Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.208$
$S = 1.11$
6407 reflections
355 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.1255P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Fe1—N2	2.059 (3)	Fe1—N4	2.066 (3)
Fe1—N1	2.061 (3)	Fe1—Cl1	2.233 (2)
Fe1—N3	2.063 (3)		
N2—Fe1—N1	87.1 (1)	N4—Fe1—Cl1	104.1 (1)
N2—Fe1—N3	86.6 (1)	C4—N1—Fe1	127.8 (2)
N1—Fe1—N3	152.3 (1)	C1—N1—Fe1	124.8 (2)
N2—Fe1—N4	152.0 (1)	C6—N2—Fe1	128.2 (2)
N1—Fe1—N4	86.3 (1)	C9—N2—Fe1	124.2 (2)
N3—Fe1—N4	86.8 (1)	C14—N3—Fe1	128.5 (2)
N2—Fe1—Cl1	103.9 (1)	C11—N3—Fe1	124.6 (2)
N1—Fe1—Cl1	103.7 (1)	C16—N4—Fe1	128.2 (2)
N3—Fe1—Cl1	104.0 (1)	C19—N4—Fe1	124.2 (2)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1017). Services for accessing these data are described at the back of the journal.

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N-(Tropon-2-yl)-1,4,7,10-tetraoxa-13-aza-cyclopentadecane with calcium thiocyanate

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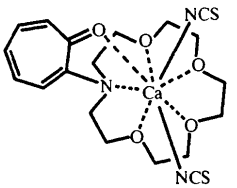
Abstract

In the title complex, [*N*-(7-oxocyclohepta-1,3,5-trien-1-yl)-1,4,7,10-tetraoxa-13-azacyclopentadecane]bis(thiocyanato-*N*)calcium, $[Ca(NCS)_2(C_{17}H_{25}NO_5)]$, the calcium ion has irregular eight coordination involving four ether O atoms, one tropone O atom, one aza-crown N atom and two thiocyanate N atoms.

Comment

Recently, we have prepared several mercurophilic dithio-crown derivatives having a tropone system and their mercury(II) salt complexes (Kato *et al.*, 1995; Mori

et al., 1996, 1998; Kubo *et al.*, 1996). We have now extended the study to aza-crown derivatives having a troponoid pendant (Takeshita *et al.*, 1995). The complexation of troponoid aza-crown ethers with metal thiocyanates as guests has been studied by UV spectroscopy. By addition of metal thiocyanates, the original absorption bands of *N*-(tropon-2-yl)-1,4,7,10-tetraoxa-13-aza-cyclopentadecane (ttapd) at 355 and 417 nm disappeared and a new absorption band appeared around 332 nm, suggesting that the conformation of the 2-aminotropone moiety changes. In order to reveal the detailed coordinated structure of ttapd, the calcium thiocyanate complex, (1), has now been investigated by X-ray crystallographic analysis.



(1)

In the title complex, the Ca^{2+} cation has an irregular eight coordination involving the O1, O7, O10 and O13 ether O atoms, the carbonyl O1′ atom of tropone, the N4 atom of aza-crown ether, and the N01 and N02 atoms of the thiocyanate anions. This geometry is similar to those observed in 15-crown-5–Ca(NCS)$_2$·H$_2$O (Wei *et al.*, 1988), benzo-15-crown-5–Ca(NCS)$_2$·H$_2$O (Owen, 1978), benzo-15-crown-5–Ca(NCS)$_2$·CH$_3$OH (Owen & Wingfield, 1976) and 2,5,8,11,14-pentaoxapentadecane–Ca(NCS)$_2$·H$_2$O (Wei *et al.*, 1987; Poonia *et al.*, 1999). Instead of an O atom from solvents such as methanol and water, the carbonyl O1′ atom of tropone coordinates to the Ca^{2+} cation. The four Ca1—O ether distances are not equal [range 2.474 (2)–2.583 (2) Å], but the average value [2.51 (5)°] is similar to those found in other complexes of crown ethers (Owen & Wingfield, 1976; Wei *et al.*, 1988) and to the sum of the ionic and van der Waals radii (2.52 Å = 1.12 + 1.40 Å; Shannon, 1976; Lide, 1990). The Ca1—O1′ distance [2.437 (2) Å] is significantly shorter than the Ca1—O ether distances. The Ca1—N4 distance [2.749 (2) Å] is longer than the sum of the ionic and van der Waals radii (2.67 Å = 1.12 + 1.55 Å; Shannon, 1976; Lide, 1990), indicating fairly strong coordination of 2-aminotropone to the Ca^{2+} cation.

