

Metal NMR Investigations on the Binding of Dicarbonyl-Ligands to Alkali and Alkaline Earth Ions

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Li, Na, K, Mg and Ca nuclear magnetic resonance measurements have been employed for the study of the interaction of these ions with the compounds $CH_3CO(CH_2)_nCOCH_3$, n being 0, 1 or 2 (diacetyl, acetylacetone, acetonylacetone). Changes in the chemical shifts of all nuclei except Mg are induced by this interaction, allowing some conclusions on the ion specificity of the ligands. Some empirical relations between the shifts and ab initio calculations on 1:1 model compounds are being discussed.

Introduction

Most of the NMR investigations on metal–ligand interactions have been carried out with respect to the metal influence on the ligand so far and comparatively few on the influence of ligand molecules on the metal. This fact was mainly due to the lack of adequate experiments, and the situation changed immediately after the rapid development of FT-NMR techniques allowing NMR studies of nuclei less suited for this technique than hydrogen. Still, due to the small sensitivity of many of the metal nuclei and the low natural abundance of their suitable isotopes, studies involving the magnetic resonance of these nuclei are quite rare. Some of them, however, have been employed widely in the study of metal–ligand interactions, as e.g. 7Li and ^{23}Na [1, 2]. The nuclei ^{39}K , ^{25}Mg and ^{43}Ca have a much lower receptivity (0.047%, 0.027% and 0.00093% compared to $^1H = 100%$) and only a few studies have made use of them up to now [3–5].

The main purpose of the work presented here was, to obtain data concerning the influence of a homologous series of chelating ligands on alkali and alkaline earth metal ions. We therefore performed metal NMR measurements on all of the above mentioned nuclei in aqueous solution of the metal chlorides containing a constant concentration of the ligands diacetyl, acetylacetone and acetonylacetone (2,5-hexanedione). These ligands can interact with the cation by two carbonyl groups and differ only

in the number of methylene groups separating these coordinative centers and thus by the ring size on chelate complex formation. Theoretical calculations on such model complexes and UV/VIS. spectra have already been performed [6] and were expected to be helpful in the interpretation of the NMR results. A previous study of the influence of various substituted amide ligands on metal ions [7] had shown the usefulness of metal NMR studies to evaluate ligand effects within series of similar ligands. In the case of the dicarbonyl compounds one could expect, therefore, results giving some interesting indications also to the ion specificity of the ligands and to the influence of the $-CH_2-$ groups inserted in the ligand molecule on the electronic structure of the complex and hence on the binding of the metal ion.

Experimental

The reagent grade salts ($LiCl$, $NaCl$, KCl , $MgCl_2$ and $CaCl_2$) have been used to prepare 1.0 *M* solutions, containing 0.02 mole of the twice distilled ligand. The measurements were performed in 10 mm spinning sample tubes, with an external standard placed in a coaxially centered 5 mm NMR tube. In the case of Li and Na , 3 *M* aqueous solutions of the chlorides were used as external standards, in the case of K , Mg and Ca 3 *M* aqueous solutions of their iodides were taken.

All spectra have been recorded at a Bruker WP 80 NMR spectrometer using the frequencies 31.093, 21.164, 3.733, 4.896 and 5.387 MHz for Li , Na , K , Mg and Ca respectively. Up to 100000 scans had to be accumulated (in the case of Ca) to obtain a good signal/noise ratio.

The observed chemical shifts were corrected for the bulk diamagnetic susceptibility.

Results and Discussion

Only one peak can be observed in all solutions, apparently due to rapid ligand exchange. This also

TABLE I. Susceptibility Corrected Metal NMR Shifts (for standards see text) in Hz.

Ion	Diacetyl	Acetylacetone	Acetylacetonone
Li	126	114	115
Na	64.3	62.4	52.4
K	45.1	46.3	50.1
Mg	0	0	0
Ca	-67.2	-70.9	-69.3

indicates that no extremely stable complex is formed with the various ligands and that the affinity of water to the ions should be of the same order of magnitude as that of the dicarbonyl ligands. The interaction with the diketones, however, causes a change in the chemical shift of all metal nuclei except Mg.

