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Acta Cryst. (1997). C53, 554–556

Bis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzo[*b*]cyclopentadecene-*O*^{1},*O*^{4},*O*^{7},*O*^{10},*O*^{13})sodium(1+) 1,1,7,7-Tetracyano-3,5-dithiahepta-1,6-diene-2,6-dithiolate(2–) (2/1)

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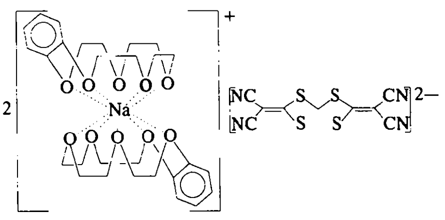
(*Received 29 May 1996; accepted 9 December 1996*)

Abstract

The cation of the title compound, $2[Na(C_{14}H_{20}O_5)_2]^+.C_9H_2N_4S_4^{2-}$, comprises two configurations of benzo-15-crown-5–sodium complex cations in which the Na atoms are sandwiched by ligands through coordinated O atoms. The Na—O distances are in the range 2.443 (4)–3.004 (3) Å. The anion portion is a partially alkylated product of isomalononitriledithiolate ($C_4N_2S_2^{2-}$). The sulfide S—C distances are in the range 1.769 (4)–1.796 (4) Å, while those of the thiol moieties are in the range 1.667 (4)–1.671 (4) Å.

Comment

We have recently reported the non-linear optical properties of compounds related to isomalononitriledithiolato (*i*-mnt) metal complexes (Long *et al.*, 1996). The starting material for isomalononitriledithiolato metal complexes is usually the alkaline metal salt. When sodium isomalononitriledithiolate was refluxed in CH_2Cl_2 with 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-pentaoxabenzo-[*b*]cyclopentadecene (benzo-15-crown-5), not only was the crown ether–sodium complex formed, but an alkylation reaction also took place on the thiolato groups. The title compound, $2[Na(C_{14}H_{20}O_5)_2]^+.C_9H_2N_4S_4^{2-}$, (I), was obtained.



(I)

The molecular structure of (I) is shown in Fig. 1. The anion is the alkylation product of *i*-mnt. Two $C_4N_2S_2$ moieties are linked by a methylene group. Configurations of the moieties are similar to that found in $Pd(i\text{-mnt})_2^{2-}$ (Long *et al.*, 1996). The S—C distances for the sulfide are between 1.769 (4) and 1.796 (4) Å, while those of the thiol group are 1.667 (4) and 1.671 (4) Å; these distances are comparable to those found in $Pd(i\text{-mnt})_2^{2-}$. There are two types of S—C—S angles. One type involves the thiol S atom, with values of 123.5 (3) and 122.9 (2)°, while the other is the central S—C—S angle of 116.0 (2)°. The former is near the value of 122.8 (3)° found in sodium salts of *i*-mnt (Hummel, 1987), while the latter is close to the S—C—S angles found in the metal complexes $Pd(i\text{-mnt})_2^{2-}$ and $M(i\text{-mnt})_2^{2-}$ [M is Pt^{II} (Hummel, 1987), Cd^{II} (Li & Amma, 1990) and Pb^{II} (Hummel & Meske, 1989)]. The alkylation reaction of the thiol with *i*-mnt in CH_2Cl_2 is partial and leaves a half group free, which may be used as a coordination group for metal complexes.

The cations are in two configurations as shown in Fig. 1. The Na1 atom is coordinated by seven O atoms and Na2 by eight O atoms. These sandwich structures are comparable to those found in Na(benzo-15-crown-5)$_2$.ClO_4 (Owen, 1980). The crown rings are coordinated through the O atoms. The Na—O

