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Hydrogen bonding in hexamminemetal(II) bromides $[M(NH_3)_6]Br_2$ ($M^{2+} = Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}$)–synergetic effect of M^{2+} ☆

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Abstract

IR spectra of isotypic hexamminemetal(II) bromide salts $[M(NH_3)_6]Br_2$ (K_2PtCl_6-type structure for $M^{2+} = Ca^{2+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}; tetragonal structure related to the K_2PtCl_6-type structure for $M^{2+} = Cu^{2+}$) and of isotopically dilute samples (5% deuterated) have been recorded in the range 400–4000 cm^{-1} with regard to the influence of M^{2+} on the strength of $N–H \cdots X^-$ hydrogen bonds. This so-called synergetic effect does not correlate simply with either the ionic radii or electron configuration of M^{2+}, but must be caused by a superposition of electronic and ionic radii effects. Arranging the metal ions with decreasing strength of their synergetic effect leads to the following series: $Cu^{2+} \gg Co^{2+} > Mn^{2+} > Fe^{2+} > Ni^{2+} = Cd^{2+} > Ca^{2+}$.

1. Introduction

Hydrogen bonding of water molecules in solid hydrates has been studied by several authors in the last decade (see, for example, the review by Lutz [1]). The strength of $O–H \cdots X^-$ hydrogen bonds is influenced by different superposing parameters, such as the acceptor strength of the anions. In addition to this, adjacent metal ions lead to a frequency downshift of the stretching modes of H_2O because the intramolecular O–H bond is weakened. This so-called synergetic effect [1] causes a higher acidity of the protons and so the strength of the hydrogen bonds increases.

In spite of intensive investigations of $O–H \cdots X^-$ hydrogen bonds of water molecules in solid hydrates, $N–H \cdots X^-$ hydrogen bonds in solid ammoniates are scarcely discussed [2–4]. Of all the possible influences on the bond strength, only the different acceptor strengths of anions in hexamminenickel (II) salts have been investigated [5]. This paper deals with the synergetic effect in hexamminemetal(II) bromides $[M(NH_3)_6]Br_2$ ($M^{2+} = Ca^{2+}$, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}). The isotypism of the hexamminemetal(II) bromides (K_2PtCl_6-type structure [6]) is used to analyse the influence of the metal ions on the $N–H \cdots X^-$ hydrogen bond strength.

IR spectroscopy is selected because the N–H and N–D stretching modes are very sensitive to the presence and strength of hydrogen bonds. The bathochrome shift caused by M^{2+} can be

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☆ Dedicated Professor G. v. Bünau, Universität-GH Siegen, on the occasion of his 65th birthday.

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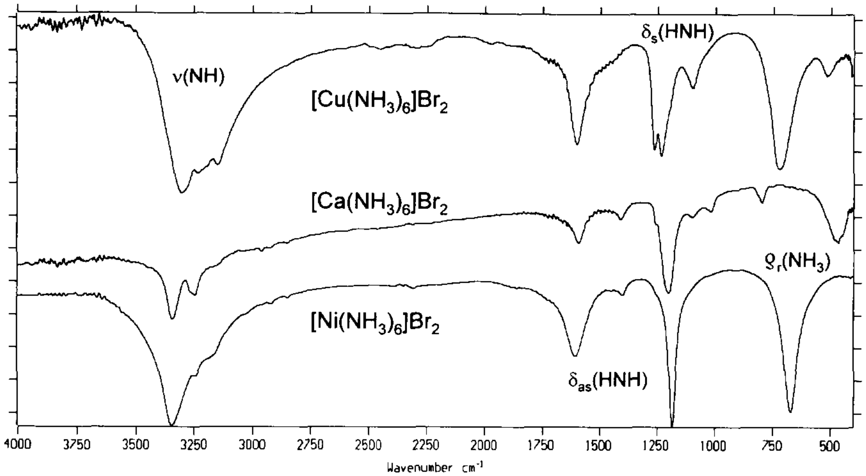

Fig. 1. IR spectra of $[M(NH_3)_6]Br_2$ ($M^{2+} = Cu^{2+}, Ca^{2+}, Ni^{2+}$) in the frequency range 400–4000 cm^{-1}.

