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# $^1$H-n.m.r. Studies on the Complex Formation of *N*,*N*-dimethylbiuret with Alkali and Alkaline Earth Salts

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$^1$H-n.m.r. spectra of *N*,*N*-dimethylbiuret in *DMSO* containing LiI, LiCl, NaI, KI, RbI, CsI, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ and $BaI_2$ have been investigated. The observed shifts of the NH-signal are relatively stronger than the shifts of the $NH_2$-signals. At high salt concentration, coalescence of the $NH_2$-signals and anion effects are observed.

*(Keywords: Biuret complexes;* $^1$H-*NMR; Salt effect, nmr of amides)*

## $^1$H-*NMR Untersuchungen zur Komplexbildung von N,N-Dimethylbiuret mit Alkali- und Erdalkalisalzen*

Protonenkernresonanzspektren von *N*,*N*-Dimethylbiuret in *DMSO*-Lösungen mit LiI, LiCl, NaI, KI, RbI, CsI, $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$ und $BaI_2$ wurden aufgenommen. Die beobachteten Verschiebungen des NH-Signals sind stärker als die der $NH_2$-Signale. Bei höheren Salzkonzentrationen wird Koaleszenz der $NH_2$-Signale und das Auftreten von Anioneffekten beobachtet.

## Introduction

In a previous paper, the tendency of complex formation between biuret and main group metal salts has been reported[1,2]. Equilibrium constants have been estimated from $^1$H-n.m.r. data and compared with the stabilization energies obtained from SCF-MO calculations. Recently, *N*,*N*-substituted biuret was considered as a model substance containing asymmetric amido groups in the same molecule[3,4].

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Within this context, more information about the complex formation of this ligand is needed. $^1$H-n.m.r. investigations were considered to be a useful method for this purpose[5–7].

## Experimental

Commercially available anhydrous salts (Fluka, Merck, Alfa-Ventron) were used without further purification. *N,N*-dimethylbiuret (*DMB*) was prepared according to Lit.[8,9] and anhydrous *DMSO* was used as a solvent. The optimal *DMB* concentration was found to be 0.5 mol · $l^{-1}$ and kept constant throughout this investigation[4]. The salt concentrations were varied until saturation. All samples were prepared under dry nitrogen atmosphere.

$^1$H-n.m.r. spectra were obtained, using a Varian EM 360 spectrometer at constant temperature. The chemical shifts were measured with respect to *TMS* as internal standard.

## Results and Discussion

Changes in the shielding of all *DMB* protons could be expected due to the complex formation of salts. In the case of rapid exchange between metal bonded and free ligand molecules, each proton will give only one average signal and its chemical shift will depend on the effect of the cations and anions. In our case, the $CH_3$-signals showed only a minor shift, whereas the NH-signal showed a remarkable shift and, to a lesser extent, also the $NH_2$-signals. The NH chemical shift as a function of metal ion to ligand ratio is shown in Fig. 1. For monovalent metal iodide, a linear dependence of the shift to higher magnetic field has been found (Fig. 1 *a*). In analogy to the metal chloride biuret system[2], shifts to lower magnetic field approaching a "saturation" value (Fig. 1 *b*) are observed due to the interaction with divalent metal chloride.

It is evident that the interaction of divalent metal salts with *DMB* is stronger than that of monovalent salts. The specific interactions of the cations can be demonstrated by the specific molar chemical shifts (cf. Table 1). The results can be explained in a similar way as in the biuret case[2], with respect to the complex stability of each system. For monovalent ions, larger shifts are observed as the cation radius increases (except in the case of cesium), whereas divalent ions show a rather ion specific interaction, which does not follow the ion radii. Magnesium ion shows the strongest shift. This shift rapidly decreases for calcium ion, but slightly increases again for strontium ion. A similar trend had been found also for the stability of analogous biuret complexes[2]. The weak interaction of barium ion is also in agreement with the low stability of its analogous biuret complex.

Generally, magnitude and direction of the chemical shift depend on various factors. At low salt concentration, the contributions from cation influence can be considered to represent the dominating factor.

