

Spectroscopic Investigations of Chelate Complexes with Dicarbonyl Ligands

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Solutions of LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ in diacetyl, acetylacetone and acetylacetonone were studied using IR- and ^1H NMR spectroscopy. The IR spectra gave evidence for complex formation only in the case of acetylacetone. The formation constants were able to be evaluated with the help of ^1H NMR spectroscopy. The NMR spectra also enabled a comparison of the interaction of the various ligands with the ions and a comparison with data obtained from MO-SCF calculations.

Introduction

In addition to the previously published UV [1] and metal NMR spectroscopy [2] experiments this work covers the results of IR and ^1H NMR spectroscopy in order to get a comprehensive survey of the effects which take place during the complexation of alkaline and alkaline earth metal ions with dicarbonyl compounds. IR spectroscopy promised to be a valuable tool in detecting complexation and determining the strength of complexation. With the help of IR spectroscopy it should be possible to ascertain, which chemical bonds were affected by complexation [3–10] and to distinguish between chelate *cis* and *trans* complexes, since the different symmetries of these forms lead to vibrations which have different IR and Raman activities.

Liquid diacetyl for example exists to 100% in the *s-trans* configuration and possesses therefore C_{2h} -symmetry [11]. Because of this symmetry (center of inversion) the exclusion principle is effective and a vibration is therefore either IR active or Raman active. As a consequence there is only one carbonyl vibration visible in the IR spectrum of diacetyl (1715 cm^{-1} $\nu_{\text{as}}\text{C}=\text{O}$) and the other one can be found in the Raman spectrum (1720 cm^{-1} $\nu_{\text{s}}\text{C}=\text{O}$). Upon chelate complex formation a rotation around the C–C axis takes place and the symmetry of diacetyl changes from C_{2h} to C_{2v} and both carbonyl vibrations become IR active. Besides the appearing of new bands as a consequence of changes in the molecular symmetry, a second effect can be expressed in the IR spectra after complexation. The change in the force

constant of the carbonyl bond leads to a shift of the IR band to lower wavenumbers. The extent of this shift is a direct measure of the strength of interaction.

A second very sensitive tool to measure the interaction between central ion and ligand is NMR spectroscopy [12–16]. In [2] we reported the effect of complexation on the central ion using metal NMR spectroscopy. Here we intend to show the influence on the ligand using ^1H NMR spectroscopy. Complexation will lead to a change in the electronic environment of the nuclei and consequently to a change of the chemical shift. If a stable complex is formed and the exchange of the ligands is slow relative to the NMR time scale, new resonance signals are expected. If the exchange is fast, only a time averaged shift of the resonance signal can be seen. The extent of this shift can also be taken as a measure of the interaction.

Experimental

The use of a solvent as in the UV experiments could be avoided by taking very thin spacers respectively using the F.M.I.R. technique (Frustrated Multiple Internal Reflection [17]). Therefore solutions of the perchlorates of Li, Na, Mg and Ca in diacetyl, acetylacetone and hexanedione-2,5 were taken for the IR as well as for the ^1H NMR experiments. The perchlorates were chosen because of their relative high solubility in organic solvents. LiClO_4 (Alfa Ventron) and NaClO_4 (Merck *p.a.*) were dried at 140°C for 48 hours.

$\text{Mg}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ were obtained from the chlorides and perchloric acid. The hydrates were twice recrystallized from water and dried *in vacuo* at 230°C . For the preparation of the solutions the strongly hygroscopic salts were handled in N_2 atmosphere.

The dicarbonyl compounds were twice distilled before use. A cell with AgCl windows and a spacer (0.015 mm) were used to record the spectra of the diacetyl solutions. In the case of acetylacetone and acetylacetonone solutions even this layer was too

