The Structural Study of the Lithium β-Diketonate Complex

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Received December 26, 1997

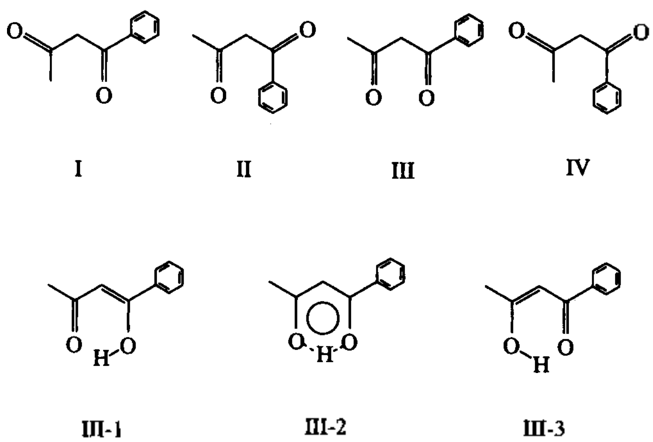
β-Diketonates have drawn constant interest in inorganic, organic, and physical chemistry. The keto-enol equilibrium, the structures of both keto and enol forms, and the intra-/inter-molecular O-H---O hydrogen bond have been extensively studied by a variety of methods, including NMR, Raman and IR sepectroscopy, X-ray and neutron diffraction, and theoretical calculations.[1] For asymmetric benzoylacetone (bzac), four conformations of the keto form are theoretically possible and the enolization of conformation III brings about two forms of *cis*-enol [forms (III-1) and (III-3)] which altenate quickly in solution via form (III-2), as shown in the Scheme 1.

An NMR study suggested that in the *cis*-enol of benzoylacetone, form(III-1) dominates in solution, and a neutron diffraction and an accurate low-temperature X-ray diffraction study indicated that within the delocalized enol ring, the C-C bond farther from the phenyl ring is slightly longer than the C-C bond closest to the phenyl ring.[2] The structure of copper complex, $[Cu(bzac)(bipy)(NO_3)]$, however, shows that the C-C bond close to the phenyl ring is longer when bzac chelates to a Cu(II) atom.[3] Herein, we report the molecular structure of lithium compound, $Li(bzac)(H_2O)_2$, having an infinite polymeric chain by hydrogen bonding.[4]

Experimental Section

General procedures. All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Butyl lithium and benzoylacetone were purchased from Aldrich and used as received.

Preparation of $Li(bzac)(H_2O)_2$. To a solution of benzoylacetone (0.34 g, 2.00 mmol) in 30 mL of hexane in a Schlenk flask was added buthyl lithium (1.6 mL of 1.6 M



Scheme 1.

in hexane) dropwise with stirring in ice bath under nitrogen. White precipitates were immediately formed. The mixture was stirred for 1h at 0 °C and for additional 2 h at ambient temperature. The white precipitate was filtered off and the resulting solvent was removed *in vacuo* to yield pale-yellow precipitate. Suitable crystals for X-ray crystallography were obtained by the slow diffusion of hexane to THF solution. Yield: 0.32 g, 91%.

X-ray Crystal Analysis. Crystallographic parameters and information related to data collection and structural refinements for the complexes are given in Reference 5. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical φ-scan method.[8] The structure were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least squares techniques (SHELXL-93). All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were idealized, assigned isotropic thermal parameters [U_{iso}(H)=1.2 U_{eq}(C)] and allowed to ride on the parent carbon atoms. All calculations were carried out on the personal computer with use of the SHELXS-86 and SHELXL-93 programs.[9] Selected bond lengths and angles are given in Table 1.

Reselts and Discussion

For the $Li(bzac)(H_2O)_2$, there are two independent molecules in an asymmetric region of the triclinic cell and the features of the two molecules are within error of being identical. One of the molecules and its labelling scheme for $Li(bzac)(H_2O)_2$ is depicted in Figure 1, and selective bond lengths and angles are given in Table 1. The local geometry around the lithium ion approximates to a distorted tetrahedral geometry.

The lithium ion is coordinated to four oxygen atoms: two oxygens from benzoylacetone, and the other two oxygens from water molecules. The average bond distance of Li-O (of bzac), [1.90 Å], is shorter than that Li-O (of water), [1.95 Å]. The O-Li-O angle of the bzac ligand is 97.6(2)° and the corresponding angle of the water molecules is 104.5(2)°. It is interesting to note that the C(2)-C(3) bond distance of 1.391(5) Å is longer than the C(3)-C(4) bond distance of 1.368(5) Å. This means that the C-C bond farther from the phenyl ring is longer than the C-C bond closest to the phenyl ring. Further, it is noteworth to compare the carbonyl bond distances.