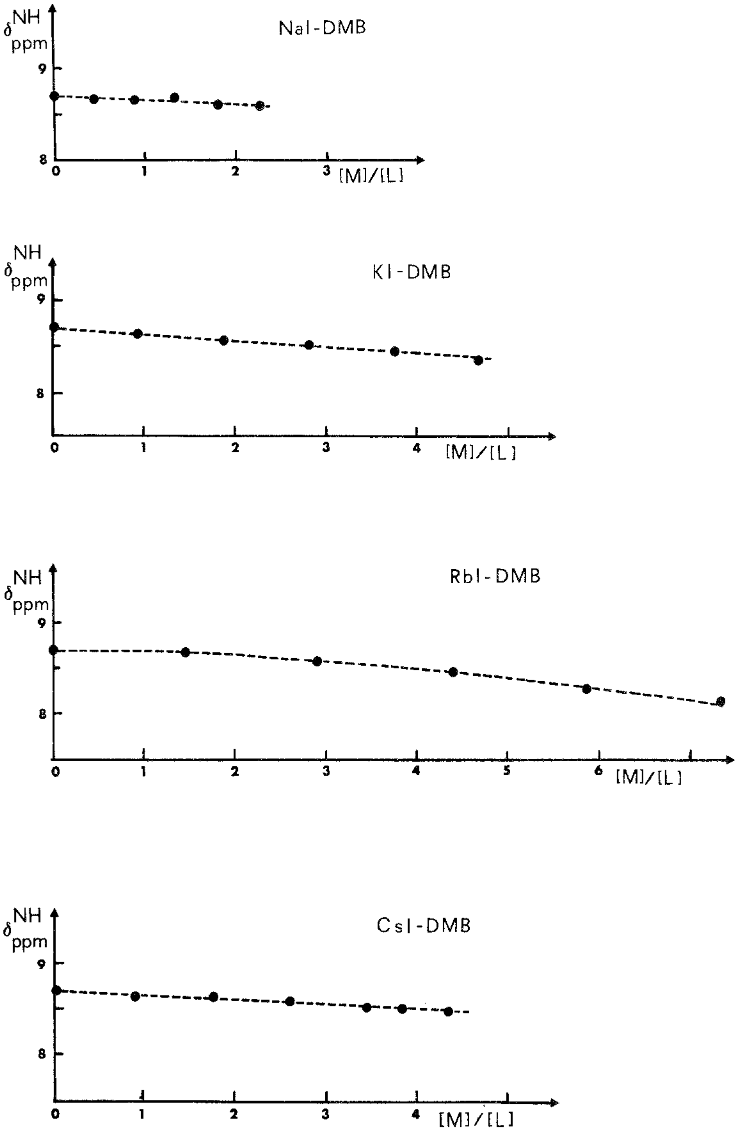


Fig. 1 a. Chemical shifts of the NH-signal as a function of monovalent metal ion to ligand ratio