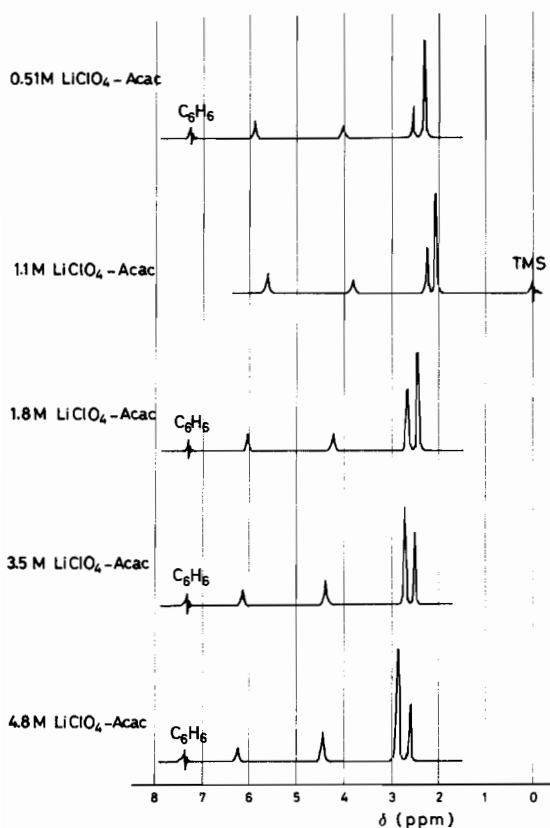


Fig. 1. ^1H NMR Spectra of LiClO_4 -Acetylacetone Solutions.

thick and it was necessary to use the F.M.I.R. technique, which allows extremely thin layers to be recorded.

The IR spectra were recorded by a Perkin Elmer 180 grating infrared spectrophotometer equipped with the F.M.I.R. unit with a Ge single crystal.

The ^1H NMR spectra were recorded in rotating 5 mm NMR tubes using a Varian EM-360 spectrometer. The chemical shift was measured against TMS as internal standard and, when TMS was not soluble enough, against benzene as external standard. Susceptibility corrections have been performed.

Results

IR Spectra

The IR spectra of the diacetyl solutions show only small deviations from the spectrum of the pure ligand. The position of the carbonyl vibration band is shifted slightly to lower wavenumbers upon addition of the salts. But there is no difference between the several cations.

The IR spectrum of liquid acetylacetone shows the presence of two tautomeric forms [18]. At room temperature 80% of acetylacetone exists in the enol form, the more stable one. Upon the addition of the

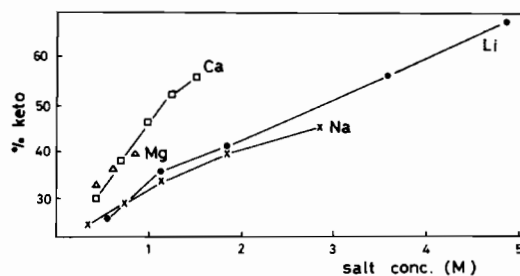


Fig. 2. % keto in dependence of the salt concentration.

salts, significant changes take place in the IR spectra: the broad enol band (1620 cm^{-1}), which dominates the spectrum of the pure ligand, diminishes and the intensity of the two carbonyl vibration bands of the keto form increases. The salts show a strong influence on the keto-enol equilibrium, which can be explained in terms of a complexation of the ions with acetylacetone in its ketoform. This explanation has been confirmed with the help of ^1H NMR studies, which also allowed a quantitative analysis of the data to estimate the complex formation constants.

The observed shifts of the carbonyl vibration bands are of the same magnitude ($1\text{--}5\text{ cm}^{-1}$) for the acetylacetone solutions as well as for the acetylacetone solutions and allow no differentiation between the pure ligand and its complexes with the various cations. The magnitude of these shifts can be compared with those obtained by Minc and Kecki [19], who made similar investigations with solutions of LiClO_4 , NaClO_4 and $\text{Ba}(\text{ClO}_4)_2$ in acetone. We thus can conclude, that — except for the case of acetylacetone, with its very peculiar keto-enol equilibrium — the IR spectra cannot be taken to ascertain the formation of ion-ligand complexes even qualitatively. The reason for this might be a much weaker complex formation of diacetyl and acetylacetone compared to acetylacetone, but also the generally small magnitude of frequency shifts upon complex formation (which is also true for acetylacetone). Hence, the NMR investigations promised to be a more appropriate tool for our investigations, since they also allow a more accurate determination of the keto-enol equilibrium in the case of acetylacetone.

