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catena-Poly[[(2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene-κ^5O)potassium]-μ-(picrato-O^1,O^2:O^5)]

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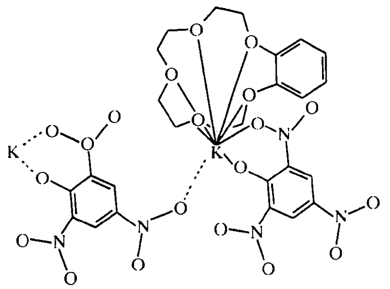
(*Received 13 October 1997; accepted 23 February 1998*)

Abstract

The title compound, $[K(C_6H_2N_3O_7)(C_{14}H_{20}O_5)]_n$, or [K(B15C5)Pic], where Pic is picrate, was synthesized and its crystal structure shown to be an infinite linear-chain polymer with the K(B15C5) moieties bridged by the picrate groups. The K^+ ion is surrounded by eight O atoms in a distorted triangular dodecahedral arrangement. The macrocycle ligand bonds to K^+ using all five O atoms [K—O 2.760 (2)–2.970 (2) Å]. The K^+ ion is bonded to the bridging picrate anion *via* a nitro and the phenolic O atom [K—O 2.808 (2) and 2.871 (2) Å, respectively], and also *via* another nitro O atom of an adjacent symmetry-related picrate anion [K—O 3.060 (2) Å].

Comment

Benzo-15-crown-5 [B15C5] is well known to form 1:2 (metal–ligand) complexes with potassium salts because the K^+ ion is too large to fit into the cavity of the 15-membered ring. Crystal structure analyses of such compounds have revealed that the K^+ ion is ten-coordinate, being 'sandwiched' between two crowns and with no interaction with the counter-anion (Mallinson & Truter, 1972; Bhagwat *et al.*, 1981; Weber & Czugler, 1982; Sheldrick & Poonia, 1986; Mao *et al.*, 1993). We now report the synthesis and crystal structure of a novel 1:1 complex of potassium picrate with benzo-15-crown-5, [K(B15C5)Pic], where Pic is picrate.



[K(B15C5)Pic]

A view of [K(B15C5)Pic] showing the K^+ coordination is given in Fig. 1. In the crystal, there is an infinite linear-chain polymer extending along the *b*-axis direction, with K(B15C5) moieties bridged by picrate anions in a head-to-tail manner to form $[K(B15C5)Pic]_\infty$ chains. We are not aware of any similar polymer in metal–crown ether complex chemistry.

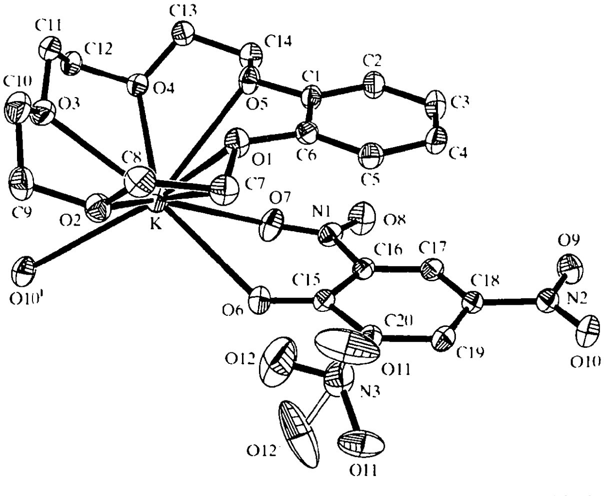


Fig. 1. A view of the asymmetric unit of the title compound with the two orientations of the disordered nitro group shown. Anisotropic displacement ellipsoids are drawn at the 30% probability level. H atoms are not shown and the symmetry code is as in Table 1.

Fig. 2 shows part of the extended chain structure in which the K^+ cation is involved in ion–dipole interactions to the five O atoms of the 15-membered ring and two interactions with a chelate picrate anion, which acts as a bidentate donor agent attached to the K^+ ion through the phenolic O and onc of the nitro O atoms, and one further interaction with one of the nitro O atoms from an adjacent symmetry-related picrate anion (Table 1). The coordination number of the K^+ ion is eight and the coordination polyhedron has a distorted triangular dodecahedral arrangement. The K^+ ion is 1.678 (1) Å from the O1–O5 mean plane, compared with 1.71 Å in the 1:2 complex [K(B15C5)$_2$Pic] (Bhagwat *et al.*, 1981).

