Proton Magnetic Resonance Studies
of Acetylacetone Metal Salt
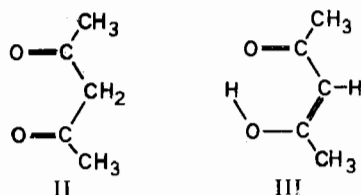
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A new metal perchlorate containing 2,4-pentanedione (AcaH), and having the formula $[Mg(AcaH)_2(H_2O)_2](ClO_4)_2$, *is reported. Proton magnetic resonance studies have been performed, with trideuterionitromethane as solvent. The keto tautomer of acetylacetone appeared to be the dominant species bonded to the magnesium ions. The free and complexed ligands of both tautomers exchange very fast in the NMR timescale, whereas the keto-enol tautomerization is slow in the temperature range of from 0 to 50°C. The behaviour of the metal-ion solvates is compared with that of the protonated acetylacetone tautomers.*

Introduction

Whereas a large number of papers have been published on β-diketonates containing Aca-anions (I):

I
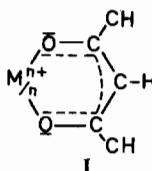
it is only very recently that attention has turned to metal complexes with β-diketones as neutral solvating molecules. In 1968 we reported[1] the complexes with the formulae $Ni(AcaH)_3(ClO_4)_2$ (AcaH = acetylacetone), $Ni(AcaH)_2(H_2O)_2(ClO_4)_2$ and $Ni(AcaH)_2$ (acetic acid)$_2(ClO_4)_2$; an adduct of $CoBr_2$ with one molecule of AcaH was given in a preliminary communication;[2] and Allred and Thompson[3] described several adducts of β-diketones with group-IV-metal tetrahalides (for some earlier work on adducts, see the references cited in their paper). In all these complexes AcaH is thought to occur as the keto (II) rather than the enol tautomer (III).

II   III

(1) P. W. N. M. van Leeuwen, *Rec. Trav. Chim.*, **87**, 396 (1968).
(2) Y. Nakamura and S. Kawaguchi, *Chem. Comm.*, 716 (1968).
(3) A. L. Allred and D. W. Thompson, A. C. S. Annual Meeting, San Francisco, April 1968.

Indications of complex formation between nickel (II) ions and the neutral AcaH keto form in solution have been found by Pearson[4] and co-workers, who have studied the reaction of nickel salts with acetylacetone and a base. That the above mentioned nickel complex $Ni(AcaH)_3(ClO_4)_2$ contains the keto form was indicated by its IR spectra. Similarly, in the case of $Ni(AcaH)_2(H_2O)_2(ClO_4)_2$ the overtone spectrum in the near-infrared region led to the same tentative conclusion. The latter complex was synthesized by reaction of hydrated nickel perchlorate and AcaH, but it can also be prepared by reaction of the acetylacetonate $Ni(Aca)_2(H_2O)_2$ and perchloric acid, which can be regarded as a reaction between a base and an acid. The basic character of acetylacetonates in relation to various solvents has been shown by Davis and Fackler.[5]

Since there are considerable differences between the NMR spectra of the two tautomers, it was thought NMR measurements could usefully be performed on solutions of compounds of this type. Consequently measurements were carried out on the magnesium(II) complex, with trideuterionitromethane being chosen as solvent because of its weak-donor properties.

Experimental Section

Proton magnetic resonance spectra of $Mg(AcaH_2)(H_2O)_2(ClO_4)_2$ were run on Varian DP–60 and HA–100 spectrometers, with tetramethylsilane used as internal standard. The trideuterionitromethane (99%) was supplied by Merck. The acetylacetone was redistilled before use.

$Mg(AcaH)_2(H_2O)_2(ClO_4)_2$ was prepared by mixing $Mg(H_2O)_{2.5}(ClO_4)_2$ (A.R., Merck) with nitromethane (previously dried on Molsieve), after which the calculated amount of AcaH was added. The mixture was heated to boiling (behind a safety screen) till all the solid had disappeared. Upon cooling, the compound $Mg(AcaH)_2(H_2O)_2(ClO_4)_2$ crystallized. Sometimes, however, needles were obtained which were found to be $Mg(H_2O)_6(ClO_4)_2$.

The formula of the former complex is based upon the X-ray powder diagram, the NMR spectrum and the magnesium content (found 5.36, calculated 5.29).