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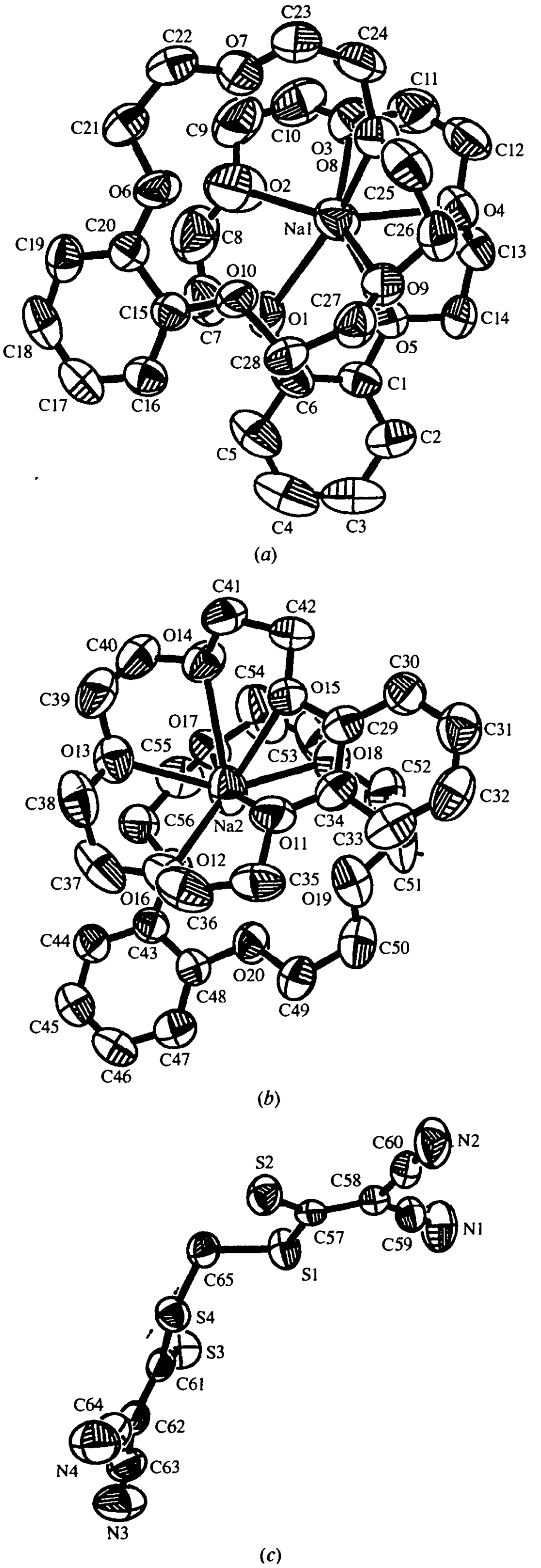
distances are in the range 2.443 (4)–2.937 (3) Å, which includes values reported for benzo-15-crown-5–sodium complexes (Bush, & Truter, 1972; Dreissig, Dauter, Cygan & Biernat, 1985; Owen, 1980; Moody & Ryan, 1979; Ward, Popov & Poonia, 1984).



(*a*)

(*b*)

(*c*)

Fig. 1. View of the title compound with H atoms omitted for clarity. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The title compound was obtained by heating $[Na_2(C_4N_2S_2)]$ with benzo-15-crown-5 in CH_2Cl_2. Single crystals were produced by slow evaporation of the solvent.

Crystal data

$2[Na(C_{14}H_{20}O_5)_2]^+ .$- $C_9H_2N_4S_4^{2-}$
$M_r = 1413.57$
Triclinic
$P\bar{1}$
$a = 11.792\ (1)$ Å
$b = 15.799\ (1)$ Å
$c = 20.925\ (2)$ Å
$\alpha = 105.31\ (1)°$
$\beta = 96.270\ (1)°$
$\gamma = 106.17\ (1)°$
$V = 3540.3\ (5)$ Å^3
$Z = 2$
$D_x = 1.326$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 3.29$–$17.84°$
$\mu = 0.220$ mm^{-1}
$T = 289\ (2)$ K
Sphere
$0.55 \times 0.55 \times 0.55$ mm
Light yellow

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
10 262 measured reflections
9711 independent reflections
5567 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.0136$

$\theta_{\max} = 23°$
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 15$
$l = -22 \rightarrow 22$
3 standard reflections every 97 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R(F) = 0.0521$
$wR(F^2) = 0.1368$
$S = 1.193$
9711 reflections
864 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.085P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.090$
$\Delta\rho_{\max} = 0.564$ e Å^{-3}
$\Delta\rho_{\min} = -0.441$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Na1—O3	2.443 (4)	S1—C65	1.796 (4)
Na1—O8	2.467 (4)	S2—C57	1.667 (4)
Na1—O2	2.476 (4)	S3—C61	1.671 (4)
Na1—O1	2.539 (4)	S4—C61	1.774 (4)
Na1—O4	2.592 (3)	S4—C65	1.791 (5)
Na1—O9	2.594 (3)	N1—C59	1.142 (5)
Na1—O5	2.673 (3)	N2—C60	1.142 (5)
Na2—O13	2.511 (4)	N3—C63	1.148 (5)