studied if isotypic hexamminmetal(II) bromides are used. As shown before [5], isotopically dilute samples (5% deuterated) are necessary to assign IR spectra correctly because in the case of the neat compounds (i) Fermi resonance of $2\delta_{as}$ with ν_s(NH), (ii) broadness of the ν(NH) stretch region, and (iii) intermolecular coupling influence ν(NH) frequencies. In contrast to this, NH_2D molecules in isotopically dilute samples are helpful in avoiding intermolecular coupling. Decoupled ν(ND) frequencies allow one to measure the lattice potential at each H position. Therefore, the number of ν(ND) correlates with the number of crystallographic different H positions which is a helpful tool for structure investigations. Finally, the halfwidth of the ND stretches ($\approx$ 20–30 cm^{-1}) decreases by a factor of ten using decoupled NH_2D molecules compared to the NH stretches of NH_3 and it is not affected by Fermi resonance.

2. Experimental

Microcrystalline hexamminemetal(II) bromides can be prepared by the reaction of MBr_2, dried at 150°C in an HBr stream, with gaseous NH_3 (Messer Griesheim, Germany, 99.8%; $p(NH_3) =$ 1 bar) at room temperature using a Hüttig tensieudiometer [7]. Decreasing the partial pressure of ammonia leads to partial decomposition within some minutes. The decomposition products cause additional bands in the IR spectra and can, therefore, be detected. Isotopically dilute samples can be prepared using a mixture of NH_3/ND_3 with 5% D (ND_3: ICON, USA 99at% D).

Table 1
IR wavenumbers (cm^{-1}) of the main NH_3 modes in $[M(NH_3)_6]Br_2$

	M^{2+}						
	Ca^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}
ν_{as}(N–H)	3347	3331	3338	3343	3348	3305	3331
ν_s(N–H)	3248	3259	3236	3230	3247	3230	3245
$2{*}\delta_{as}$(HNH)	3150	3155	3150	3156	3165	3152	3153
δ_{as}(HNH)	1593	1600	1593	1600	1608	1602	1628
δ_s(HNH)	1203	1238	1256	1172	1187	1265/1235	1206
$\rho_r(NH_3)$	471	580	605	645	662	728	592

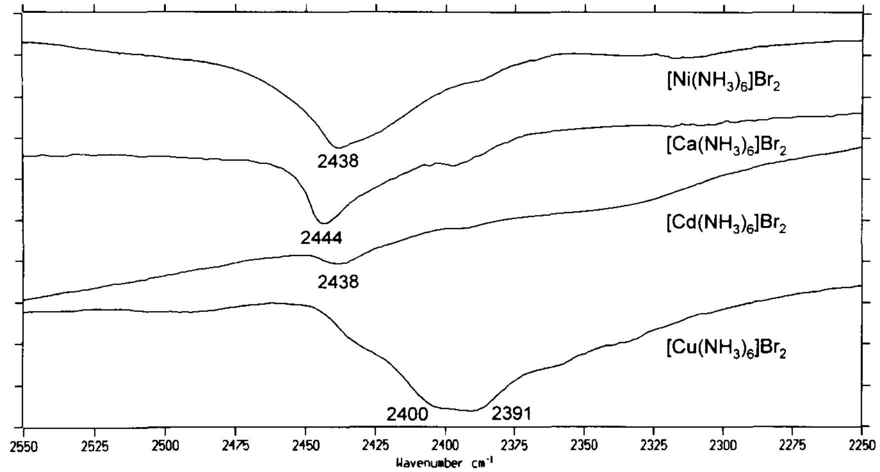

Fig. 2. IR spectra of the ν(ND) region of isotopically dilute samples of [M(NH$_3$)$_6$]Br$_2$ (M^{2+} = Ca^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}).

The compounds were characterized by X-ray diffraction in a closed glass tube using the Debye–Scherrer technique (Fa. Richard Seifert). IR spectra were recorded on either a Bruker IFS 113v (400–4000 cm^{-1}, resolution <1 cm^{-1}) or a Bruker IFS 25 (400–4000 cm^{-1}, resolution <2cm^{-1}) using three-layered KBr discs (the first layer was pure KBr, the second KBr with the sample and the third pure KBr) as well as Nujol mulls. Wavenumbers of hexamminemetal(II) bromides of mulls and discs showed no difference. To avoid reaction with moisture and air the samples must be handled in a glove box filled with dried argon.

3. Results

Typical IR spectra of hexamminemetal(II) bromides in the frequency range 400–4000 cm^{-1} are shown in Fig. 1. The most intense bands are assigned as ν(NH), δ_{as}(HNH), δ_s(HNH) and ρ_r(NH$_3$) [5]. Their frequencies are presented in Table 1.

