ALCOCK, N. W., KEMP, T. J. & WIMMER, F. L. (1981). *J. Chem. Soc. Dalton Trans.* pp. 635–638.

ALCOCK, N. W. & NELSON, J. H. (1985). *Acta Cryst.* C41, 1743–1750.

ARESTA, M., BALLIVET-TKATCHENKO, D., BONNET, M. C., FAURE, R. & LOISELEUR, H. (1985). *J. Am. Chem. Soc.* 107, 2994–2995.

BONDOUX, D., MENTZEN, B. F. & TKATCHENKO, I. (1981). *Inorg. Chem.* 20, 839–848.

BONDOUX, D., TKATCHENKO, I., HOUALLA, D., WOLF, R., PRADAT, C., RIESS, J. G. & MENTZEN, B. (1978). *J. Chem. Soc. Chem. Commun.* pp. 1022–1024.

BONNET, M. C., AGBOSSOU, S., TKATCHENKO, I., FAURE, R. & LOISELEUR, H. (1987). *Acta Cryst.* C43, 445–448.

BONNET, M. C., TKATCHENKO, I., FAURE, R. & LOISELEUR, H. (1983). *Nouv. J. Chim.* 7, 601–6f3.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE.* Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee, USA.

FERGUSON, G., McCRINDLE, R., McALEES, A. J. & PARVEZ, M. (1982). *Acta Cryst.* B38, 2679–2681.

FRENZ, B. A. (1982). *SDP Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (10⁻¹). Vol. IV, pp. 99–101, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

MARTIN, L. L. & JACOBSON, R. A. (1971). *Inorg. Chem.* 10, 1795–1798.

NEWCOME, J. R., EVANS, D. W. & FRONCZEK, F. R. (1987). *Inorg. Chem.* 26, 3500–3506.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A24, 351–359.

RIESS, J. G. (1986). *Phosphorus,* 27, 93–107.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

WACHTER, J., RIESS, J. G. & MITSCHLER, A. (1984). *Organometallics,* 3, 714–722.

Structure of Bis(1,10-phenanthroline)trifluoromethanesulfonatolithium

BY SOON W. LEE AND WILLIAM C. TROGLER*

Department of Chemistry, D-006, University of California at San Diego, La Jolla, California 92093, USA

Abstract. $[Li(CF_3O_3S)(C_{12}H_8N_2)_2]$, $M_r = 516 \cdot 43$, monoclinic, $P2_1/n$, $a = 10 \cdot 540$ (4), $b = 15 \cdot 403$ (6), $c = 14 \cdot 624$ (6) Å, $\beta = 90 \cdot 55$ (3)°, $V = 2374 \cdot 1$ (17) Å³, $Z = 4$, $D_x = 1 \cdot 44$ g cm⁻³, $\lambda(\text{Mo }K\alpha) = 0 \cdot 71073$ Å, $\mu = 1 \cdot 80$ cm⁻¹, $T = 298$ K, $F(000) = 964$. $R = 0 \cdot 053$ for 2221 reflections with $I > 3 \cdot 0\sigma(I)$ (4197 unique observations). The Li is trigonal-bipyramidally coordinated to two phenanthroline molecules and one trifluoromethanesulfonate, with one equatorial Li—O bond [$2 \cdot 072$ (9) Å] and four Li—N [$2 \cdot 115$ (9)–$2 \cdot 166$ (9) Å] bonds. The dihedral angle between the two planar 1,10-phenantholine rings is $59 \cdot 5°$.

Introduction. Alkali-metal cations usually form 1:1 complexes with the 1,10-phenanthroline (phen) ligand, except for the *o*-nitrophenolates of Na⁺, K⁺, Rb⁺ and Cs⁺, to which two molecules of phenanthroline are added (Layton, Nyholm, Banerjee, Fenton, Lestas & Truter, 1970; Poonia & Bajaj, 1979; Fenton, 1985). The relatively small Na⁺ and K⁺ cations form 1:2 complexes only when the reaction mixture contains foreign proton-donor species which stabilize the counter anion (Poonia, 1977). In this paper, we report that the small Li⁺ cation forms a stable complex with

two equivalents of 1,10-phenanthroline in a non-protonic solvent, CH_2Cl_2, by use of the weakly basic trifluoromethanesulfonate counter ion (Nitschke, Schmidt & Trogler, 1985).