Na2—O17	2.524 (3)	N4—C64	1.136 (6)
Na2—O12	2.572 (4)	C57—C58	1.396 (5)
Na2—O18	2.601 (4)	C58—C59	1.413 (6)
Na2—O14	2.768 (4)	C58—C60	1.431 (6)
Na2—O11	2.773 (4)	C61—C62	1.395 (5)
Na2—O16	2.937 (3)	C62—C64	1.400 (7)
Na2—O15	3.004 (3)	C62—C63	1.419 (6)
S1—C57	1.769 (4)		

C58—C57—S2	124.4 (3)	C62—C61—S4	113.0 (3)
C58—C57—S1	112.7 (3)	S3—C61—S4	123.5 (3)
S2—C57—S1	122.9 (2)	C61—C62—C64	123.2 (4)
C57—C58—C59	123.8 (4)	C61—C62—C63	121.1 (4)
C57—C58—C60	120.7 (4)	C64—C62—C63	115.8 (4)
C59—C58—C60	115.5 (4)	N3—C63—C62	177.2 (6)
N1—C59—C58	179.3 (5)	N4—C64—C62	178.0 (5)
N2—C60—C58	177.8 (5)	S4—C65—S1	116.0 (2)
C62—C61—S3	123.5 (3)		

Data were collected with a scan speed of $<7.00°\ \mathrm{min}^{-1}$ and a scan width of $(0.60 + 0.35\tan\theta)°$ (in ω). The structure was solved by direct methods. The Na atom was located in the *E* map and the remaining non-H atoms were deduced from successive Fourier syntheses. The structure was refined by full-matrix least-squares techniques. H atoms were positioned geometrically and not refined. All calculations were performed on a PC 486 computer.

Data collection: *XSCANS* (Siemens, 1994*a*). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1994*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was supported by grants from the National Science Foundation of China.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 556–559

Bis[(1,1,2,3,3-pentacyanopropenido-*N*^{1}:*N*^{2})-bis(triphenylphosphine-*P*)copper(I)]

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(*Received 30 May 1996; accepted 9 December 1996*)

Abstract

The title complex, $[Cu(C_8N_5)(C_{18}H_{15}P)_2]_2$, is a dimer. The two Cu atoms are bridged by the $C(CN)_2$ units of the pentacyanopropenide moiety. The coordination polyhedron of the Cu^I atoms is a distorted tetrahedron with a CuN_2P_2 chromophore.

Comment

In connection with our investigations on the ambidentate behaviour of $C(CN)_2$-modified derivatives of inorganic oxoacids, we have been interested in the coordination behaviour of pentacyanopropenide towards singly charged metal ions. Discussing the fragments $C(CN)_2$ and CCN as pseudo-chalcogen or pseudo-pnictogen (Jäger & Köhler, 1992), the ions NO_2^-, $[NOC(CN)_2]^-$, $[N\{C(CN)_2\}_2]^-$ and $[NCC\{C(CN)_2\}_2]^-$ can be considered as a homologous series.

Depending on the character of the metal atom, dicyanomethanidonitrite, like nitrite, forms coordinative bonds through the central N (Re^I; Fritsch, Polborn, Sünkel, Beck, Köhler & Jäger, 1992) or O atom (Cu^{II}; Hvastijová, Kožíšek, Kohout, Mroziński, Jäger & Svoboda, 1997). On the other hand, from $[N\{C(CN)_2\}_2]^-$ we know complexes in which the ionic ligand is coordinated exclusively through the terminal N atom (Cu^I, Ag^I; Jäger & Tretner, 1997). To the best of our knowledge, for $[NCC\{C(CN)_2\}_2]^-$ only the structure of $[CuCl(bipy)_2][NCC\{C(CN)_2\}_2]$ (Jensen & Jakobson, 1981) has been described. Here, the corresponding ligand exists as an uncoordinated counterion. For $[NCC\{C(CN)_2\}_2]^-$, quantum-chemical investigations predict coordinative bonds *via* terminal N atoms of the $C(CN)_2$ groups. Coordination *via* the central nitrile group end seems to be rather improbable (Jäger, Schädler, Grobe, Köhler & Nefedov, 1992). The title compound, (I), consists of discrete dimeric units.

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