^1H NMR Spectra

^1H NMR spectra of diacetyl solutions

The proton magnetic resonance spectrum of diacetyl shows a singlet at 2.34 ppm relative to TMS. Only solutions of LiClO_4 in diacetyl showed significant changes because of the poor solubility of the other perchlorates. The addition of LiClO_4 produces a shift to lower field (+0.09 ppm in a 0.8 M LiClO_4 solution).

TABLE I. Complex Formation Constants.

	Li	Na	Ca
K_2	$3.7 (M^{-1})$	$0.043 (M^{-1})$	$10^{5.9} (M^{-1})$
K_3	$1.0 (M^{-1})$	$20 (M^{-1})$	$10^{6.2} (M^{-1})$
$K_t = K_2 \cdot K_3$	$3.7 (M^{-2})$	$0.85 (M^{-2})$	$10^{12} (M^{-2})$

¹H NMR spectra of acetylacetonone solutions

The ¹H NMR spectrum of acetylacetonone shows five resonance signals, which are produced by the two tautomeric forms:

The keto form gives rise to two signals:

2.16 ppm resulting from $-\text{CH}_3-$

3.62 ppm resulting from $-\text{CH}_2-$

The enol configuration produces the remaining signals:

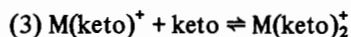
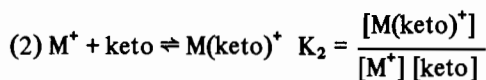
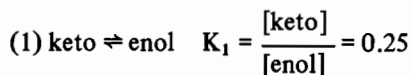
2.03 ppm resulting from $-\text{CH}_3$

5.57 ppm resulting from $=\text{CH}-$

15.53 ppm resulting from $-\text{OH}\cdots$

(all values relative to TMS).

The ratio of concentration of the two forms can be determined very easily by integration. The spectra of the LiClO_4 -acetylacetonone solutions are shown in Fig. 1 as an example. The concentration of the keto form increases continuously with increasing salt concentration, as is shown in Fig. 2. Recording of $\text{Mg}(\text{ClO}_4)_2$ solutions at higher concentrations than those shown in Fig. 2 is not possible because of the precipitation of a solid complex. The isolation of this compound confirmed the assumption that the changes in the IR and ¹H NMR spectra are produced by complex formation [20]. For a qualitative description of the system and evaluation of complex formation constants, one has to assume at least the following three equilibrium reactions:



$$K_3 = \frac{[\text{M}(\text{keto})_2^+]}{[\text{M}(\text{keto})^+][\text{keto}]}$$

The total concentrations $[]_T$ can be expressed as follows:

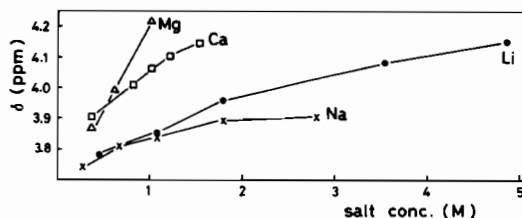
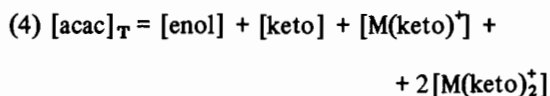


Fig. 3. Chemical shift of the methylene group of acetylacetonone in its perchlorate solutions.

$$(5) [\text{keto}]_T = [\text{keto}] + [\text{M}(\text{keto})^+] + 2[\text{M}(\text{keto})_2^+]$$

$$(6) [\text{M}^+]_T = [\text{M}^+] + [\text{M}(\text{keto})^+] + [\text{M}(\text{keto})_2^+]$$

Equations (2) and (3) substituted in (5) give:

$$(7) [\text{keto}]_T = [\text{keto}](1 + K_2[\text{M}^+](1 + 2[\text{keto}]K_3))$$

and equations (2) and (3) substituted in (6) give:

$$(8) [\text{M}^+] = \frac{[\text{M}^+]}{1 + [\text{keto}]K_2(1 + [\text{keto}]K_3)}$$

The combination of eqns. (8) and (7) leads to:

$$(9) [\text{keto}]_T = [\text{keto}] \left(1 + \frac{K_2[\text{M}^+](1 + 2[\text{keto}]K_3)}{1 + [\text{keto}]K_2(1 + [\text{keto}]K_3)} \right)$$

$[\text{keto}]_T$, and $[\text{M}^+]_T$ are known from the starting conditions of the experiment, $[\text{keto}]$ can be determined from the NMR spectra. Equation (9) was programmed and the values for K_2 and K_3 were evaluated by a least squares procedure. The results are listed in Table I.