(4) R. G. Pearson (private communication), to be published.
(5) T. S. Davis and J. P. Fackler, *Inorg. Chem.*, **5**, 242 (1966).

Table I. Chemical Shifts of Solutions* of Mg(AcaH)₂(H₂O)₂(ClO₄)₂ and AcaH in CD₃NO₂ at a temperature of 40°C.

Sample	H₂O/Mg	ratios			chemical shifts in ppm				
		total AcaH / Mg	total keto / Mg	total enol / Mg	CH₃–keto	CH₂–keto	CH₃–enol	CH–enol	H₂O
1	2.2	2.0	1.8	0.2	2.48	4.34	2.16	5.76	5.0
2	**	6.0	3.6	2.4	2.35	4.03	2.09	5.69	**
3	»	9.8	5.3	4.5	2.29	3.89	2.05	5.67	(15)
4	»	12.0	6.0	6.0	2.23	3.82	2.03	5.66	(15)
5	»	15.0	7.2	7.8	2.24	3.82	2.04	5.66	15

* [Mg²⁺]=0.1 mole.l⁻¹. ** The water signal at 5 ppm broadens upon addition of enol, due to exchange reaction (6). The signal ultimately disappears, whereupon the collapsed signal at ≈ 15 ppm is observed. At lower temperatures the enol–OH and water signals split again.

The compound is powder-isomorphous with the corresponding nickel perchlorate. The single-crystal pictures, however, show differences. The mull infrared spectrum shows the presence of carbonyl groups, hydroxyl groups, methyl groups, and the perchlorate anion. The compound is very hygroscopic.

Mg(H₂O)₂(AcaH)₂(ClO₄)₂ is only slightly soluble in trideuterionitromethane and solutions of 0.1 mole . l⁻¹ were obtained after heating to 60°C. The spectra at room temperature were taken on subcooled solutions. Further reduction of the temperature was impossible because this was immediately followed by crystallization. The solubility could be increased, however, by the addition of AcaH.

Results

Solution of the pure compound. A solution of the pure compound Mg(AcaH)₂(H₂O)₂(ClO₄)₂ in CD₃NO₂ gives three strong signals at 2.48 ppm, 4.3 ppm, and 4.95 ppm downfield from tetramethylsilane. The spectrum is shown in Figure 1 (a) and the chemical shifts are given in Table I, (sample 1). The intensities are in the ratio 6:3:2. Unfortunately, the signal at 4.3 coincides with a small solvent quintiplet of CD₂HNO₂ at 4.35. After correction for this the ratio is between 6:1:2 and 6:2:2. Clearly the high-field signal must be assigned to methyl groups and the low-field signal to water. The latter asignment can be proved by the addition of small amounts of water, as a result of which the intensity of the 4.95 signal increases. If a sufficient amount of water is added, the hydrate Mg(H₂O)₆(ClO₄)₂ crystallizes and the usual spectra of the free keto and enol tautomers are observed with intensities in the ratio 2:3.

The assignment of the peak at 4.3 ppm, however, is problematic. On the basis of the spectrum obtained it is impossible to decide whether it is the keto or the enol form that is present in the complex. Besides giving rise to an olefinic C–H peak between 4 and 6 ppm the presence of the enol tautomer should also give rise to a signal at 15 ppm downfield, due to the alcoholic proton, but this is not found. However, this signal is usually very broad and it may have been too weak to be observed in the dilute solution. In order to solve the tautomer .problem and to assign the 4.3 absorption, therefore, spectra were also taken of the complex in solutions with an excess of acetylacetone.
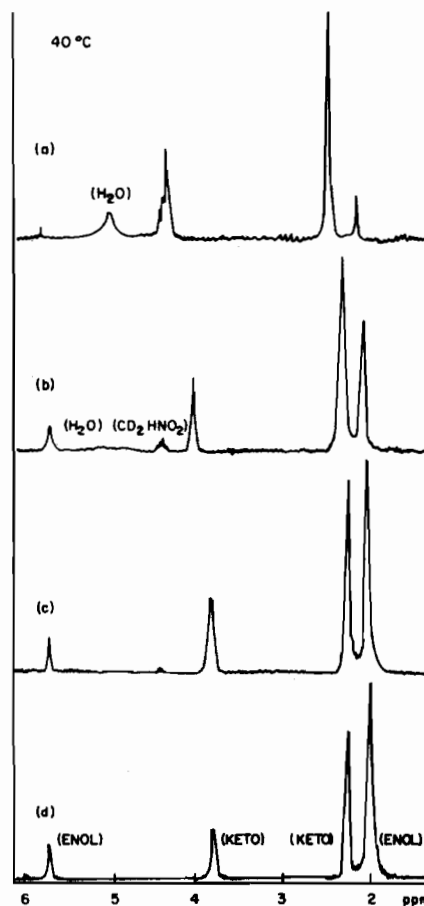