The O(1)-C(2) bond distance of 1.296(5) Å is shorter than the O(2)-C(4) bond distance of 1.324(5) Å. Therefore, the short-long pattern of the O(1)-C(2), C(2)-C(3), C(3)-C(4), C(4)-O(2) bond lengths is found for Li complex (Scheme 2). As mentioned, the reverse tendency is, however, observed in the copper compound. In the copper com-

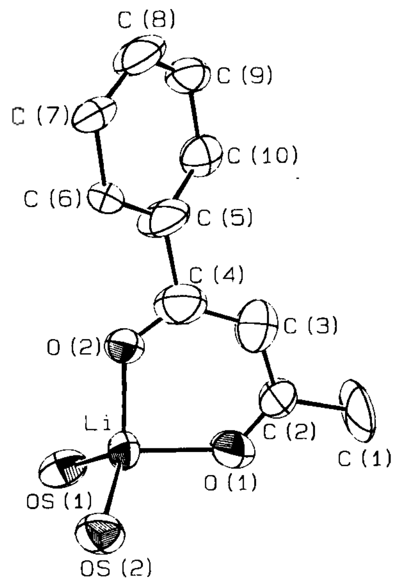


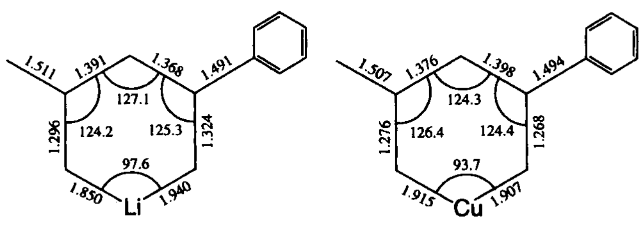
Figure 1. ORTEP drawing of the crystal structure of Li(bzac)$(H_2O)_2$ showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Li(bzac)$(H_2O)_2$

Li(1)-O(1)	1.85(1)	Li(1)-O(2)	1.94(1)
Li(1)-OS(1)	1.96(1)	Li(1)-OS(2)	1.94(1)
O(1)-C(2)	1.296(5)	O(2)-C(4)	1.324(5)
C(1)-C(2)	1.511(6)	C(2)-C(3)	1.391(5)
C(3)-C(4)	1.368(5)	C(4)-C(5)	1.491(5)
O(1)-Li(1)-O(2)	97.6(2)	OS(1)-Li(1)-OS(2)	104.5(2)
Li(1)-O(1)-C(2)	124.9(2)	Li(1)-O(2)-C(4)	120.7(2)
O(1)-C(2)-C(1)	115.3(2)	O(1)-C(2)-C(3)	124.2(2)
O(2)-C(4)-C(3)	125.3(2)	O(2)-C(4)-C(5)	116.3(2)
C(2)-C(3)-C(4)	127.1(2)		

pound, [Cu(bzac)(bipy)(NO_3)], the C-C bond farther from the phenyl ring, 1.376 Å, is shorter than the closest one, 1.398 Å. In addition the C-O bond distance close to the phenyl ring, 1.268 Å, is shorter than the other C-O bond distance, 1.276 Å.

The plane defined by the phenyl ring forms a dihedral angle of 39° with the plane of the β-diketonate and Li atom. The dihedral angle of 39° for the Li(bzac)$(H_2O)_2$ is different from the dihedral angle of 23°found in the crystal structure of the Cu(bzac)(bipy)(NO_3). The C(4)-C(5) distance of 1.491(1) Å suggests that this bond is a single bond and thus no conjugation between the phenyl ring and the plane of the bzac ligand. The O(1)---O(2) distance is 3.09 Å and the



Scheme 2.

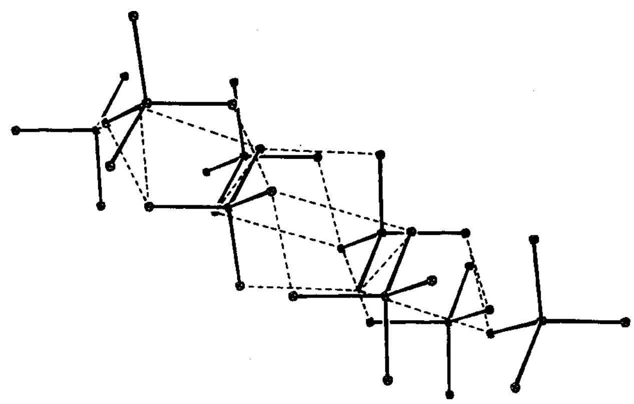


Figure 2. Crystal packing digram of Li(bzac)$(H_2O)_2$ showing the intermolecular hydrogen bonding along the z axis. Only Li and four oxygen atoms are shown for clarity.

