1.484 Å), and the C—O—C angles (average 114.1°) are unremarkable. Apart from the C9—C10—O6 segment, all C—O torsion angles are *trans* and all C—C torsion angles are *gauche* and alternating in sign (average absolute values: C—O—C—C 171.8 and O—C—C—O 62.2°). In the aforementioned segment, two successive *gauche* torsion angles of the same sign constitute a conformational corner (Dale, 1973) and induce an exceptionally large bond angle at C10 [O5—C9—C10—O6 −58.8 (4), C9—C10—O6—C11 −82.8 (4) and C9—C10—O6 111.7 (3)°].

As in (4), the anion Z^- of (1) approximates to C_s symmetry. The C and S atoms are essentially coplanar, the largest deviation from their mean plane and their mean out-of-plane distance being 0.055 (1) (for S1) and 0.032 Å, respectively. The N atom lies 0.129 (3) Å out of the same plane [in (4): 0.310 (2) Å]; its trigonal-pyramidal coordination is described by the appropriate bond angles in Table 1 and its distance, 0.380 (3) Å, from the plane defined by Na, S1 and S2.

Experimental

1,2-Benzenedisulfonylimide (HZ) was obtained as previously described (Blaschette, Jones *et al.*, 1993). Dissolving 0.50 g (2.3 mmol) of HZ and 0.09 g (2,3 mmol) of NaOH in 60 ml of deionized water, evaporating the heated solution until the onset of turbidity and storing at ambient temperature, afforded $NaZ.H_2O$ (92% yield), which was dehydrated *in vacuo* over P_4O_{10} (24 h, 353 K). To prepare complex (1), a solution of 0.48 g (2.0 mmol) of NaZ and 0.43 g (1.9 mmol) of 15-crown-5 in 60 ml of dry methanol was evaporated *in vacuo* to *ca* 10 ml and stored at 253 K; the product crystallized in a yield of 0.65 g (74%); m.p. 446 K. Elemental analysis: found C 41.68, H 5.27, N 3.00, S 13.62%; $C_{16}H_{24}NNaO_9S_2$ requires C 41.64, H 5.24, N 3.04, S 13.90%. ^1H NMR (200 MHz, DMSO-d_6): δ 3.55 (*s*, 20H, 15-crown-5), 7.67–7.78 p.p.m. (4H, aromatic H).

Crystal data

[$Na(C_6H_4NO_4S_2)$-($C_{10}H_{20}O_5$)]
$M_r = 461.47$
Monoclinic
$P2_1/n$
$a = 14.963$ (4) Å
$b = 9.780$ (3) Å
$c = 15.734$ (5) Å
$\beta = 115.76$ (2)°
$V = 2073.7$ (11) $Å^3$
$Z = 4$
$D_x = 1.478$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 54 reflections
$\theta = 10.0$–11.5°
$\mu = 0.326$ mm^{-1}
$T = 143$ (2) K
Rhombus
0.7 × 0.4 × 0.3 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
3806 measured reflections
3660 independent reflections
2795 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

$\theta_{max} = 25.02°$
$h = -8 \rightarrow 17$
$k = -6 \rightarrow 11$
$l = -18 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.117$
$S = 1.030$
3660 reflections
262 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 2.0518P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.309$ e $Å^{-3}$
$\Delta\rho_{min} = -0.309$ e $Å^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Na—O7	2.407 (3)	Na—N	2.610 (3)
Na—O5	2.412 (3)	Na—O1	2.627 (3)
Na—O6	2.434 (3)	S1—N	1.588 (3)
Na—O8	2.438 (3)	S2—N	1.584 (3)
Na—O9	2.444 (3)		
O7—Na—O6	69.48 (9)	O7—Na—O1	89.63 (9)
O5—Na—O6	69.23 (10)	O5—Na—O1	135.20 (10)
O7—Na—O8	67.45 (10)	O6—Na—O1	89.77 (9)
O5—Na—O9	68.42 (11)	O8—Na—O1	88.93 (10)
O8—Na—O9	66.95 (12)	O9—Na—O1	139.79 (10)
O7—Na—N	145.14 (10)	N—Na—O1	55.71 (8)
O5—Na—N	90.17 (9)	S2—N—S1	115.75 (16)
O6—Na—N	103.48 (9)	S2—N—Na	135.74 (16)
O8—Na—N	111.00 (10)	S1—N—Na	94.80 (12)
O9—Na—N	102.06 (10)	S1—O1—Na	98.01 (12)
C16—O9—C7—C8	−179.7 (3)	O6—C11—C12—O7	−66.0 (4)
C9—O5—C8—C7	−167.1 (3)	C12—O7—C13—C14	173.3 (3)
O9—C7—C8—O5	65.0 (4)	C15—O8—C14—C13	−160.6 (4)
C8—O5—C9—C10	−179.9 (3)	O7—C13—C14—O8	58.0 (5)
C11—O6—C10—C9	−82.8 (4)	C14—O8—C15—C16	161.8 (4)
O5—C9—C10—O6	−58.8 (4)	C7—O9—C16—C15	−179.1 (3)
C10—O6—C11—C12	175.0 (3)	O8—C15—C16—O9	−59.8 (4)
C13—O7—C12—C11	169.8 (3)		

The index ranges given above were not covered fully; however, a complete quadrant of data is present. H atoms were treated as riding. Elongated ellipsoids of some crown ether atoms may indicate the typical conformational flexibility of a large ring system.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990).

Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1019). Services for accessing these data are described at the back of the journal.

References

Blaschette, A., Jones, P. G., Hamann, T., Näveke, M., Schomburg, D., Cammenga, H. K., Epple, M. & Steppuhn, I. (1993). *Z. Anorg. Allg. Chem.* **619**, 912–922.

Blaschette, A., Nagel, K.-H. & Jones, P. G. (1993). *Z. Naturforsch. Teil B*, **48**, 893–897.

Blaschette, A., Nagel, K.-H. & Jones, P. G. (1994). *Z. Naturforsch. Teil B*, **49**, 36–42.

Dale, J. (1973). *Acta Chem. Scand.* **27**, 1115–1129.

Hamann, T., Blaschette, A. & Jones, P. G. (1997). *Z. Anorg. Allg. Chem.* In the press.

Jones, P. G., Moers, O. & Blaschette, A. (1997). *Acta Cryst.* C**53**, 1809–1811.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *XP. Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments, Inc., Madison, USA.

Stoe & Cie (1992*a*). *DIF4. Diffractometer Control Program.* Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU4. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). C**53**, 1813–1815

Dichloro[2,3,5,6-tetra(2-pyridyl)pyrazine]-copper(II), [$CuCl_2(C_{24}H_{16}N_6)$]

Jozef Kožíšek,[a] Jaromír Marek,[b] Zuzana Baloghová[a] and Dušan Valigura[a]

[a]*Department of Inorganic Chemistry, Faculty of Chemical Technology, Radlinského 9, Slovak Technical University, 812 37 Bratislava, Slovakia, and* [b]*Department of Inorganic Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic. E-mail: kozisek@cvt.stuba.sk*

(*Received 14 May 1997; accepted 22 August 1997*)

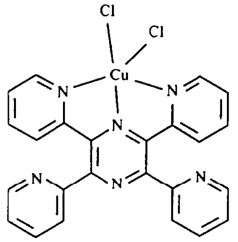
Abstract

In molecules of [$Cu(TPPZ)Cl_2$] [TPPZ is 2,3,5,6-tetra(2-pyridyl)pyrazine], the central Cu^{II} atom has a square-pyramidal coordination environment, defined by three TPPZ N atoms and by two chloro ligands, one of which is apical. The other three TPPZ N atoms remain uncoordinated. The Cu—N distances are in the range 1.975 (2)–2.058 (2) Å and the Cu—Cl bond lengths are 2.214 (1) and 2.465 (1) Å.

Comment

Tetra(2-pyridyl)pyrazine (TPPZ), known for nearly 30 years, attracts the attention of chemists because it could act as a bis-tridentate ligand. However, this would require all five aromatic rings to be coplanar. Mutual steric hindrance of neighbouring pyridine rings (due to H atoms on their β-C atoms) does not allow a coplanar arrangement and the bis-tridentate bonding mode can be achieved only by twisting the pyrazine ring (Graf, Greaves & Stoeckli-Evans, 1993; Valigura, Ondrejovič & Anderson, 1997).

Complexes with metal-to-TPPZ ratios of 1:1 and 1:2 can be obtained. The 1:1 complexes may be either mononuclear or polynuclear through the formation of infinite chains. The crystal structure of [$Cu(TPPZ)Cl_2$], (I), has been determined in order to distinguish between these two possibilities.



(I)

The crystal consists of discrete [$Cu(TPPZ)Cl_2$] molecules and is isostructural with [$Zn(TPPZ)Cl_2$], (II) (Graf, Greaves & Stoeckli-Evans, 1993) (see Table 1). The metal-coordination polyhedra of (I) and (II) are best described as tetragonal pyramids, showing trigonality τ parameters (Addison *et al.*, 1984) of 0.11 and 0.07, respectively. The basal planes are formed by three TPPZ N atoms and by one chloro ligand; deviations from the best basal plane are less than 0.030 (2) Å for (I) and less than 0.076 (2) Å for (II). The longer *M*—Cl bond in each complex involves the apical chloro ligand. The displacement of this ligand from the basal plane varies only slightly, from 2.752 (1) Å in (I) to 2.811 (2) Å in (II). The displacements of the metal atom from the basal plane are 0.327 (1) and 0.572 (2) Å for (I) and (II), respectively. The greater displacement of the Zn atom, together with the similar sizes of the coordination polyhedra of both complexes, result in the *M*—Cl(apical) distance being shorter in (II) than in (I) (see Table 1). The difference in the central-atom displacements from the basal plane may be explained by the difference in their covalent radii (r_{Cu} = 1.17 and r_{Zn} = 1.25 Å).