Figure 1. Proton magnetic resonance spectra of Mg(AcaH)₂-(H₂O)₂(ClO₄)₂ in CD₃NO₂ with and without excess AcaH. (a) Mg:AcaH=1:2 (Sample 1, Table I; no extra AcaH); (b) Mg:AcaH=1:6 (Sample 2, Table I); (c) Mg:AcaH= 1:15 (Sample 5, Table I); (d) pure AcaH.

Solutions with an excess of acetylacetone. In the NMR spectrum of pure acetylacetone dissolved in trideuterionitromethane both the keto and the enol tautomers are observed (Figure 1 (d), the ratio of keto to enol being about 2:3. The keto form absorbs at 2.2 (CH₃) and at 3.8 ppm (CH₂) from tetramethylsilane, while the enol absorptions are found at 2.0 (CH₃) and 5.6 ppm (CH), with a broad signal at 15 ppm (OH).

A solution of the complex Mg(AcaH)₂(H₂O)₂(ClO₄)₂ and AcaH in trideuterionitromethane with an AcaH/

Mg ratio of 15 leads to a spectrum which is very similar to that of the solution of the free ligand AcaH, except for the keto/enol ratio. The spectrum is shown in Figure 1 (c) and the chemical shifts are given in Table I (sample 5). It will be seen that in this sample with magnesium perchlorate the amount of keto tautomer is proportionally slightly higher, and when the extra amount of AcaH added to a solution of $Mg(AcaH)_2(H_2O)_2(ClO_4)_2$ is decreased (see Figure 1 (b)), we observe a steady increase of the keto/enol ratio. The chemical shifts and tautomer/Mg ratios for a number of different mixtures are given in Table I.

The table and figure clearly show that the 4.3 absorptio nin Figure 1 (a) must be assigned to the keto form. Furthermore we observe in Figure 1 (a) very small absorption peaks due to the enol form (at 2.16 an 5.76 ppm).

Discussion

As the two tautomers are observed separately, it may be concluded that in solutions with an excess of acetylacetone the keto-enol tautomerism is low in the NMR line-broadening time-scale. This is not surprising, since also in mixtures with perchloric acid and water the tautomerism is in the slow-exchange region between 0 and 60°C. Thus:

$$keto \rightleftarrows enol \qquad (slow) \qquad (1)$$
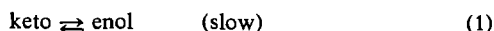
Furthermore the fact that the chemical shifts of the AcaH tautomers change when the AcaH/Mg ratio is varied, indicates that some kind of complex formation occurs. Roughly speaking, we have four forms in which the AcaH molecules can occur, namely the keto-form bonded to magnesium(II), the free keto-form, and the same two possibilities for the enol-form. (Other forms resulting from presumably weaker interactions such as enol-anion, keto-water, enol- water, and interactions and differences in cation coordination may be ignored here). Yet in spite of the wide range of possibilities, we still only observe one set of absorption peaks that can be assigned to the keto tautomer, and likewise for the enol tautomer. This means that the exchange reaction (5) (or dissociation reaction (2)) between the free and bonded forms of the complex is fast within the NMR timescale. Thus we have the following fast reactions:

$$(keto)(Mg) \rightleftarrows keto + (Mg) \qquad (2)$$

$$(enol)(Mg) \rightleftarrows enol + (Mg) \qquad (3)$$

$$(H_2O)(Mg) \rightleftarrows H_2O + (Mg) \qquad (4)$$

The « free » compounds appear without parentheses. In addition we have the exchange reaction:

$$keto^* + (keto)(Mg) \longrightarrow keto + (keto^*)(Mg) \qquad (5)$$
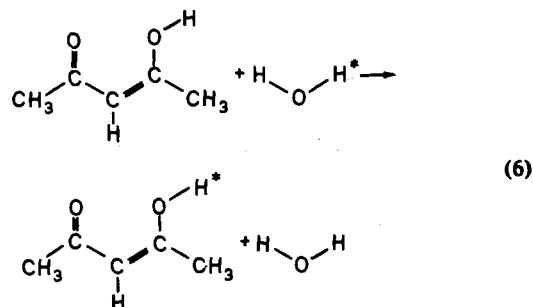
and many more combinations with other molecules or ions.