Experimental. Addition of 0·60 g (3·32 mmol) of 1,10-phenanthroline dissolved in 30 mL of CH_2Cl_2, to a stirred white slurry of 0·25 g (1·60 mmol) of Li-(O_3SCF_3) in 30 mL of CH_2Cl_2, gave a yellow solution. After 18 h the solution was filtered, concentrated under vacuum, and layered with pentane to yield (0·51 g, 62%) white crystals of $Li(O_3SCF_3)(phen)_2$. Analysis. Calculated for $C_{25}H_{16}N_4O_3F_3SLi$: C 58·15; H 3·12; N 10·85%. Found: C 58·37; H 3·13; N 10·95%. m.p. 512–514 K.

X-ray data were collected with the use of a Nicolet $R3m/V$ automated diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined from 25 machine-centered reflections with $15 < 2\theta < 30°$. The intensities of three check reflections (222, 105, 043) were monitored after every 100 reflections and showed statistical variations within 2%. Data were corrected for Lorentz and polarization effects. No absorption correction was

---

* To whom correspondence should be addressed.

Table 1. X-ray data collection and structure refinement for $Li(O_3SCF_3)(N_2C_{12}H_8)_2$

Crystal size (mm)	0·6 × 0·3 × 0·2
Scan type	ω–2θ
Scan speed (° min⁻¹)	3·01–15·00
2θ range (data collection) (°)	3–45
Range of hkl	$0 \le h \le 13, 0 \le k \le 19, -18 \le l \le 18$
No. of reflections measured	4197
No. of reflections with $I > 3\sigma(I)$	2221
No. of parameters refined	382
Weight = $[\sigma^2(F_o) + g(F_o)^2]^{-1}$	0·005874
Max. Δ/σ	0·069
Max., min., in $\Delta\rho$ (e Å⁻³)	0·31, −0·28
S (goodness of fit)	0·9211
R	0·053
wR	0·060

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) in $Li(O_3SCF_3)(N_2C_{12}H_8)_2$

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Li	334 (7)	2734 (5)	1065 (5)	61 (3)
S	233 (1)	3063 (1)	3319 (1)	53 (1)
O(1)	1491 (3)	2760 (3)	3489 (3)	92 (2)
O(2)	−132 (4)	3802 (2)	3835 (3)	90 (2)
O(3)	−106 (3)	3119 (2)	2382 (2)	81 (1)
C(100)	−770 (6)	2208 (4)	3739 (4)	73 (2)
F(1)	−534 (4)	2054 (2)	4626 (3)	123 (2)
F(2)	−1977 (3)	2401 (3)	3665 (4)	131 (2)
F(3)	−583 (4)	1468 (2)	3323 (2)	103 (2)
N(1)	−1271 (3)	1875 (3)	1066 (3)	62 (1)
C(1)	−2506 (4)	2037 (4)	1097 (5)	83 (2)
C(2)	−3432 (6)	1417 (5)	1217 (5)	89 (3)
C(3)	−3097 (5)	580 (4)	1290 (4)	73 (2)
C(4)	−1798 (5)	357 (3)	1262 (3)	57 (2)
C(5)	−1353 (6)	−511 (3)	1316 (3)	70 (2)
C(6)	−122 (6)	−705 (3)	1245 (3)	69 (2)
C(7)	816 (5)	−24 (3)	1122 (3)	58 (2)
C(8)	2114 (6)	−188 (4)	1023 (3)	72 (2)
C(9)	2919 (6)	472 (5)	914 (4)	80 (2)
C(10)	2460 (5)	1329 (4)	898 (3)	69 (2)
N(2)	1234 (3)	1510 (2)	990 (2)	57 (1)
C(11)	414 (4)	837 (3)	1088 (3)	52 (1)
C(12)	−926 (4)	1030 (3)	1145 (3)	49 (1)
N(3)	1889 (3)	3647 (3)	954 (2)	58 (1)
C(13)	2830 (5)	3802 (4)	1548 (3)	71 (2)
C(14)	3725 (5)	4446 (4)	1433 (4)	75 (2)
C(15)	3659 (5)	4950 (4)	683 (4)	70 (2)
C(16)	2690 (4)	4823 (3)	31 (3)	53 (1)
C(17)	2531 (5)	5331 (3)	−786 (4)	65 (2)
C(18)	1577 (5)	5198 (3)	−1378 (4)	66 (2)
C(19)	662 (4)	4529 (3)	−1217 (3)	54 (2)
C(20)	−372 (5)	4361 (4)	−1802 (3)	67 (2)
C(21)	−1178 (5)	3718 (4)	−1604 (4)	71 (2)
C(22)	−1000 (5)	3226 (3)	−829 (3)	63 (2)
N(4)	−44 (3)	3358 (2)	−226 (2)	52 (1)
C(23)	784 (4)	4001 (3)	−433 (3)	47 (1)
C(24)	1819 (4)	4151 (3)	203 (3)	48 (1)

