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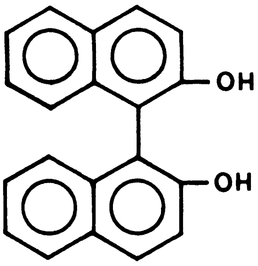
Crystalline Inclusion Compounds of 2,2'-Dihydroxy-1,1'-binaphthyl with Alkali Metal Hydroxides and Ammonia

Fumio TODA,* Koichi TANAKA, Man Chaun WONG,† and Thomas C. W. MAK*†

Department of Industrial Chemistry, Faculty of Engineering,
Ehime University, Matsuyama 790
†Department of Chemistry, The Chinese University of Hong Kong,
Shatin, New Territories, Hong Kong

2,2'-Dihydroxy-1,1'-binaphthyl, $C_{20}H_{14}O_2$, forms crystalline inclusion compounds of stoichiometries $1\frac{1}{2}C_{20}H_{14}O_2\cdot 3MOH\cdot 8H_2O$ (M = Li,Na,K), $C_{20}H_{14}O_2\cdot CsOH\cdot 6H_2O$, and $2C_{20}H_{14}O_2\cdot 2NH_3\cdot CH_3OH$. In the crystal structure of the NH_3 complex, the three molecular components are interlinked by hydrogen bonds to form a column with a hydrophilic stem and a hydrophobic sheath.

2,2'-Dihydroxy-1,1'-binaphthyl ($C_{20}H_{14}O_2$, commonly known as bis-β-naphthol), **1**, has been found to be a very effective host compound for the isolation[1] and optical resolution[2] of a wide range of organic guest species through the formation of crystalline inclusion complexes.[3] We now report the preparation and structural characterization of a series of new inclusion compounds (formulas **2** to **6**) of **1** with alkali metal hydroxides and ammonia.



$C_{20}H_{14}O_2$ (**1**)

2 $1\frac{1}{2}C_{20}H_{14}O_2\cdot 3LiOH\cdot 8H_2O$

3 $1\frac{1}{2}C_{20}H_{14}O_2\cdot 3NaOH\cdot 8H_2O$

4 $1\frac{1}{2}C_{20}H_{14}O_2\cdot 3KOH\cdot 8H_2O$

5 $C_{20}H_{14}O_2\cdot CsOH\cdot 6H_2O$

6 $2C_{20}H_{14}O_2\cdot 2NH_3\cdot CH_3OH$

Typical procedures in preparing the complexes are as follows. When a mixture of **1** (1 g) and 20% aqueous NaOH solution (5 ml) was kept at room temperature for 12 h, colorless prisms (1.5 g, mp not clear) of **3** was obtained.

In a similar manner, 6 was obtained as colorless prisms (1.7 g, mp not clear) when a mixture of 1 (1 g) and 5 ml of methanol saturated with ammonia was kept at room temperature for 12 h.

Compounds 2 - 5 are air-sensitive but may be kept for weeks in a sealed tube without apparent decomposition. The alkali metal contents of 2 - 5 were determined by the flame emission technique using a Varian AA-4 atomic absorption spectrophotometer. In each instance a freshly prepared sample was quickly dried by pressing between filter paper and immediately weighed and dissolved for triplicate analysis. In the determination of cesium, a known excess of potassium was added as an ionization suppressor to enhance its emission intensity in the air-acetylene flame. The experimental results (% by weight: Li, 3.57; Na 9.92; K, 15.72; Cs 24.19) obtained for 2 - 5 were consistent with those (Li, 3.23; Na, 9.94; K, 15.81; Cs 24.42) calculated from the stoichiometric formulas $1\tfrac{1}{2}\mathrm{C_{20}H_{14}O_2\cdot 3MOH\cdot 8H_2O}$ (M = Li,Na,K) and $\mathrm{C_{20}H_{14}O_2\cdot CsOH\cdot 6H_2O}$. The formulation of the isomorphous sodium and potassium complexes was substantiated by X-ray crystallographic analysis, but the lithium and cesium complexes did not yield suitable crystals for unit-cell and density measurements.

X-Ray crystallographic studies of 3, 4, and 6 proceeded in the same manner. Densities were determined by flotation in a mixture of hexane and carbon tetrachloride. A selected crystal was sealed inside a 0.5 mm Lindemann glass capillary, and intensity data were collected on a Nicolet R3m diffractometer using Mo-K_α radiation (λ = 0.71069 Å) as described previously.4) For 3 and 4 the intensities declined rapidly with increasing Bragg angle.

