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The Crystal Structure of the Dimeric Complex of 24⟨O_5-2_4. [(4′,4″)-1,8-Diphenylnaphthalenol]coronand-5⟩* with KNCS

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Introduction

The title ligand and its ‘stereologues’ [2] contain ether O atoms and additional aromatic π donor centres. Hence they form stable complexes with Ag^+ and with alkali cations [2]. On coordinating to K^+, the bulky 1,8-diarylnaphthalene entity might be a steric hindrance, though aromatic interactions to potassium have been reported [3]. A structural investigation of the current compound therefore seemed interesting.

Experimental

A sample was kindly provided by Dr. R. Leppkes and Prof. F. Vögtle, University of D-5300 Bonn (F.R.G.). Colourless rods were grown from methanol. *Crystal data:* $C_{30}H_{30}O_5$·KNCS, M_r = 576.75, triclinic, space group P1, a = 9.480(3), b = 12.256(4), c = 13.732(4) Å, α = 107.70(4), β = 94.59(3), γ = 105.39(3)°, Z = 2, $d_{calc.}$ = 1.307 Mg m^{-3}, $\mu(MoK_\alpha)$ = 0.289 mm^{-1}.

4256 unique profile-fitted [4] diffractometer data points were collected from a crystal *ca.* 0.4 × 0.2 × 0.2 mm, up to 2θ = 47° with monochromated MoK_α-radiation (λ = 0.71069 Å). The structure was solved by direct methods and subsequent Fourier syntheses [5] and refined anisotropically using 2918 observed $[F > 3\sigma(F)]$ reflections. A difference map then revealed all H atoms which were included in idealised positions (C–H = 0.96 Å) with $U(H_i)$ kept fixed at 1.2 $U_{eq}(C_i)$ during further refinement. The final R was 0.068 and R_w = 0.056 with $w^{-1} = \sigma^2(F_o) + 3 \times 10^{-4} F_o^2$.

Atom parameters are listed in Table I; a view of the dimer is given as Fig. 1. Further data may be obtained from GW on request.

TABLE I. Atomic Coordinates (× 10^4) and Isotropic Thermal Parameters ($Å^2 \times 10^3$).

	x	*y*	*z*	*U*
K	6187(1)	5548(1)	3764(1)	66(1)
S	6095(1)	1655(1)	3941(1)	85(1)
C	5305(4)	2710(4)	4124(3)	64(2)
N	4710(4)	3428(3)	4252(3)	78(2)
O(1)	6791(3)	3779(2)	1645(2)	66(1)
C(2)	7679(4)	3244(4)	2133(3)	61(2)
C(3)	9098(4)	4178(4)	2702(3)	74(2)
O(4)	8846(3)	4968(3)	3621(2)	78(1)
C(5)	10137(5)	5952(4)	4209(4)	104(3)
C(6)	10217(5)	7016(4)	3926(4)	110(3)
O(7)	8963(3)	7401(3)	4167(2)	88(2)
C(8)	8956(5)	8413(4)	3885(4)	107(3)
C(9)	7559(5)	8688(4)	4088(4)	99(3)
O(10)	6374(3)	7729(2)	3389(2)	72(1)
C(11)	4991(6)	7962(4)	3447(3)	76(2)
C(12)	3887(4)	7037(3)	2558(3)	64(2)
O(13)	3661(3)	5869(2)	2651(2)	59(1)
C(14)	2712(4)	4916(3)	1846(3)	48(2)
C(15)	2427(4)	3792(3)	1944(3)	48(2)
C(16)	1488(4)	2792(3)	1168(3)	48(2)
C(17)	822(4)	2888(3)	264(3)	45(2)
C(18)	1111(4)	4028(3)	200(3)	51(2)
C(19)	2033(4)	5045(3)	975(3)	52(2)
C(20)	−239(4)	1846(3)	−595(3)	46(2)
C(21)	165(4)	915(3)	−1318(3)	48(2)
C(22)	−1002(4)	31(3)	−2129(3)	61(2)
C(23)	−2457(4)	104(4)	−2189(3)	75(2)
C(24)	−2796(4)	988(4)	−1502(3)	76(2)
C(25)	−1689(4)	1878(4)	−696(3)	61(2)
C(26)	1628(4)	778(3)	−1316(3)	54(2)
C(27)	1835(5)	−182(4)	−2067(3)	68(2)
C(28)	683(5)	−1030(4)	−2847(3)	78(2)
C(29)	−702(4)	−923(4)	−2871(3)	72(2)
C(30)	2988(4)	1591(3)	−532(3)	45(2)
C(31)	3601(4)	1137(3)	149(3)	55(2)
C(32)	4867(4)	1836(3)	884(3)	57(2)
C(33)	5554(4)	2998(4)	938(3)	52(2)
C(34)	4976(4)	3448(3)	231(3)	51(2)
C(35)	3715(4)	2750(4)	−490(3)	51(2)

