^{81}Br NQR for Uncoordinated Br^- ions in *trans*-$[CoBr_2(en)_2]$ $[H_5O_2]Br_2$ and *trans*-$[CoBr_2(en)_2]$ $[D_5O_2]Br_2$ *

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The temperature dependence of the ^{81}Br NQR frequencies (ν_D) for uncoordinated Br^- ions in *trans*-$[CoBr_2(en)_2]$ $[D_5O_2]Br_2$ (**D**) has been determined by a continuous-wave spectrometer. ν_D amounted to 16.200 MHz at 273 K. This is lower by 418 kHz than the ^{81}Br NQR frequency (ν_H) for *trans*-$[CoBr_2(en_2]$ $[H_5O_2]Br_2$ (**H**). The frequency difference ($\Delta\nu = \nu_H - \nu_D$) remained almost constant in the temperature range studied. A shortening of the O–H bond length caused by deuteration could explain the magnitude and the sign of $\Delta\nu$ on the basis of a point charge model calculation. The compounds **D** and **H** yielded ^{81}Br NQR lines in the range 110–320 K and 90–343 K, respectively. As to the ^{59}Co NQR frequencies ν_1 (7/2–5/2), the observed isotope frequency shifts ($\Delta\nu_1 = \nu_{1H} - \nu_{1D}$) between **D** and **H** were smaller than 5 kHz. Below 160 K, ^{59}Co resonances were only available by pulsed experiments. ^{59}Co NQR spin-lattice relaxation times T_{1Q} of 0.54 ms at 194 K and 4.8 s at 77 K for **H** have been observed.

Key words: ^{81}Br NQR; ^{59}Co NQR; ^{1}H–^{2}D isotope effect; H-bonding; Ubbelohde effect.

We have recently reported that the electric field gradient (EFG) at uncoordinated Br^- ions in the crystal of *trans*-dibromobis (ethylenediamine) cobalt (III) diaquahydrogen bromide (**H**) arises from $O-H \cdots Br^-$ and $N-H \cdots Br^-$ H-bonds [1]. The Br^- ions can be considered to be almost purely ionic, however rather high ^{79}Br NQR frequencies (e.g. 19.954 MHz at 293 K) were observed for the ions. For covalently bonded halogen atoms, the NQR frequency is mainly determined by the nature of the bond, effects of H-bonds to the halogens being small. For ionic crystals, however, H-bonds themselves determine the NQR frequencies of halogens in the crystals. Therefore relatively large ^{1}H–^{2}D isotope effect on the halogen NQR frequency should be observed in ionic crystals. There have been only few studies on ionic crystals focusing on the ^{1}H–^{2}D isotope effects on the halogen NQR frequencies [2–4]. The present study has been undertaken to examine the ^{1}H–^{2}D isotope shifts of ^{81}Br NQR frequencies between **H** and its deuterated analogue *trans*-$[CoBr_2(en)_2]$ $[D_5O_2]Br_2$ (**D**).

Results

D was prepared in a dry box by dissolving *trans*-$[CoBr_2(en)_2]Br$ in 6 M of deuterated hydrobromic acid. Resulted crystals were filtered off and washed with acetone and absolute ether. Examination of the sample by IR spectra indicated the deuteration of O–H protons and remaining of N–H protons undeuterated.

A single ^{81}Br NQR line was observed by the cw-method for **D** which is consistent with the crystal structure reported for **H** [5]. The line was fairly broad with a frequency $\nu_D = 16.200$ MHz at 273 K. A corresponding ^{79}Br NQR line was observed at 19.292 MHz at the same temperature. Despite of imperfect deuteration of the samples, ν_D showed nearly the same or narrower widths than those of ν_H, suggesting that the widths arise from the local magnetic field at Br^- produced by neighboring protons [1]. Pulsed experiments were also examined on bromine nuclei for **H**. However, there was no FID or echo signal appearing after the spectrometer's dead time (ca. 30 µs). The cw-method was only feasible for detecting the broad lines of the Br^- ions in this sample. Figure 1 shows the temperature dependence of ν_H and ν_D. Measurements of ν_H were repeated in this work in order to determine the deuteration shift $\Delta\nu$ more accurately. Experiments

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on ^{81}Br were chosen because of higher sensitivity of our apparatus around 16 MHz. The observed $\Delta\nu$ amounted to 418 kHz at 273 K. The curve of ν_D is almost parallel to that of ν_H, showing the usual negative temperature coefficients. The intensity of the NQR lines was practically the same for both complexes and showed a maximum ($S/N \approx 20$) around 170 K. As departing from this temperature, the lines became gradually weaker, showing $S/N \approx 5$ at arond 140 and 300 K. The observable temperature range of the line, however, differed significantly: ν_D, 110–320 K; ν_H, 90–343 K.