Crystal data: 3, FW = 693.81, tetragonal, space group $I4_1/a$, a = 19.298(5), c = 37.357(8) Å, V = 13912(6) Å^3, Z = 16, F(000) = 5839, D_m = 1.341, D_c = 1.325 g cm^{-3}, crystal size 0.40 x 0.24 x 0.20 mm^3, μ = 1.27 cm^{-1}, $2\theta_{max}$ = 40°, 2401 unique reflections, 1450 observed, R = 0.218; 4, FW = 741.94, a = 19.303(6), c = 37.549(8) Å, V = 13991(7) Å^3, F(000) = 6223, D_m = 1.393, D_c = 1.409 g cm^{-3}, crystal size 0.42 x 0.40 x 0.32 mm^3, μ = 4.49 cm^{-1}, $2\theta_{max}$ = 40°, 2554 unique data, 1617 observed, R = 0.275; 6, FW = 638.76, monoclinic, space group $P2_1/c$, a = 11.136(2), b = 19.853(5), c = 15.314(3) Å, β = 91.36(1)°, V = 3384.7(9) Å^3, Z = 4, F(000) = 1352, D_m = 1.250, D_c = 1.254 g cm^{-3}, crystal size 0.56 x 0.52 x 0.46 mm^3, μ = 0.87 cm^{-1}, 4848 unique reflections, 3671 observed, R = 0.059. The structures were solved by direct phase determination guided by negative quartets.5) All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL package.6,7)

In the crystal structure of 3 and 4, one host molecule (1) occupies Wyckoff position 8(*e*) of site symmetry 2, whereas the other is in a general position. The structure is highly disordered, such that two alkali metal atoms and three of the water/hydroxide oxygen atoms failed to appear in a difference Fourier map. The single ordered metal atom is coordinated to a phenolic oxygen atom and two water/hydroxide oxygen atoms, but other atoms occupying the remaining ligand sites could not be located. The occurrence of liquid-like regions in the solid lattice may be a common structural feature of the newly-discovered crystalline inclusion compounds formed by phenol- and propynol-type hosts with alkali metal and ammonium hydroxides.8)

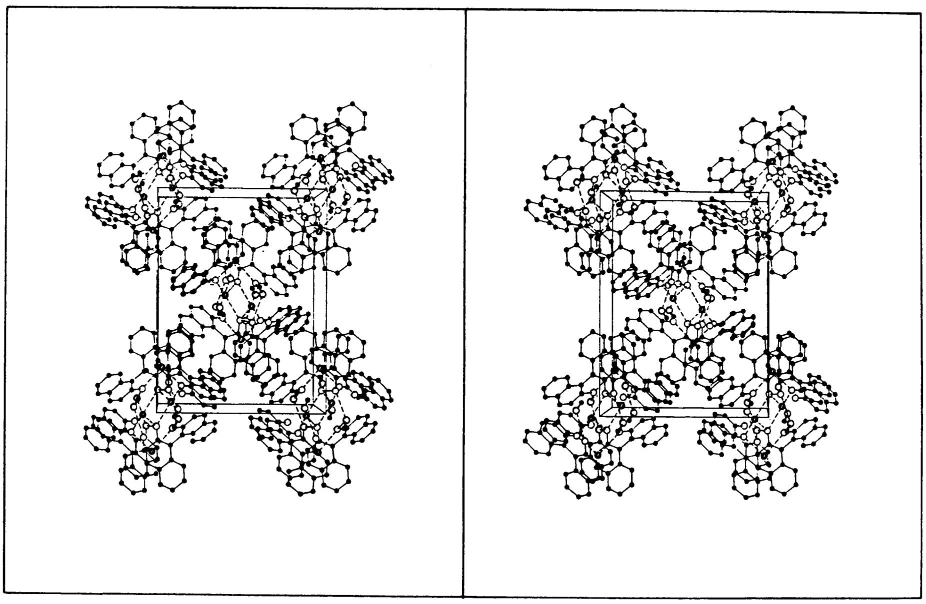
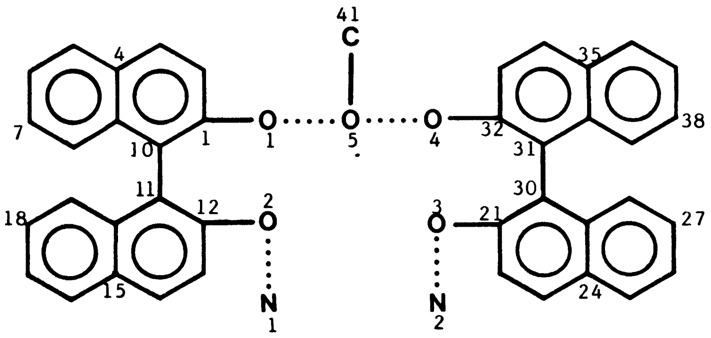