In most cases the halfwidth of ν(NH) is more than 200 cm^{-1} and is influenced by the metal ion. The wavenumbers of ν_s(NH) are affected by Fermi resonance with the first overtone of δ_{as}(HNH), but it is clear that ν_s(NH) and ν_{as}(NH) are bathochromically shifted compared to gaseous ammonia (ν_{as}(NH) = 3443 cm^{-1}, ν_s(NH) = 3337 cm^{-1} [4]).

The wavenumbers of δ_s(HNH) and δ_{as}(HNH) are scarcely affected by the metal ion, but in the case of hexamminecopper(II) bromide δ_s(HNH) splits off. This is caused by a Jahn–Teller distortion of the NH$_3$ octahedron around the Cu^{2+} ion [8], which leads to two crystallographically different ammonia molecules. Therefore, δ_s(HN(1)H) and δ_s(HN(2)H) were observed. The existence of two different ammonia molecules is in agreement with the spectra of the isotopically dilute samples

Table 2
ν(N–D) (cm^{-1}) of isotopically dilute [M(NH$_3$)$_6$]Br$_2$ (5% deuterated) and radii, r (Å) of the M^{2+} ions [9] with low spin (LS) or high spin (HS) configuration

	M^{2+}						
	Ca^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}
ν(N–D)	2444	2434	2435	2431	2438	2391/2400	2438
r(LS)	1.14	0.81	0.75	0.79	0.83	0.87	1.09
r(HS)		0.97	0.92	0.89			

(Fig. 2). It can be seen (Fig. 2) that copper causes a greater downshift of ν(ND) and enlarges the half-width of ν(ND) more than the other characterized metal ions (see Table 2).

4. Discussion

Isotopically dilute spectra of hexammine-metal(II) bromides show that decoupled ν(ND) stretches are influenced by metal(II) ions. They decrease the strength of the N–H(D) bonds and, therefore, cause a higher acidity and a higher donor strength of the protons. Copper shows the greatest effect on the hydrogen bond strength, but because of the tetragonal distortion of $[Cu(NH_3)_6]^{2+}$ the downshift of ν(ND) for hexamminecopper(II) bromide results in a synergetic effect as well as a coordination effect.

Arranging the metals with decreasing strength of the $N-H\cdots Br^-$ hydrogen bonds leads to the following series:

$$Cu^{2+} \gg Co^{2+} > Mn^{2+} > Fe^{2+} > Ni^{2+} = Cd^{2+} > Ca^{2+}$$

The synergetic effect does not simply correlate the ionic radii of M^{2+} in an octahedral environment with either a high spin or low spin arrangement (see Table 2). On the contrary, there is no simple relationship between the stability of the hexammine complexes or the electron configuration of M^{2+} and $\Delta\nu$(ND). Thus, it can be assumed that several effects, e.g. electronic effects as well as radii effects, should be superposed to obtain the resulting synergetic effect.

It should be noted that the influence of the synergetic effect on the strength of $N-H\cdots X^-$ hydrogen bonds is much smaller than the influence of the acceptor strength of the anions [5]. Finally, it is difficult to compare the strength of the synergetic effect on hydrates with that on ammoniates because hexaaquametal(II) complexes crystallize in different structures types (not the K_2PtCl_6-type structure), so that the small change in the synergetic effect is superposed by other dominating effects. In spite of this, the large synergetic effect of Cu^{2+} ions is verified for both classes of compounds.

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References

[1] H.D. Lutz, Struct. Bonding, 69 (1988) 97.
[2] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley, New York, 1978.
[3] K. Nakamoto, M. Margoshes and R.E. Rundle, J. Am. Chem. Soc., 77 (1955) 6480.
[4] I. Fujita, K. Nakamoto and M. Kobayashi, J. Am. Chem. Soc., 78 (1956) 3295.
[5] R. Eßmann, J. Mol. Struct., 351 (1995) 87.
[6] R.W.G. Wyckhoff, Crystal Structures, Vol. 3, Robert E. Krieger, Malabar, Florida, 1981, pp. 783–784.
[7] G.F. Hüttig, Z. Anorg. Allg. Chem., 114 (1920) 161.
[8] T. Distler and P.A. Vaughan, Inorg. Chem., 6 (1967) 126.
[9] R.D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751.