^{59}Co NQR frequencies ν_1 (7/2-5/2) at typical temperatures are listed in Table 1 for **D** and **H**. A pulsed NQR spectrometer was also employed at several temperatures in order to confirm the frequency measurements of ν_1 by the cw-spectrometer. Observed isotope frequency shifts for ^{59}Co, $\Delta\nu_1$, are very small compared to those for ^{81}Br, $\Delta\nu$, and smaller than 5 kHz in the whole temperature range studied. At 273 K, ν_{1D} and ν_{1H} showed nearly the same intensity of $S/N \sim 15$. Upon cooling, the line became gradually broad and finally disappeared; resonance was observable down to 140 K for ν_{1D} and down to 121 K for ν_{1H}, showing a maximum intensity of $S/N \sim 40$ at around 240 K for both complexes. In the pulse experiments, however, the ^{59}Co NQR FID's for ν_{1H} were observable even at 77 K. Preliminary measurements showed that ^{59}Co NQR T_{1Q} for ν_{1H} changes rapidly between 194 K (0.54 ms) and 77 K (4.8 s) and exceeds 1 s below ca. 110 K. This suggests that the fading out of the signals at the low temperatures in the cw-experiments is attributable to the saturation effect of the resonance absorption. On heating, both ν_{1D} and ν_{1H} faded out at around 360 K, where the samples began to decompose.

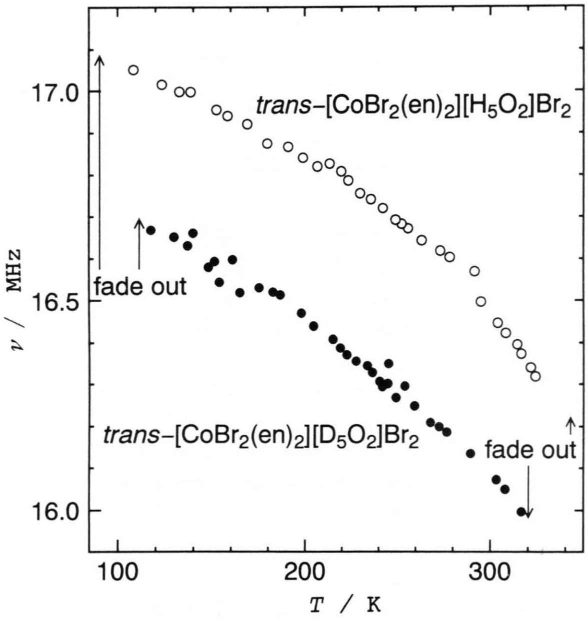

Fig. 1. Temperature dependence of ^{81}Br NQR frequencies observed for uncoordinated Br$^-$ ions in *trans*-[CoBr$_2$ (en)$_2$] [H$_5$O$_2$]Br$_2$ and *trans*-[CoBr$_2$(en)$_2$] [D$_5$O$_2$]Br$_2$.

Discussion

The uncoordinated Br$^-$ ions are almost purely ionic. Therefore, the observed fairly large non-zero EFG at the Br$^-$ nuclei is thoroughly attributable to H-bond formation between Br$^-$ and surrounding protons. Similar systems have already been studied by NQR for alkylammonium halides [2], anilinium bromides [3], and chloroanilinium iodides [4]. In these compounds the isotope frequency shifts, $\Delta\nu$, amount to several hundred kHz.

The ^{1}H–^{2}D isotope effect has also been studied by NQR for H-bonded systems in which the halogen atoms are involved in covalent or coordination bonds [6–10]. The EFG's at halogens are mainly determined by the nature of the covalent or coordination bond. Therefore, $\Delta\nu$ is relatively small: of the order 10 kHz for ^{35}Cl [7–9] and smaller than 200 kHz for ^{81}Br [10].

Table 1. ^{59}Co NQR frequencies ν_1 (7/2–5/2) in *trans*-[CoBr$_2$(en)$_2$] [H$_5$O$_2$]Br$_2$ and *trans*-[CoBr$_2$(en)$_2$] [D$_5$O$_2$] Br$_2$ at various temperatures.

Compound	Frequency/MHz (±0.001)					
	77 K	110 K	160 K	200 K	230 K	273 K
trans-[CoBr$_2$(en)$_2$] [H$_5$O$_2$]Br$_2$	15.902	15.860	15.810	15.727	15.672	15.568
trans-[CoBr$_2$(en)$_2$] [D$_5$O$_2$]Br$_2$	15.906	15.865	15.813	15.731	15.670	15.567

In the discussion of the ^{1}H$-^2$D isotope effect on the halogen NQR frequencies in O$-$H$\cdots$X H-bond systems, two important effects must be taken into consideration. One is the effect of the zero-point energy of the O$-$H vibration, which makes the O$-$D distance shorter than the O$-$H distance. In strong but asymmetric H-bonds, the deuteration causes further elongations of the O$\cdots$X distance (Ubbelohde effect) [11]. This effect has been introduced to interpret rather larger $\Delta\nu$ [3, 4, 12]. The other concerns the torsional amplitudes of water molecules and has been successful to explain rather small magnitudes of $\Delta\nu$ [7, 9, 10]. Deuteration reduces the amplitude and makes the D$\cdots$X distance shorter than the H$\cdots$X one, contrary to the former effect [7]. This latter effect is strongly temperature dependent and is predominant at lower temperatures.