The tropone moiety of (1) shows pronounced bond alternation similar to that of tropone (Barrow & Mills, 1973). The tropone ring system deviates from planarity; the angle of the intersection between least-squares planes *A* (defined by C1′, C2′, C7′ and O1′) and *B* (defined by C2′, C3′, C6′ and C7′) is 16.2 (2)°, while that between least-squares planes *B* and *C* (defined by C3′, C4′, C5′ and C6′) is 7.1 (2)°.

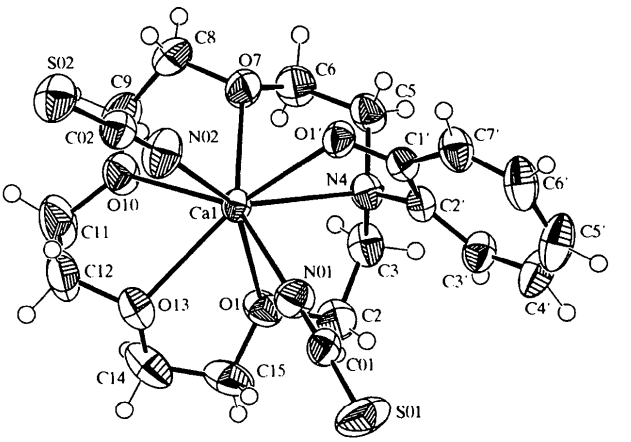


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids.

Experimental

Single crystals of complex (1) were obtained by crystallization of an equimolar mixture of Ca(NCS)$_2$ and ttapd in CH$_3$CN.

Crystal data

[Ca(NCS)$_2$(C$_{17}$H$_{25}$NO$_5$)]
M_r = 479.62
Orthorhombic
Pbca
a = 13.356 (5) Å
b = 23.060 (5) Å
c = 14.719 (5) Å
V = 4533 (2) Å^3
Z = 8
D_x = 1.405 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 22.0–42.1°
μ = 4.412 mm^{-1}
T = 296 (2) K
Prism
0.57 × 0.33 × 0.30 mm
Yellow

Data collection

Enraf–Nonius FR590 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
T_{min} = 0.221, T_{max} = 0.266
4292 measured reflections
4292 independent reflections

3370 reflections with $I > 2\sigma(I)$
θ_{max} = 70°
h = 0 → 16
k = 0 → 28
l = 0 → 17
3 standard reflections
frequency: 120 min
intensity decay: 4.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.117
S = 1.04
4292 reflections
272 parameters
H atoms constrained

$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 5.5 (5) × 10^{-4}

$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 3.4824P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ca1—N01	2.412 (2)	N02—C02	1.153 (3)
Ca1—N02	2.415 (2)	O1′—C1′	1.247 (3)
Ca1—O1′	2.437 (2)	S01—C01	1.629 (3)
Ca1—O7	2.474 (2)	S02—C02	1.630 (3)
Ca1—O10	2.493 (2)	C1′—C7′	1.436 (4)
Ca1—O1	2.502 (2)	C1′—C2′	1.464 (4)
Ca1—O13	2.583 (2)	C2′—C3′	1.363 (4)
Ca1—N4	2.749 (2)	C3′—C4′	1.404 (4)
Ca1—C1′	3.226 (3)	C4′—C5′	1.352 (5)
N4—C2′	1.434 (3)	C5′—C6′	1.401 (5)
N01—C01	1.139 (3)	C6′—C7′	1.346 (4)
N01—Ca1—N02	94.53 (9)	O1′—Ca1—N4	60.83 (6)
N01—Ca1—O1′	76.26 (8)	O7—Ca1—N4	67.18 (6)
N02—Ca1—O1′	85.21 (8)	O1—Ca1—N4	65.01 (6)
O7—Ca1—O10	65.17 (6)	N01—C01—S01	177.4 (3)
O10—Ca1—O13	63.45 (7)	N02—C02—S02	178.6 (3)
O1—Ca1—O13	64.28 (6)		
O1—C2—C3—N4	60.7 (3)	O10—C11—C12—O13	−49.5 (4)
N4—C5—C6—O7	62.0 (3)	O13—C14—C15—O1	−57.0 (4)
O7—C8—C9—O10	53.7 (3)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1014). Services for accessing these data are described at the back of the journal.

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