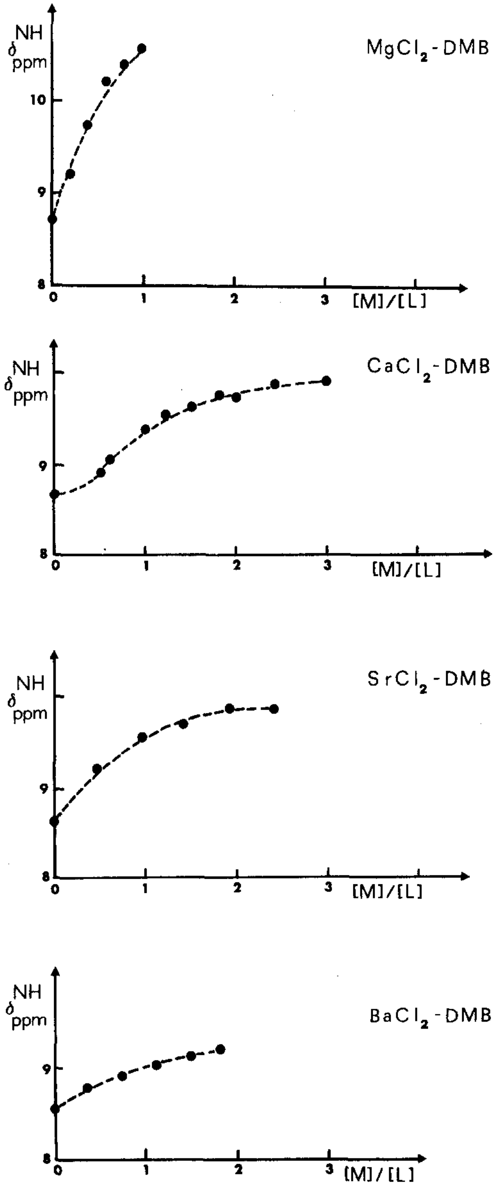


Fig. 1 b. Chemical shifts of the NH-signal as a function of divalent metal ion t ligand ratio

Table 1. *Specific molar chemical shifts of NH-signal due to complex formation:* $\delta_{spec} = (\delta_{MDMB} - \delta_{DMB})/C_m$

| $MX_n$ | $\delta_{spec}$ (ppm mol$^{-1}$) | $MX_n$ | $\delta_{spec}$ (ppm mol$^{-1}$) |
|---|---|---|---|
| LiI | +0.108 | LiCl | −1.15 |
| NaI | +0.115 | $MgCl_2$ | −6.20 |
| KI | +0.137 | $CaCl_2$ | −2.05 |
| RbI | +0.155 | $SrCl_2$ | −3.15 |
| CsI | +0.092 | $BaCl_2$ | −0.95 |
| $BaI_2$ | +0.099 | | |

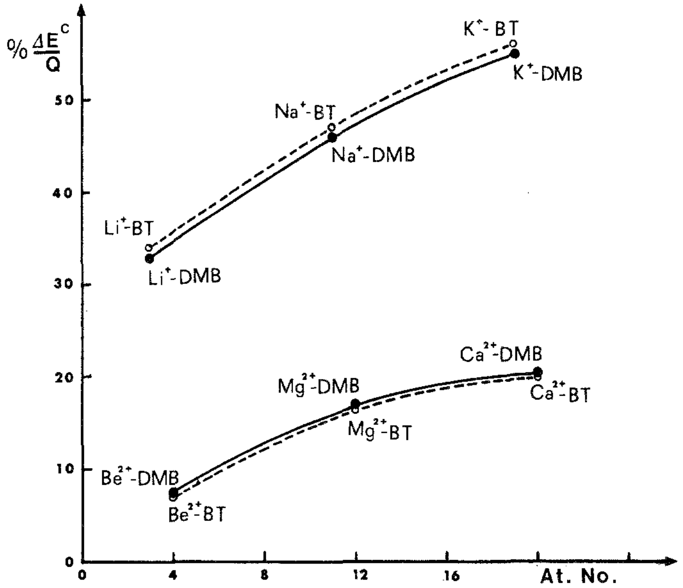


Fig. 2. Calculated SCF-stabilization energies of the 1:1 *DMB* complexes (solid line) and the 1:1 biuret complexes (broken line) as a function of atomic number

This influence can be interpreted also using the results of the MO-SCF calculations of the 1:1 complexes[4]. The different way of complex formation found for alkali and alkaline earth ions is clearly demonstrated in Fig. 2. The tendency to form chelate complexes is appearently higher for divalent ions, but not so evident for monovalent ions. It is reasonable to assume that the stronger effect of divalent ions on the NH-shift occurs due to the chelate ring formation, but this cannot explain yet the different direction of the shifts.