On the basis of experience during the synthesis of this compound it is concluded that the equili-brium (4) must lie far over to the left and it is in fact assumed throughout the paper that the unit $Mg(H_2O)_2^{2+}$ remains unaffected.

For the sake of completeness we should also mention the exchange reaction:

(6)

which explains the behaviour of the absorption due to water (see note to Table I).

The last point to be discussed is the meaning of the chemical shifts found for the solution of the compound $Mg(H_2O)_2(AcaH)_2(ClO_4)_2$. The question is whether the chemical shifts for sample 1 in Table I are indeed the ones for AcaH bonded to divalent magnesium or whether dissociation appreciably distorts the picture. As outlined above, the keto form (II) dominates in this solution. Now, if it is assumed that the free ligand (originating from dissociation) occurs in a keto/enol ratio of 2/3, it may be concluded that the amount of free keto must be very small. About 10% occurs in the enol form in sample 1. Sometimes less enol is found in freshly prepared solutions. It should be noted, however, that not all the enol observed necessarily occurs as free ligand, since the NMR absorptions show a marked shift. This leads to even smaller free keto quantities, and it is therefore concluded that about 5% of the keto tautomer is present as free ligand and that this is mainly due to traces of water (see Table I, sample 1). This means that the chemical shifts attributed to the keto tautomer bonded to magnesium(II) as given in Table I are indeed significant. The presence of 5% free keto causes a shift of only 0.015 ppm of the collapsed signals of free and bonded keto AcaH. From the fast-exchange behaviour of sample 2 it can be deduced that the exchange rate constant is higher than 10^{-3} s^{-1}.l.mole^{-1} at 40°C.

The assumption that the free ligand occurs in the tautomer ratio 2/3 is supported by a rough calculation of average chemical shifts.
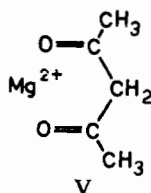
Concluding remarks. On comparing the diprotonated AcaH (IV)[7]

IV
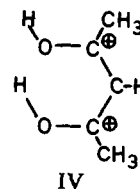
(6) T. R. Stengle and C. H. Langford, *Coordin. Chem. Rev.*, 2, 349 (1967).
(7) D. M. Brouwer, *Rec. Trav. Chim.*, 87, 225 (1968).

with the keto-AcaH bonded to Mg^{2+} (V)

we see a marked difference in the influence of protons and magnesium ions on the chemical shifts. For the complexes IV and V the methyl resonances are found at 3.41 and 5.47, respectively, and the methylene resonances at 2.48 and 4.34, respectively. We tentatively conclude therefore that protonation on the oxygen causes a higher positive charge on the carbon atom than coordination with a magnesium ion does. However, metal ions with the same coordination number, a smaller radius and a higher charge, such as aluminium(III) and chromium(III), may be expected to have a more pronounced effect.

The positive charge induced on the ligand by magnesium(II) may be closely associated with catalysis of the tautomerism. Unfortunately the effect of the catalysis on the line-broadening is too small at 60°C and the catalysis also increases with time, indicating decomposition of the complex. Furthermore, a compound containing water is not suitable for studies of this nature, since it has been observed that addition of the hydrated magnesium perchlorate caused a small increase in the tautomerism rate, with the result that we cannot distinguish between a direct influence of the magnesium(II) ions and the hydrated ions. On the basis of the chemical shifts of IV and V it is concluded that protonation is more effective, particularly as the proton attacking a keto-oxygen maintains its position when the enol form is obtained, whereas a magnesium(II) ion has to be replaced by a proton to give the enol form after dissociation of one of the methylene protons.

The above considerations bring us to the general problem of acid-catalysis by metal salts. The chemical shifts suggest that protonation of oxygen-containing compounds is more effective in producing positive charges on the organic moiety than complex formation with magnesium(II). The interaction of less polar organic molecules (such as alkenes) with metal salts (containing e.g. Li^+, Be^{2+}, Mg^{2+}, Al^{3+}, B^{3+}) is much weaker than the interaction of these Lewis acids with oxygen-containing organic molecules. Evidently, the acidic activity of the metal salts is brought about by Brönstedt acids formed with water. Only in the case of polar organic groups and strong Lewis acids can the direct interaction be an important factor in catalysis.