Crystalline Inclusion Compounds of 2,2'-Dihydroxy-1,1'-binaphthyl with Alkali Metal Hydroxides and Ammonia
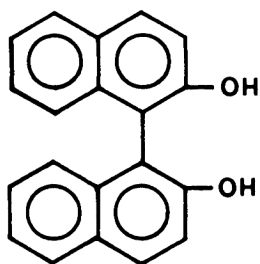
Fumio TODA,[*] Koichi TANAKA, Man Chaun WONG,[†] and Thomas C. W. MAK[*†]

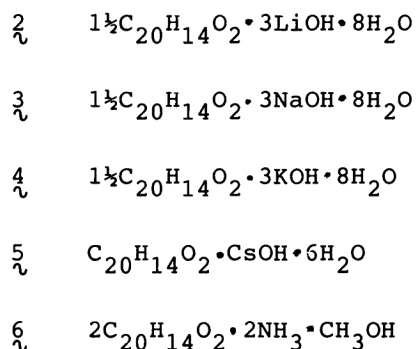Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
[†]Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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), $\underset{\sim}{1}$, 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 $\underset{\sim}{2}$ to $\underset{\sim}{6}$) of $\underset{\sim}{1}$ with alkali metal hydroxides and ammonia.

$C_{20}H_{14}O_2 \quad (\underset{\sim}{1})$

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

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

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

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

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

Typical procedures in preparing the complexes are as follows. When a mixture of $\underset{\sim}{1}$ (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 $\underset{\sim}{3}$ 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 $1\frac{1}{2}C_{20}H_{14}O_2 \cdot 3MOH \cdot 8H_2O$ (M = Li,Na,K) and $C_{20}H_{14}O_2 \cdot CsOH \cdot 6H_2O$. 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]
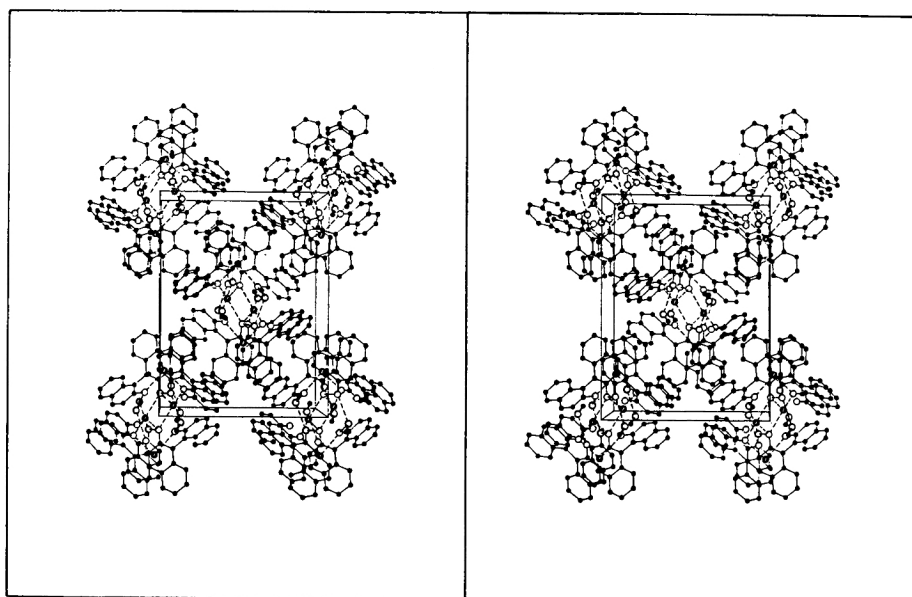
Fig. 1.   Stereodrawing of the crystal structure of $2C_{20}H_{14}O_2 \cdot 2NH_3 \cdot CH_3OH$, 6. The origin of the unit cell lies at the upper left corner, with a pointing towards the reader, b downwards, and c from left to right. The blackened, shaded, and open cirles represent C, N, and O atoms, 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.
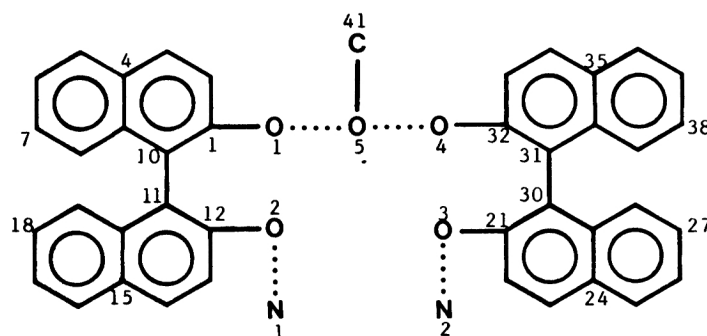
Atom numbering scheme for the asymmetric unit in 6.