Due to the relatively small number of data no accurate constants can be expected, their order of magnitude however can be determined in this way. The formation constant of $\text{Mg}(\text{ClO}_4)_2(\text{acac})_2$ could not be evaluated at all because of the precipitation of a solid compound, but from Fig. 2 it can be estimated to be of the same order as the stability constant for $\text{Ca}(\text{ClO}_4)_2(\text{acac})_2$.

The significant difference between alkaline and alkaline earth ions could also be found in the calculated chelate effect resulting from MO-SCF calculations [1]. In addition, in Fig. 3 the dependency of the chemical shifts of the methylene group of acetylacetonone on the salt concentration is shown. Since the chemical shift depends on the electronic environment of the nucleus, a correlation between the chemical

TABLE II. Specific Chemical Shifts δ_s (ppm/M) and Calculated Changes of the Charge Density δ_q (e^-).

		Acetylacetone	Acetylacetonate
Li	δ_s	0.28	0.105
	δ_q	-0.0547	-0.0448
Na	δ_s	0.26	0.074
	δ_q	-0.0465	-0.0386
Mg	δ_s	0.56	0.150
	δ_q	-0.105	-0.0888
Ca	δ_s	0.44	0.160
	δ_q	-0.094	-0.0733

shift difference and the changes of the electronic density (Mulliken populations evaluated by the MO-SCF calculations [1]) was of some interest. To enable this comparison, a specific chemical shift had to be evaluated by dividing the change of the chemical shift by the complex concentration. The so obtained specific chemical shifts (δ_s) and the changes of the net charges (δ_q) are listed in Table II.

The qualitative correlation between calculated changes in electronic density and observed changes of the chemical shifts seems to be a further proof of the validity of the assumed model compounds of the MO calculations [1] for the description of ion-ligand interactions in the system being investigated here.

¹H NMR spectra of acetylacetonate solutions

The proton resonance spectrum of acetylacetonate shows two sharp singlets at 2.76 ppm ($-\text{CH}_3$) and at 2.22 ppm ($-\text{CH}_2-$) relative to benzene as external standard. The addition of perchlorates leads again to a deshielding of the nuclei and therefore to a shift to lower field. The dependence of the chemical shift upon salt concentration is shown in Fig. 4. The graph shows a nearly linear relationship. Again specific chemical shifts δ_s (ppm/M) have been evaluated and compared with the changes of the charge density (Table II). The correlation is satisfactory again. The much lower values of the specific chemical shifts for acetylacetonate compared to those of acetylacetone give some more evidence that this ligand is much less interacting with the ions than acetylacetone.

Conclusion

Among the ligands being investigated, the tendency to form complexes with IA and IIA metal ions seems to follow the order: acetylacetonate \gg acetylacetonate $>$ diacetyl where IIA metal com-

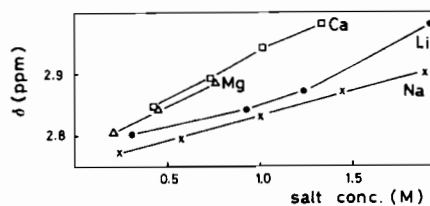


Fig. 4. Chemical shift of the methylene group of acetylacetonate in its perchlorate solutions.

plexes seem to be more stable by several orders of magnitude. Apparently the increased stability of 6-membered rings compared to 5- and 7-membered rings seems to hold also for rings, where one member is represented by an ion in chelate position, although for this ion (especially IA and IIA metal ions) strong 'overlapping' or participating in electronic 'resonance' cannot be stressed as explanation as is done for organic ring compounds. This can be shown easily by the results of the MO calculations [1], which on the other hand did not yet provide another satisfactory explanation for this favor for 6-rings.

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