For the present complexes **H** and **D**, the observed $\Delta\nu$ are fairly large and almost temperature independent. The position of the protons has not been determined, however rather strong O$-$H$\cdots$Br$^-$ H-bonds are presumable from the structure of *trans*-[CoCl$_2$(en)$_2$] [H$_5$O$_2$] Cl$_2$ [1, 5, 13]. Therefore we conclude that the Ubbelohode effect is larger than the effect of the torsional amplitude. Deuteration of the protons makes the O$-$D distance shorter than the O$-$H distance and further increases the O$\cdots$Br$^-$ and D$\cdots$Br$^-$ distances by the Ubbelohde effect. Since the EFG arises from the surrounding protons or deutrons, the shorter H$\cdots$Br$^-$ distance gives rise to positive $\Delta\nu$. We observed the usual negative temperature coefficients of ν_H and ν_D. Unusual positive temperature coefficients of NQR frequencies have sometimes been observed for the O$-$H$\cdots$X H-bonded systems in which protons reside in the direction of p_π lone pair orbitals of halogens [14]. The observation of the usual negative temperature coefficients in the present study indicates that the thermal motions of the Br$^-$ ions take place about the principal axis of the EFG, which almost coincides with the shortest H-bond vector [1], so as to average out the largest component of the EFG.

It must be noticed that there is another kind of compounds such as HCl [15] and [HCl$_2$]$^-$ [12, 16] which yield large and negative $\Delta\nu$. In these compounds the hydrogens are directly bonded to the chlorine atoms. Therefore the anharmonicity in the H$-$Cl vibration reduces the H$-$Cl bond distance by deuteration, which produces the contrary effect on $\Delta\nu$ to the case for the ionic crystals [2$-$4] and for the present complexes.

In order to obtain more quantitative features about $\Delta\nu$, a point charge model calculation of the EFG has been carried out for the determination of the reduction factor, ζ of the O$-$H bond length on deuteration

$$d_{\mathrm{O-D}} = \zeta\, d_{\mathrm{O-H}}\,, \tag{1}$$

where $d_{\mathrm{O-H}}$ and $d_{\mathrm{O-D}}$ represent the O$-$H (terminal) and O$-$D (terminal) distances in [H$_5$O$_2$]$^+$ and [D$_5$O$_2$]$^+$, respectively. The unknown protonic positions for **H** have been deduced from the known structure of *trans*-[CoCl$_2$(en)$_2$] [H$_5$O$_2$] Cl$_2$ [13]. Since only the position of the oxygen atoms has been determined for [H$_5$O$_2$]$^+$ [5], the orientation of the ion has been assumed to fix the position of the O$-$H protons and the angle O$-$H$\cdots$Br$^-$ to be the same as the O$-$H$\cdots$Cl$^-$ angle (174.6°) in *trans*-[CoCl$_2$(en)$_2$] [H$_5$O$_2$] Cl$_2$. Since the nuclear quadrupole coupling constants of ^{59}Co are nearly the same for both **H** and *trans*-[CoCl$_2$(en)$_2$] [H$_5$O$_2$] Cl$_2$ [17], the same charges on the halogens and on the other atoms in the cations were assumed for the two complexes: Co($+0.60$), ligand Br(-0.50), N(-0.35), C(-0.35), N$-$H($+0.34$), C$-$H($+0.18$) [18]. As for the charge distribution within the [H$_5$O$_2$]$^+$ ion, the results of a CNDO/2 calculation have been employed: O(-0.26), central H($+0.39$), terminal H($+0.28$) [19]. The same value of η has been assumed for **H** and **D.** Furthermore,

$$\nu_H/\nu_D = e q^0_H / e q^0_D \tag{2}$$

has been assumed, because ν_H and ν_D show almost the parallel temperature dependence. Here, eq^0_H and eq^0_D represent the maximum components of the static EFG at a Br$^-$ ion for **H** and **D**, respectively. The value of the EFG produced by all the ions within a radius of 10 Å about Br$^-$ was calculated and found to amount to $eq^0_H = 0.1622 \times 10^{14}$ esu cm^{-3}. For the frequency ratio, the data at 273 K were employed, giving $\nu_H/\nu_D = 1.026$. The parameter ζ in (1) was varied so that the EFG calculations satisfy $eq^0_D = 0.1581 \times 10^{14}$ esu cm^{-3}. The resulting value of $\zeta \sim 0.98$ explains well the tendency of the effect of the shortening of O$-$H bonds by deuteration. No significant difference was found in the calculated EFG at the central Co(III) atoms between **H** and **D** by using the value $\zeta = 0.98$.

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