Table 3. Bond distances (Å) and bond angles (°) in $Li(O_3SCF_3)(N_2C_{12}H_8)_2$

Li—O(3)	2·072 (9)	Li—N(1)	2·148 (8)
Li—N(2)	2·115 (9)	Li—N(3)	2·166 (9)
Li—N(4)	2·153 (9)	S—O(1)	1·425 (4)
S—O(2)	1·421 (4)	S—O(3)	1·415 (4)
S—C(100)	1·800 (6)	C(100)—F(1)	1·339 (7)
C(100)—F(2)	1·310 (7)	C(100)—F(3)	1·308 (6)
N(1)—C(1)	1·326 (7)	N(1)—C(12)	1·356 (6)
C(1)—C(2)	1·377 (9)	C(2)—C(3)	1·341 (9)
C(3)—C(4)	1·412 (7)	C(4)—C(5)	1·419 (7)
C(4)—C(12)	1·397 (6)	C(5)—C(6)	1·336 (9)
C(6)—C(7)	1·453 (8)	C(7)—C(8)	1·400 (8)
C(7)—C(11)	1·395 (7)	C(8)—C(9)	1·335 (9)
C(9)—C(10)	1·406 (9)	C(10)—N(2)	1·330 (6)
N(2)—C(11)	1·357 (6)	C(11)—C(12)	1·446 (6)
N(3)—C(13)	1·334 (6)	N(3)—C(24)	1·347 (6)
C(13)—C(14)	1·380 (8)	C(14)—C(15)	1·346 (8)
C(15)—C(16)	1·404 (7)	C(16)—C(17)	1·437 (7)
C(16)—C(24)	1·407 (6)	C(17)—C(18)	1·336 (8)
C(18)—C(19)	1·433 (7)	C(19)—C(20)	1·403 (7)
C(19)—C(23)	1·409 (6)	C(20)—C(21)	1·340 (8)
C(21)—C(22)	1·374 (8)	C(22)—N(4)	1·348 (6)
N(4)—C(23)	1·355 (5)	C(23)—C(24)	1·446 (6)
O(3)—Li—N(1)	89·6 (3)	O(3)—Li—N(2)	114·1 (4)
N(1)—Li—N(2)	78·7 (3)	O(3)—Li—N(3)	93·5 (3)
N(1)—Li—N(3)	175·0 (4)	N(2)—Li—N(3)	103·6 (3)
O(3)—Li—N(4)	130·3 (4)	N(1)—Li—N(4)	97·8 (3)
N(2)—Li—N(4)	115·6 (4)	N(3)—Li—N(4)	77·2 (3)
O(1)—S—O(2)	115·2 (2)	O(1)—S—O(3)	114·5 (2)
O(2)—S—O(3)	113·4 (2)	O(1)—S—C(100)	104·4 (3)
O(2)—S—C(100)	104·0 (2)	O(3)—S—C(100)	103·4 (2)
Li—O(3)—S	145·6 (3)	S—C(100)—F(1)	110·8 (4)
S—C(100)—F(2)	112·3 (4)	F(1)—C(100)—F(2)	106·9 (5)
S—C(100)—F(3)	112·8 (4)	F(1)—C(100)—F(3)	105·6 (4)
F(2)—C(100)—F(3)	108·1 (5)	Li—N(1)—C(1)	131·1 (4)
Li—N(1)—C(12)	112·4 (3)	C(1)—N(1)—C(12)	116·1 (4)
N(1)—C(1)—C(2)	124·8 (6)	C(1)—C(2)—C(3)	119·4 (6)
C(2)—C(3)—C(4)	119·1 (5)	C(3)—C(4)—C(5)	123·2 (5)
C(3)—C(4)—C(12)	117·5 (4)	C(5)—C(4)—C(12)	119·2 (5)
C(4)—C(5)—C(6)	121·8 (5)	C(5)—C(6)—C(7)	120·7 (5)
