

A Reinvestigation of some Alkali Chelates

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Abstract

Alkali metal derivatives of several 1,3-diketones have been synthesized and their infrared and far-infrared spectra recorded. The spectra showed 1) that there is no difference in the bonding between hydrated and anhydrous compounds; and 2) that both the carbonyl and metal-oxygen absorptions are typical of compounds with ionic bonding. It was concluded that any differences in chemical behavior between the hydrated and anhydrous forms must be due to steric or solvent replacement factors.

Introduction

It is generally accepted that alkali metal derivatives of organic compounds behave as simple salts. Thus most salts of alcohols, acids and 1,3-diketones have high melting points, are white powders, are soluble in water and insoluble in organic solvents. There are, however, some organic compounds capable of forming not only the common alkali salts, but also alkali "complexes," which are appreciably soluble in organic solvents and have low melting points. Thus, Sidgwick and Brewer (6) found that sodium benzoylacetate has the properties of a common salt in that it is water soluble, insoluble in nonpolar solvents, and has a high melting point. If recrystallized from 95% ethanol, however, a dihydrated species is formed which is appreciably soluble in benzene and toluene. The authors concluded that therefore the dihydrate is a chelate. Since this first report, other papers (2, 9) also indicate an apparent dual chemical behavior, and subsequent references (1, 7) cite solubility differences as the only criterion for chelation.

Chelation, though etymologically meaning a claw-like structure, is, however, not a mere cage compound, but one in which strong metal bonds are formed to at least two ligand points. Thus the infrared spectrum of the sodium salt of acetylacetone shows weak ligand-metal interactions ($\nu_{C=O} = 1622 \text{ cm}^{-1}$; $\nu_{M-O} = 405 \text{ cm}^{-1}$); whereas the chelate copper acetylacetate does show strong metal-ligand interactions ($\nu_{C=O} = 1577 \text{ cm}^{-1}$, $\nu_{M-O} = 451 \text{ cm}^{-1}$) (4).

In an attempt to shed new light on the chemical behavior of alkali, 1,3-diketones, particularly the postulated hydrated chelates, the infrared and far-infrared spectra of eight such pairs were studied.

Experimental

Preparations

All compounds were prepared according to published procedures (6, 8). The 1,3-diketone was dissolved in NaH-dried acetone and allowed to react with a stoichiometric amount of the metal. The white salts were washed several times under strictly anhydrous conditions

and vacuum dried. Dihydrated species were obtained through recrystallization of the anhydrous compounds from 95% ethanol.

No hydrated complex of sodium salicylaldehyde can be obtained. Instead an adduct between a neutral salicylaldehyde molecule and sodium salicylaldehyde may be prepared by allowing the metal to react in an excess of salicylaldehyde.

Spectra

The infrared spectra were recorded on a Perkin Elmer Infracord spectrophotometer using Nujol mulls between NaCl disks. Far-infrared spectra were obtained on a Perkin Elmer spectrophotometer, Model 621 using a Nujol film between paraffin sheets.

Results

Absorption data for the compounds under investigation as well as those for the parent chelating agents and for copper acetylacetonate appear in Table 1. Spectra for the hydrated and anhydrous compounds were identical except for the absorptions noted in the Table, and the characteristic high frequency absorption due to water in the former. Two carbonyl frequency values appear for acetylacetone in conformity with the tautomeric enol and keto forms. In some cases the metal-oxygen column has two frequency values, reflecting the general uncertainty in assignments and the fact that neither value represents a pure metal-oxygen stretch. Modes in this region are usually coupled with ring deformation and C-CH₃ stretching modes. Metal-oxygen absorption values for the salicylaldehyde pair have been omitted due to assignment uncertainties.