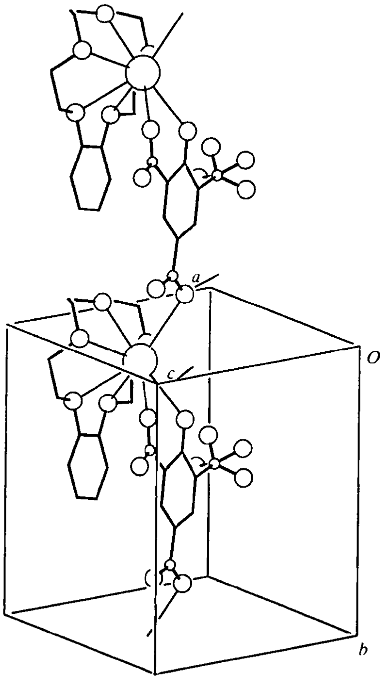


Fig. 2. A view of part of the chain of [K(B15C5)Pic] units with the unit cell indicated.

It is worth noting that the distance from the K^+ ion to one of the O atoms of the bridging nitro group [K—O10(x, $y-1$, z)] is significantly longer than the bonds from the other picrate O atoms, indicating a weaker interaction. Other intermolecular contacts correspond with normal van der Waals distances.

Experimental

The synthesis of the title compound was carried out by reaction of benzo-15-crown-5 (B15C5, 0.134 g) and potassium picrate (KPic, 0.401 g) (molar ratio 1:3) in acetone solution (115 ml) for 24 h at 333 K. The solvent was partially evaporated and the crystalline complex obtained was filtered, washed with 3 × 10 ml acetone and dried *in vacuo* at room temperature over P_2O_5 (yield: 75%; decomposition temperature 450.5–451.5 K). Crystals were obtained by slow evaporation of an acetone solution at room temperature.

Crystal data

$[K(C_6H_2N_3O_7)(C_{14}H_{20}O_5)]$
$M_r = 535.51$
Triclinic
$P\bar{1}$
$a = 7.074\,(1)$ Å
$b = 11.052\,(1)$ Å
$c = 15.086\,(2)$ Å
$\alpha = 90.22\,(1)^\circ$
$\beta = 91.85\,(1)^\circ$
$\gamma = 105.37\,(1)^\circ$
$V = 1136.6\,(2)$ Å^3
$Z = 2$
$D_x = 1.565$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 4.95$–19.52°
$\mu = 0.307$ mm^{-1}
$T = 296\,(2)$ K
Prism
0.58 × 0.42 × 0.42 mm
Yellow

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction:
ψ scan (Koptman & Huber, 1968)
$T_{\min} = 0.839$, $T_{\max} = 0.879$
4834 measured reflections
4452 independent reflections
3425 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\max} = 25.99^\circ$
$h = 0 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: 3.55%

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.139$
$S = 1.203$
4452 reflections
345 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0830P)^2 + 0.2863P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.772$ e Å^{-3}
$\Delta\rho_{\min} = -0.759$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.012 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

K—O2	2.760 (2)	K—O6	2.871 (2)
K—O7	2.808 (2)	K—O4	2.886 (2)
K—O1	2.855 (2)	K—O5	2.970 (2)
K—O3	2.862 (2)	K—O10^{i}	3.060 (2)
O1—K—O2	59.40 (6)	O4—K—O7	90.27 (6)
O1—K—O10^{i}	139.50 (6)	O4—K—O10^{i}	98.67 (6)
O2—K—O3	60.99 (6)	O5—K—O10^{i}	153.00 (6)
O2—K—O10^{i}	80.10 (6)	O6—K—O7	56.13 (6)
O3—K—O4	61.24 (5)	O6—K—O10^{i}	108.77 (6)
O3—K—O10^{i}	70.24 (6)	O7—K—O10^{i}	121.31 (7)
O4—K—O5	55.59 (5)	N2^{i}—O10^{i}—K	108.6 (2)

Symmetry code: (i) $x, y-1, z$.