closest Li---Li separation in the chain is 3.98 Å. The O(1)---O(2) distances of the intramolecular hydrogen bonded Hacac are in the range of 2.40 and 2.70 Å.[6] This indicates that the lengthening of the O(1)---O(2) distance of Li(bzac)$(H_2O)_2$ results in the widening of both O(1)-C(2)-C(3) and C(3)-C(4)-O(2) angles which are 124.2°and 125.3°, respectively. The structure consists of an extended network by the complicated hydrogen bonding interactions. All four coordinated oxygen atoms have the intermolecular hydrogen bonding interactions. The O(1) atom has two hydrogen bonding interactions and the O(2) atom has one hydrogen bonding interaction. In addition each of two water molecules has three hydrogen bonding interactions. These complicated hydrogen bonding interactions give an extended structure shown Figure 2.[7]

Recently, Umetani group has reported that the distance between the two donating oxygens in β-diketonates affects the acidity of the ligand itself and its ability to separate lanthanides.[10] A semi-emperical MNDO-H calculation[11] shows that the anionic form of the benzoylacetone has the O---O distance of 3.10 Å which is quite consistent with the O---O distance of 3.09 Å of the Li(bzac)$(H_2O)_2$. Further studies are in progress to investigate the relationship betwen the O---O distances of the β-diketonates and the separation of the lanthanide metals.

Acknowledgment. Financial support of Korea Ministry of Education (1997-1998) is gratefully acknowledged. This research was partly supported by Grant for Institute-University Collaborative Project from the Korean Research Institute of Standards and Science.

Supporting Information Available. Experimental details of X-ray crystal structure determination, crystallographic tables, listing of atomic coordinates, thermal parameters, and bond distances and angles.

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5. Crystal data for $[Li(bzac)(H_2O)_2]$; triclinic P1-bar(# 2), a =8.8951(3), b=10.0583(5), c=14.215(2) Å, α=101.80(2), β=92.78(2), γ=116.08(3)°, V=1104(1) $Å^3$. The structure was solved by a heavy atom method and refined to R1= 0.066 and wR2=0.1551 against 2736 observed $[I>2\sigma(I)]$ reflections.
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Preparative Scale Separation of Enantiomers on an MPLC Chiral Column

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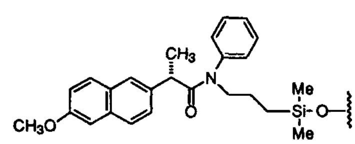
Received January 22, 1998

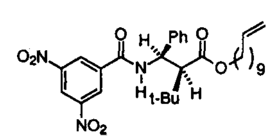
The two enantiomers of chiral drugs often show different pharmacological effects in living systems.[1] Consequently, the individual enantiomers of chiral compounds should be studied for their own pharmacological and toxicological properties during the process of drug development as required by the drug regulatory authorities.[2] In this context, the techniques of separating enantiomers and the analytical means of evaluating enantiomeric purity of chiral compounds are demanded very much. Among others, liquid chromatographic separation of enantiomers on chiral stationary phases (CSPs) have been known as the most convenient means to meet such demands because this technique can be successfully utilized in separating enantiomers and in evaluating enantiomeric purity simultaneously.[3] In addition, the technique of separating enantiomers on liquid chromatographic CSPs is very attractive in that the technique can be easily extended to the preparative scale separation of enantiomers and consequently can be employed as an alternative to preparing pure enantiomers using large chiral column packed with a suitable CSP.[4]

The successful use of liquid chromatographic CSPs for the preparative scale separation of enantiomers mostly depends on their availability in a substantial amount and their chiral recognition ability. Consequently, CSPs which have been employed in the preparative scale separation of enantiomers are limited to those usually derived from readily available chiral compounds such as amino acids,[4a,5] and cellulose derivatives.[6] In this aspect, CSP **1**, which was recently reported to be prepared from inexpensive and readily available (S)-naproxen and to show high enantioselectivity for the enantiomers of racemic compounds containing π-acidic aromatic functional groups,[7] is expected to be successfully utilized in the preparative scale separation of enantiomers.

In this study, we wish to show that an MPLC chiral column packed with CSP **1** is useful to separate enantiomers in a preparative scale (up to 2 g at one run) with an easily assembled and inexpensive MPLC system. In order to extend the use of HPLC CSP **1** to an MPLC system, CSP **1** was prepared by bonding the chiral selector, (S)-naproxen derivative, to large particle size silica gel (230-400 mesh) *via* the procedure described in the previous study.[7] CSP **1** thus prepared was dry packed into an MPLC glass column (2.5 cm ID × 60 cm length) and used for the separa-



CSP **1**



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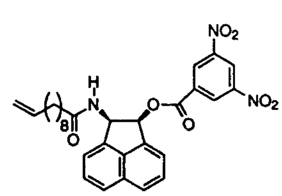

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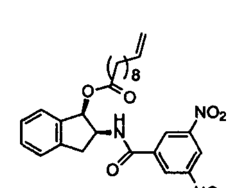

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