TABLE 1. *Carbonyl and metal-oxygen absorption frequencies.*

Compound	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$
¹ H (acac)	1700, 1610	—
Cu (acac) ₂	1577 (Ref. 4)	451, 612 (Ref. 4)
Na (acac)	1622	405, 525
Na (acac) • 2H ₂ O	1620	410, 525
K (acac)	1630	410, 520
K (acac) • 2H ₂ O	1630	410, 520
² H (bzac)	1610	—
Na (bzac)	1590	425
Na (bzac) • 2H ₂ O	1590	422
K (bzac)	1590	424
K (bzac) • 2H ₂ O	1590	424
³ H (salald)	1650	—
Na (salald)	1650	
Na (salald) • H (salald)	1650	

¹ H (acac) = acetylacetone; ² H (bzac) = benzoylacetone; ³ H (salald) = salicylaldehyde.

Discussion

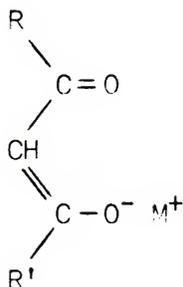
The carbonyl stretch for a strong chelate such as copper acetylacetonate appears at the relatively low value of 1577 cm⁻¹. Such

lowering from the normal C=O stretching frequency of 1700 cm^{-1} is attributed to a drain of electrons away from the C=O group into the M-O bond. The resulting weak C=O force constant causes the observed lower vibrational energy. Similarly, the M-O bond is strengthened by the gain of electrons causing a relatively high stretching frequency. For these reasons copper acetylacetonate is a strong chelate with considerable covalent bonding.

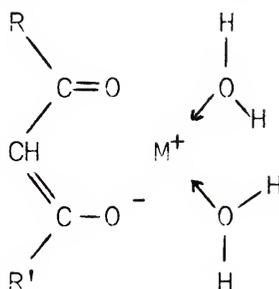
The carbonyl absorption frequency values for the alkali derivatives are relatively high indicating a relatively minor electron drain. Thus, while the absorption frequency for copper acetylacetonate is 1577 cm^{-1} , those for the alkali derivatives of acetylacetonate lie between $1620\text{--}1630\text{ cm}^{-1}$. From the preceding discussion one might thus conclude that the alkali derivatives of acetylacetonate are more ionic in nature than copper acetylacetonate.

No frequency shifts are observed within any of the anhydrous-hydrated pairs under investigation. Thus the C=O stretch for sodium benzoylacetate occurs at 1590 cm^{-1} and its M-O stretch at 425 cm^{-1} , while those of the hydrated analog occur at approximately the same values. Similar comparisons between the other pairs also show no substantial frequency shifts. It is therefore concluded that the differences in chemical behavior between the hydrated and non-hydrated species cannot be due to any differences in metal-ligand bonding.

It is quite obvious from Structure I, that the alkali ion of the anhydrous form is fairly exposed to the solvent system, whereas in the hydrated form, Structure II, the ion is shielded. Since solubility depends on the interaction of solvent molecules with the exposed parts of the solute molecule, it is easy to see that in Structure I the metal ion and its charge will come in rather direct contact with



Structure I



Structure II

the solvent molecule. A non-polar solvent will resist the presence of polarized molecules and prevent solvation. On the other hand, compounds such as represented in Structure II, where the ion and its charge are engulfed by several groups, thus shielding these from the solvent, can experience increased solubility in non-polar solvents. The dissolution process may be envisioned as occurring through re-

placement of the water molecules; through an increased solvent attack on the organic constituent of the salt; or through possible hydrogen bonding between solvent and water molecules. It is not clear whether one or all of these mechanisms are operative, or to what extent they affect solubility, but there is little doubt that solution does not occur due to a different type of M-O bonding in the hydrated species.

There are several recent reports which support the dissolution processes proposed above. For example, the potassium ion in KAuCl_4 may be complexed by valinomycin, thus rendering the salt soluble in organic solvents (5). Similarly, the sodium ion in NaCl has been complexed with an organic "crown of oxygen atoms," thus achieving solubility of the salt in organic solvents (3).

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