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

Results and Discussion

It may be deduced from geometrical considerations (mean K^+..O *ca.* 2.8, O..O *ca.* 2.8 Å), and has been confirmed by stability constant measurements [6] and X-ray investigations [*e.g.* 7–9], that 18-crown-6 and its derivatives provide a cavity of optimal geometry for the uptake of K^+. With the smaller benzo-15-crown-5, however, a 2:1 ‘sandwich’ complex is formed [10] in which the K^+..bond valences [11] sum to 1.26 (*cf.* 0.90 in 18-crown-6·KSCN [7]), and the cation is totally shielded from the anion.

The title ligand also contains only five donor atoms but a 1:1 stoichiometry is nevertheless found. Closest distances C(30)..C(17) = 2.996(6), C(30)..C(16) = 3.032(7) and C(35)..C(17) = 3.036(6) Å

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*For nomenclature see [1].

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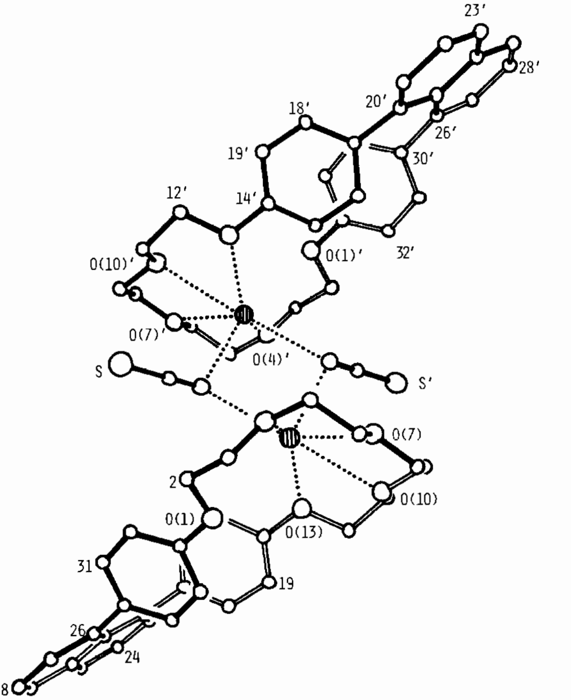

Fig. 1. A perspective view of the dimer. Radii are arbitrary. Primed atoms are related to unprimed ones by inversion at 1/2, 1/2, 1/2. Coordination distances (Å) are to O(1): 3.254(3), to O(4): 2.801(4), to O(7): 2.867(4), to O(10): 2.836(4), to O(13): 2.916(3), to N: 2.905(5), to N': 2.929(5).

(dihedral angle between aryl planes: 17(1)°, to naphthalene plane: 69(1)° each) despite systematically widened angles C(16)–C(17)–C(20): 123.8(3), C(17)–C(20)–C(21) = 125.1(3), C(20)–C(21)–C(26) = 126.3(3), C(21)–C(26)–C(30) = 125.3(3) and C(26)–C(30)–C(35) = 123.6(4) probably reflect the repulsion between the two aryl groups in the 1,8 positions of the naphthalene nucleus. The O(1)..O(13) distance is thus widened from *ca.* 2.4 Å [corresponding to C(20)..C(26)] to 4.452(4) Å, a value close to the 1..7 distance (*ca.* 4.85 Å) in a hexagonal arrangement of O atoms preferred by K$^+$.

However, only four O atoms out of the five are coplanar to within ±0.15 Å, O(1) deviating by 1.82(1) Å (K$^+$: –0.83(1) Å; *cf.* 1.67 in (benzo-15-crown-5)$_2$·KI [10]). Accordingly, this 'apical' atom shows the weakest coordination (if any) to K$^+$. The five K$^+$..O contacts (mean distance 2.86 Å, neglecting K$^+$..O(1) = 3.254(3); *cf.* 2.86 in (benzo-15-crown-5)$_2$·KI [10] and 2.80 in 18-crown-6·KSCN [7]) yield a sum of K$^+$..O bond valences of only 0.55, indicating a rather weak linkage between host and guest. It seems that this lack of strong interactions can only be compensated for by the twofold binding of each K$^+$ to two anions resulting in a four-membered ⌞K–N–K–N⌟ ring. Similar geometries have occasionally been observed with potassium [12, 13], particularly in the binuclear dibenzo-24-crown-8·2KNCS complex [3]. In contrast to the latter, additional π..K$^+$ interactions are not obvious in the current structure since the shortest contact between an aromatic carbon and K$^+$ is >3.8 Å.

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