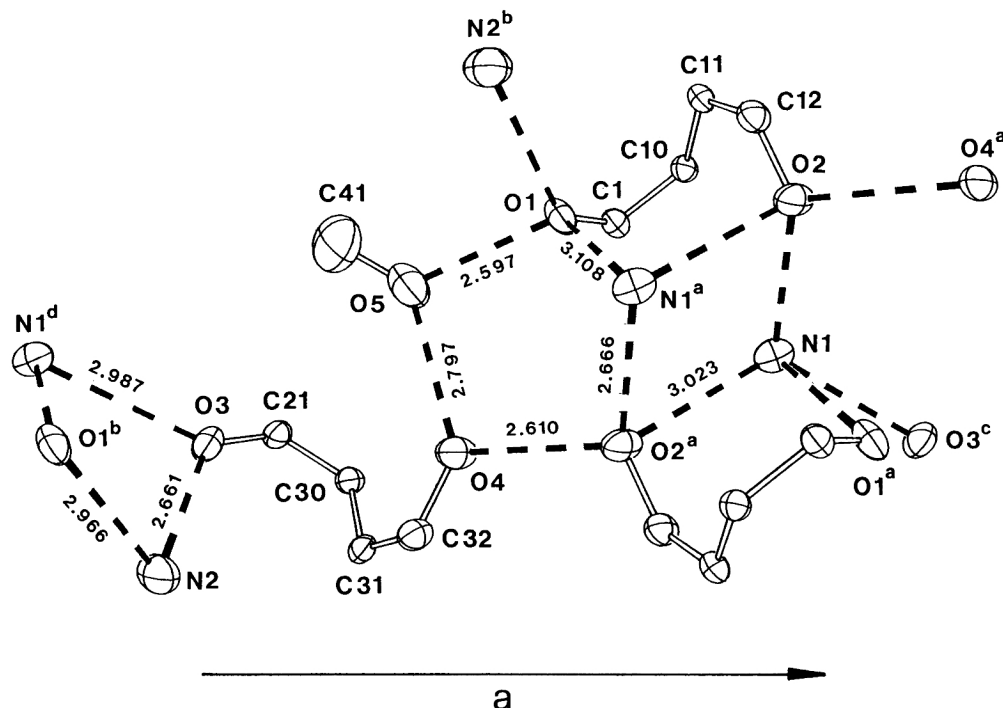Fig. 2.   Details of the hydrogen bonding in the hydrophilic stem of a column in the crystal structure of 6. For clarity the aromatic rings have been omitted, so that molecule 1 [torsion angles C(1)-C(10)-C(11)-C(12) = 86.8(3)° and C(21)-C(30)-C(31)-C(32) = -101.3(3)°] appears like 1,4-butanediol. Symmetry 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.

References

1)   F. Toda, K. Tanaka, G. Ulibarri Daumas, and M.C. Sanchez, Chem. Lett., 1983, 1521.

2)   F. Toda, K. Tanaka, and S. Nagamatsu, Tetrahedron Lett., 25, 4929 (1984).

3)   F. Toda, K. Tanaka, and T.C.W. Mak, Chem. Lett., 1984, 2085.

4)   F. Toda, K. Tanaka, and T.C.W. Mak, Bull. Chem. Soc. Jpn., 58, 2221 (1985).

5)   G.T. DeTitta, J.W. Edmonds, D.A. Langs, and H. Hauptman, Acta Crystallogr., Sect. A, 31, 472 (1975).

6)   G.M. Sheldrick, "Computational Crystallography," ed by D. Sayre, Oxford University Press, New York (1982), p. 506.

7)   The atomic coordinates have been deposited with the Cambridge Crystallo- graphic Data Centre. Structure factors are obtainable from the last author.

8)   F. Toda, "Molecular Inclusion and Molecular Recognition - Clathrates I," (Topics in Current Chemistry, Vol. 140), ed by E. Weber, Springer-Verlag, Berlin (1987), pp. 43-69.