C(6)—C(7)—C(8)	123·3 (5)	C(6)—C(7)—C(11)	119·0 (5)
C(8)—C(7)—C(11)	117·7 (5)	C(7)—C(8)—C(9)	119·8 (6)
C(8)—C(9)—C(10)	119·9 (6)	C(9)—C(10)—N(2)	121·9 (5)
Li—N(2)—C(10)	128·9 (4)	Li—N(2)—C(11)	112·9 (4)
C(10)—N(2)—C(11)	118·1 (4)	C(7)—C(11)—N(2)	122·4 (4)
C(7)—C(11)—C(12)	119·3 (4)	N(2)—C(11)—C(12)	118·2 (4)
N(1)—C(12)—C(11)	123·1 (4)	N(1)—C(12)—C(11)	117·0 (4)
C(4)—C(12)—C(11)	119·9 (4)	Li—N(3)—C(13)	128·8 (4)
Li—N(3)—C(24)	113·6 (3)	C(13)—N(3)—C(24)	117·5 (4)
N(3)—C(13)—C(14)	123·7 (5)	C(13)—C(14)—C(15)	118·9 (5)
C(14)—C(15)—C(16)	120·3 (5)	C(15)—C(16)—C(17)	124·5 (4)
C(15)—C(16)—C(24)	116·9 (4)	C(17)—C(16)—C(24)	118·5 (4)
C(16)—C(17)—C(18)	122·5 (5)	C(17)—C(18)—C(19)	120·4 (5)
C(18)—C(19)—C(20)	123·5 (4)	C(18)—C(19)—C(23)	119·5 (4)
C(20)—C(19)—C(23)	117·0 (4)	C(19)—C(20)—C(21)	119·6 (5)
C(20)—C(21)—C(22)	120·3 (5)	C(21)—C(22)—N(4)	123·4 (5)
Li—N(4)—C(22)	129·5 (4)	Li—N(4)—C(23)	114·1 (3)
C(22)—N(4)—C(23)	116·3 (4)	C(19)—C(23)—N(4)	123·3 (4)
C(19)—C(23)—C(24)	119·5 (4)	N(4)—C(23)—C(24)	117·2 (4)
N(3)—C(24)—C(16)	122·6 (4)	N(3)—C(24)—C(23)	117·9 (4)
C(16)—C(24)—C(23)	119·5 (4)		

applied. The systematic absences $h0l$ ($h+l = 2n+1$) and $0k0$ ($k = 2n+1$) unambiguously indicated $P2_1/n$ as the space group.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculation of F's, initially with isotropic and finally with anisotropic temperature factors for the non-H atoms. All H atoms were located in a difference Fourier map and refined with fixed isotropic thermal parameters. The shortest refined C—H distance was 0·78 (6) Å and the longest was 1·13 (5) Å. Refinement converged with $R = 0·053$ and $wR = 0·060$. All calculations were carried out on a

Fig. 1. ORTEP drawing (Johnson, 1965) of $Li(O_3SCF_3)$-$(N_2C_{12}H_8)_2$ showing the atom-labeling scheme and 50% probability thermal ellipsoids.