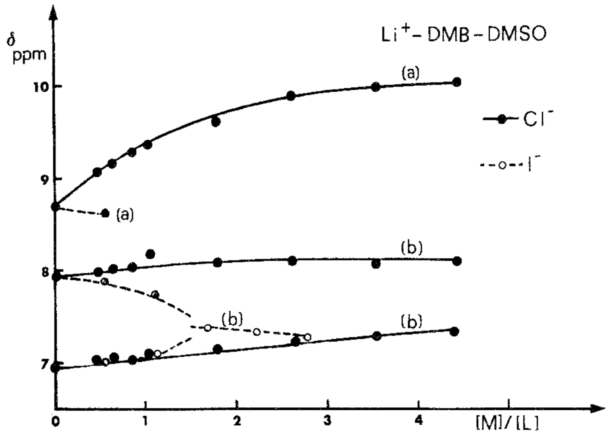
Thus, the influence of the anions should be taken into consideration, too. At high salt concentration, this effect is expected to dominate, expecially concerning the shape of the $NH_2$-signals (cf. Fig. 3). Coalescence of $NH_2$-signals is observed for iodide salts, but decreasing line widths of NH- and $NH_2$-signals without coalescence are found in the case of chlorides.

The different influence of iodide and chloride ions can be explained considering the differences in size and polarizability, and the possibility to form H-bonds to the ligand's hydrogen atoms. According to the most stable *cis-DMB* geometry[3,4], iodide ion can interact simultaneously with NH- and $NH_2$-protons due to its size. This should lead to a gain of electron density at the protons, compensating the influence of the cations. Thus, a small chemical shift to higher magnetic field would result in the case of monovalent iodide salts and, to a lesser extent, for $BaI_2$. On the other hand, the relatively short optimal distance to the protons in the case of $Cl^-$ bonded to $—NH_2$ and the more rigid character of this H-bond does not allow a simultaneous interaction with the NH-proton. Therefore, the influence on the shift of the NH-signals should be determined in this case mainly by the cations. The possibility of the typical H-bond formation of chloride to the amido protons[10–12] seems to act also as an additional factor on the shift to lower field of the $NH_2$-signals.

The coalescence of the $NH_2$-signals at higher $I^-$ concentration also supports the assumption of a rather widespread interaction of this anion with all NH-protons of the ligand and the assumption, that $I^-$, in contrast to $Cl^-$, acts rather as an electron donor for these protons, due to its size and polarizability (i.e. its "soft character"[13] compared to $Cl^-$).

The cation induced specific chemical shifts, regarding to the tendency of complex formation, can be compared with the previous results, i.e. the calculated stabilization energies and the changes of the rotational barriers[4], by assuming anions and other effects as a constant factor. In this sense, the specific chemical shifts of the considered cations give the following series, for monovalent ions: $Cs > Li > Na > K > Rb$, and for divalent ions: $Mg > Sr > Ca > Ba$.

These series show a good agreement with the calculated stabilization energies of the 1:1 complexes ($Li > Na > K$ and $Be > Mg > Ca$). For the ion induced changes of rotational barriers, the experimentally obtained order was $Na > Rb > Cs > K$ and $Mg > Ba > Ca > Sr$. From these data, we can conclude, therefore, that the specific chemical shift is a measure for the complex stability, but that the observed changes in rotational barriers result from several influences among which stabilization is surely an important but not dominating factor.



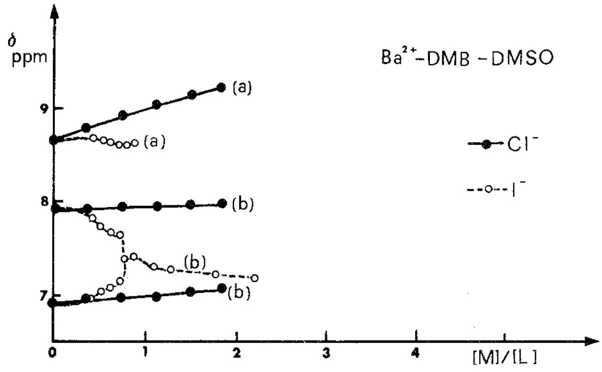


Fig. 3. The influence of anions on the chemical shifts of *a* NH-signal and *b* $NH_2$-signals

As for the large cations as $Cs^+$, there might exist the possibility of simultaneous interaction with two coordination centers, leading to other complex conformations and thus to a stronger influence on the chemical shift.

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