Several attempts have been made up to now to correlate metal NMR shifts with various properties of ligands (mainly solvents), but this has been successful in only a few cases, especially for Na [8], or if the ligands were very similar in chemical structure [7]. Since the components contributing to the chemical shift of metal nuclei are quite complex and theoretically not well known, also a comparison with quantum theoretical calculations was and is restricted to more or less empirical correlations between shifts and calculated quantities (*e.g.* ref. 7). It is to be expected, that the contributions to the chemical shifts depend also quite strongly on the ion, even within a series like the alkaline earth metal ions, where Be and Ca show a remarkable shift sensitivity to solvent and counterion, whereas in the case of Mg such effects could not be observed in previous studies too [8]. This makes a comparison of shifts of different metal nuclei also quite problematic.

The susceptibility corrected shifts are listed in Table I. Comparing the values for the shifts of Li, Na and K, the decrease of the ligand influence with increasing atomic number is evident. The interaction energies decrease in the same order from Li to K [9], but the shift of Ca cannot be included into this consideration, since a different standard had to be used.

For reasons mentioned above (mainly the shift composition), the observed shifts of the different nuclei can hardly be compared directly. It rather seemed to be reasonable to compare the effect of ligand variation (*i.e.* insertion of one or two methylene groups) on the shifts of the various ions (Table II). As a first step of correlation to quantum chemically calculated quantities, these effects are also compared with the calculated change in total electron

TABLE II. Shift Differences upon Methylene Group Insertion into the Ligand (relative to diacetyl) and *ab initio* Calculated Changes in Electron Population at the Metal (shifts in Hz, densities in elementary units).^a

Ion	Δs (upon insertion of $-\text{CH}_2-$ (I) and $-(\text{CH}_2)_2$ (II))		Δq	
	I	II	I	II
Li	-12.5	-11.5	-0.00587	-0.00619
Na	-1.9	-1.9	-0.04790	-0.04510
K	+1.2	+5.0	-0.01040	-0.00480
Mg	0.0	0.0	-0.19060	-0.18880
Ca	-3.7	-2.1	-0.03320	-0.02440

^aPositive sign denote Upfield shifts.

density (Mulliken population) of the metal ions in their 1:1 complexes upon variation of the ligand [9]. These density differences are also listed in Table II.

Regarding the shift differences the most remarkable result seems to be the deviating behaviour of potassium, whose shielding increases with the number of inserted methylene groups, whereas for the other ions a low frequency shift is observed. A somewhat similar situation is observed in the UV/VIS. spectra where for K a hypsochromic shift on the $n-\pi^*$ band of acetylacetonone is found, whereas the other ions induce all bathochromic shifts [9]. Also *ab initio* calculations of the chelate effect indicate for K a stronger stabilization in the diacetyl complex than in the acetylacetonone complex, whereas all other ions show a bigger chelate effect for the latter ligand [7]. An interpretation based on the assumption, that the shifts are determined strongly by the ion specificity of the ligand and the strength of interaction seems to be one of the possible explanations.

Regarding the electron density at the ion (which is surely only one of the components influencing the metal NMR shift), no direct relation can be established at the first glance. It is obvious, however, that the expected increase of the density difference from Li over Na to K is not found, but that there is a reversal of the trend after Na, which might be related to the different shift direction of K. This assumption agrees also with the observation of a stronger high frequency shift for K/acetylacetonone, where the density decrease is smaller than with acetylacetonone. For Ca the same trend is observed, but in this case the smaller density decrease just induces a smaller low frequency shift. The very similar density differences for acetylacetonone and acetylacetonone in the case of Li and Na correspond to the very similar shift differences observed for these ions.

No explanation can be given so far for the relation between the absolute magnitude of the shift differences and the magnitude of the density differences. Also the question, why Mg does not show any shift differences despite the remarkable density differences resulting from the calculations, remains still completely unsolved and will have to be examined further by a much more exact analysis of the chemical shift of metal nuclei.

The results of this work seem to indicate, that the metal NMR chemical shifts can be regarded to some extent as a semiquantitative measure of the strength of the ion–ligand interaction, at least within series of homologous ligands. Further, they show once more, that some correlations can be established between electron populations at the metal and its NMR shift, but that the factors determining this chemical shift should be of quite different nature and/or importance even within metals of the same valence electron configuration.

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