Fig. 1. Stereodrawing of the crystal structure of $2C_{20}H_{14}O_2\cdot 2NH_3\cdot CH_3OH$, **6**. The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right. The blackened, shaded, and open cirles represent C, N, and O atoms, respectively. Hydrogen bonds are indicated by broken lines.

The crystal structure of **6** is shown in Fig. 1. The phenolic groups, ammonia molecules, and methanol molecules are interlinked by hydrogen bonds to form a column with a hydrophilic stem and a hydrophobic sheath. Geometrical details of the hydrogen bonding in the stem are illustrated in Fig. 2. The crystal lattice is constructed from a lateral packing of such infinite columns, all of which are oriented in the direction of the a axis.



Atom numbering scheme for the asymmetric unit in **6**.

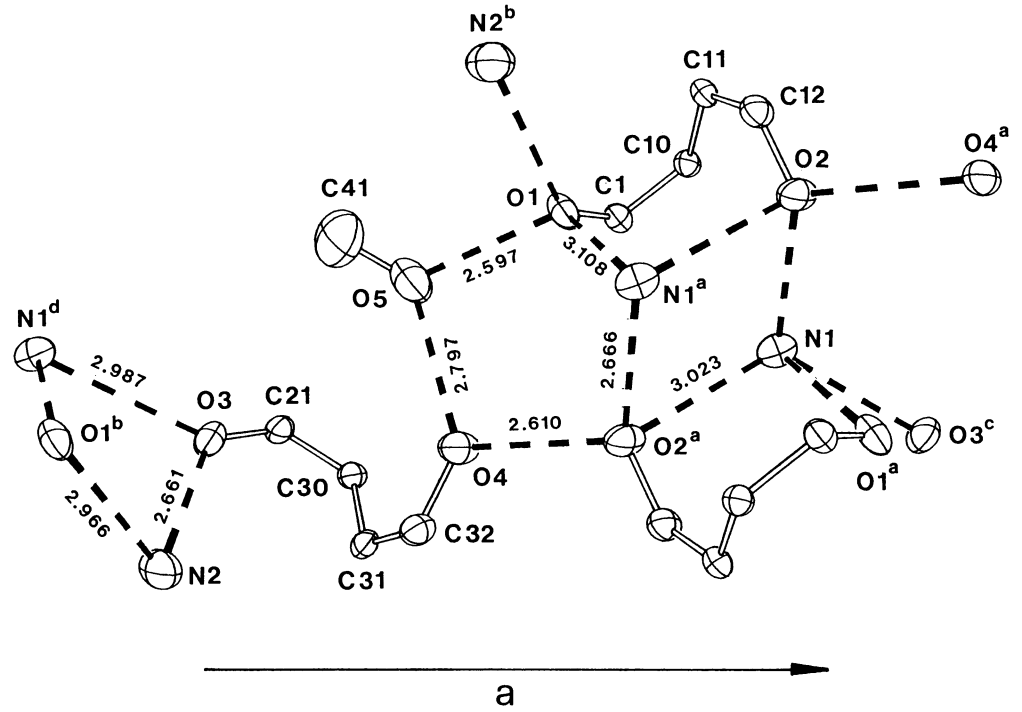


Fig. 2. Details of the hydrogen bonding in the hydrophilic stem of a column in the crystal structure of **6**. For clarity the aromatic rings have been omitted, so that molecule **1** [torsion angles C(1)-C(10)-C(11)-C(12) = 86.8(3)° and C(21)-C(30)-C(31)-C(32) = −101.3(3)°] appears like 1,4-butanediol. Symmetry transformations: ^{a} $1-x$, $1-y$, $1-z$; ^{b} $-x$, $1-y$, $1-z$; ^{c} $1+x$, y, z; ^{d} $-1+x$, y, z. The standard deviation of each hydrogen bond length is about 0.007 Å.

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