The O atoms of one of the nitro groups (N3, O11, O12) are disordered unequally over two sites. This was allowed for during refinement and the O-atom occupancies refined to 0.613 (9) (O11 and O12) and 0.387 (9) (O11′ and O12′). H atoms were allowed for as riding atoms using standard *SHELXL*93 (Sheldrick, 1993) defaults.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985).

Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

We acknowledge the National Natural Science Foundation of China and the Doctorial Point Foundation of the State Education Commission of China (9573005) for their grants in support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1402). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1418-1419

A *closo*-12-Vertex Dinickelaborane: [$(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$]

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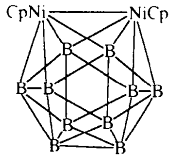
(*Received 5 January 1998; accepted 16 March 1998*)

Abstract

In the title compound, 1,2-di-η^5-cyclopentadienyl-1,2-dinickela-*closo*-dodecaborane, [$Ni_2(B_{10}H_{10})(C_5H_5)_2$], the cluster has a *closo*-twelve-vertex icosahedral {Ni_2B_{10}} framework. The Ni atoms occupy adjacent vertices of the polyhedron and each Ni atom is coordinated by a η^5-cyclopentadienyl ring.

Comment

Di- or polymetallaborane clusters are well known in metallaborane chemistry (Crook *et al.*, 1982; Pipal & Grimes, 1977, 1979*a*,*b*; Bowser *et al.*, 1979), but twelve-vertex metallaborane species are rare. There are two methods for the synthesis of these species. One is *nido*-cage closure, as used in the preparation of dicobalta- (Schubert *et al.*, 1988) and diplatinaboranes (Cheek *et al.*, 1985). The other, developed by Hawthorne's group, is *closo*-polyhedral cage expansion; Hawthorne and co-workers reported the synthesis of *closo*-[$(C_5H_5)_2Ni_2B_{10}H_{10}$] and *closo*-[$(C_5H_5)_2NiCoB_{10}H_{10}$]$^-$ (Leyden *et al.*, 1978), which were characterized by NMR spectroscopy. We have previously isolated and characterized the novel *closo*-twelve-vertex dinickelaborane [$(\mu\text{-}1,2\text{-}Cl)\text{-}3\text{-}Cl\text{-}6\text{-}(PPh_3)\text{-}(\mu\text{-}1,4\text{-}Ph_2PC_6H_4)\text{-}(\mu\text{-}2,8\text{-}Ph_2PC_6H_4)\text{-}1,2\text{-}Ni_2B_{10}H_6$] (Dou *et al.*, 1997) by X-ray diffraction analysis. We now report the crystal and molecular structure of *closo*-[$(\eta^5\text{-}C_5H_5)_2Ni_2B_{10}H_{10}$], (I).



(I)

The structure of the title compound consists of a *closo*-twelve-vertex icosahedral {Ni_2B_{10}} framework. The Ni atoms occupy adjacent vertices of the polyhedron. Although the Ni—Ni distance of 2.4233 (6) Å is similar to that found in another *closo*-twelve-vertex

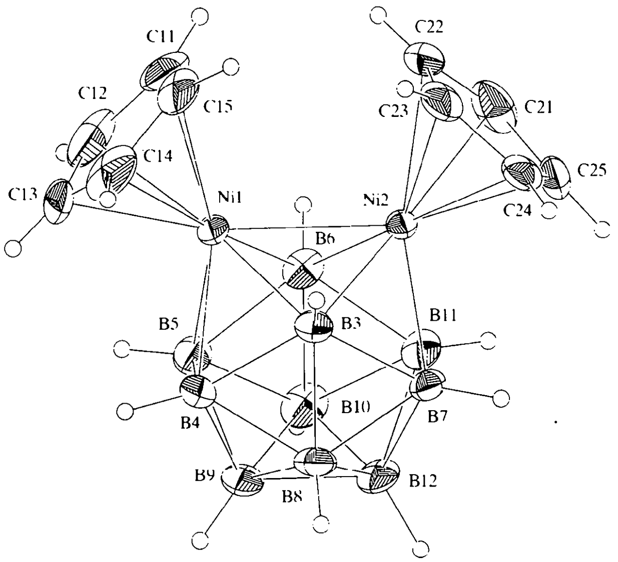


Fig. 1. View of the title compound with 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998