MicroVAX II computer with use of the *SHELXTL-Plus* program package (Sheldrick, 1988) with atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates are given in Table 2, bond distances and angles in Table 3.* The molecular structure and atomic-numbering scheme are shown in Fig. 1. The geometry about the Li^+ ion can be classified as trigonal bipyramidal. The O(3), N(2) and N(4) atoms occupy equatorial positions in the trigonal plane, while the remaining N(1) and N(3) atoms occupy axial positions. Equatorial placement of the $CF_3SO_3^-$ ion is dictated by the preference of the phenanthroline ligand for chelation, with N—Li—N angles near 80°. The Li^+ ion is coplanar with respect to the least-squares plane defined by the three equatorial atoms, and deviation from the plane is 0·026 Å. Although the in-plane angles differ from the ideal (120°) of a regular trigonal bipyramid, the sum of the three angles is 360°. The Li—N-distance ranges are 2·115 (9)–2·166 (9) Å and the short Li—O bond distance of 2·072 (9) Å reflects a strong electrostatic attraction between the lithium and trifluoromethanesulfonate ions (Humphrey, Lamanna, Brookhart & Husk, 1983). The dihedral angles between the equatorial plane and the two phenanthroline molecular planes are 100·4 and 79·5°.

---

* Fractional atomic coordinates for H atoms, anisotropic temperature factors for non-H atoms, least-squares-planes information and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51792 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Chemically equivalent bond distances and angles in the two phenanthroline ligands are normal and in good agreement with each other. The two ligands are essentially planar, with maximum deviations of atoms from their least-squares planes of 0·027 and 0·051 Å, respectively. The dihedral angle between these ligands is 59·5°. Bond distances and angles within the $CF_2SO_3^-$ ion are normal (Lawrance, 1986).

References

FENTON, D. E. (1985). *Comprehensive Coordination Chemistry*, Vol. 3, pp. 6–14. Oxford: Pergamon Press.
HUMPHREY, M. B., LAMANNA, W. M., BROOKHART, M. & HUSK, G. R. (1983). *Inorg. Chem.* 22, 3355–3358.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
LAWRANCE, G. A. (1986). *Chem. Rev.* 86, 17–33.
LAYTON, A. J., NYHOLM, R. S., BANERJEE, A. K., FENTON, D. E., LESTAS, C. N. & TRUTER, M. R. (1970). *J. Chem. Soc. A,* pp. 1894–1896.
NITSCHKE, J., SCHMIDT, S. P. & TROGLER, W. C. (1985). *Inorg. Chem.* 24, 1972–1978.
POONIA, N. S. (1977). *Inorg. Chim. Acta,* 23, 5–12.
POONIA, N. S. & BAJAJ, A. V. (1979). *Chem. Rev.* 79, 389–445.
SHELDRICK, G. M. (1988). *SHELXTL-Plus.* Structure determination software programs. Nicolet Instrument Corp., Madison, Wisconsin, USA.

The Structure of the 15-Crown-5–NaClO$_4$ (1/1) Complex

BY G. SHOHAM AND N. COHEN

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Abstract. 1,4,7,10,13-Pentaoxacyclopentadecane–sodium perchlorate (15-C-5/NaClO$_4$), $C_{10}H_{20}O_5$.NaClO$_4$, $M_r = 342·71$, monoclinic, $P2_1/c$, $a = 9·928$ (1), $b = 10·162$ (1), $c = 15·944$ (2) Å, $\beta = 97·35$ (1)°, $V = 1595·4$ (2) Å^3, $Z = 4$, $D_x = 1·43$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 2·54$ cm^{-1}, $F(000) = 716·0$, room temperature, $R = 0·053$ and $S = 2·18$ for 2006 independent reflections. The Na cation forms a 1/1 complex with 15-C-5. In this complex, Na$^+$ is seven-coordinated to the five macrocyclic O atoms (av. Na—O 2·42 Å) and two of the O atoms of the bidentate perchlorate anions (av. Na—O 2·51 Å). The Na$^+$ ion lies 0·77 Å above the least-squares plane of the ether O atoms. All structural parameters of the crown ether are