Bromine-79 NQR for uncoordinated Br⁻ ions in trans-[CoBr₂(en)₂][H₅O₂]Br₂*

A. Sasane, T. Matsuda, H. Honda, and Y. Mori
Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390, Japan

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A single ⁷⁹Br NQR line showing a frequency of 19.594 MHz at room temperature has been observed in the crystals of trans-[CoBr₂(en)₂][H₅O₂]Br₂ and assigned to the Br⁻ ions which are not coordinated to the central Co(III) atom. The electric field gradient (EFG) at the Br⁻ nuclei arises from O–H···Br⁻ hydrogen bond formation between the Br⁻ ions and the terminal O–H hydrogen atoms in [H₅O₂]⁺ ions. The induced EFG is greater for the present bromine complex than that for the isostructural chlorine complex. A point charge model calculation explains well the relative magnitude of the EFG in the two crystals by introducing Sternheimer’s antishielding factors for the halogen ions.

Key words: ⁷⁹Br NQR frequency, Br⁻ ion, hydrogen bonding, electric field gradient (EFG), Sternheimer effect.

Introduction

Crystals of trans-dibromobis(ethylenediamine)cobalt(III)diaquahydrogen bromide belong to the space group, P₂₁/c and consists of three units of ions, trans-[CoBr₂(en)₂]⁺, [H₂O···H···OH₂]⁺, and Br⁻ [1]. Hydrogen bonds are formed between terminal O–H hydrogen atoms in [H₂O₂]⁺ and the uncoordinated Br⁻ ions. The corresponding chlorine complex, trans-[CoCl₂(en)₂][H₂O₂]Cl₂ forms isomorphous crystals with the bromine complex [2, 3]. Recently, neutron diffraction experiments have been carried out about the chlorine complex including the determination of the protonic position in the crystal [4, 5].

Hartmann et al. were the first to investigate the ⁵⁹Co and halogen NQR in trans-[CoX₂(en)₂][H₂O₂]X₂ (X = Cl, Br) [6–8]. They discussed the nature of the metal-ligand halogen bonds especially for the chlorine complex [7] and gave in the next paper a ³⁵Cl NQR frequency of 2.843 MHz and the asymmetry parameter η = 0.904 at room temperature for the uncoordinated Cl⁻ ions [8]. Brill and Hugus evaluated the lattice EFG at the site of Co(III) nucleus in complexes containing the [CoCl₂(en)₂]⁺ cation [9]. The nature of the metal and chlorine bonds in trans-[MCl₂(en)₂][H₂O₂]Cl₂ (M = Rh, Co, Cr) has been discussed by Schreiner and Brill [10]. Shirley and Hugus measured the temperature dependences of ⁵⁹Co, ligand chlorine and bromine NQR frequencies of trans-[CoX₂(en)₂][H₂O₂]X₂ and explained the results by the network of hydrogen bonds in the crystals [11]. Recently, the nature of the hydrogen bonds involving the ligand chlorine atoms has been further clarified by the study of ⁵⁹Co and ³⁵Cl NQR for the deuterated complex, trans-[CoCl₂(D₂NC₂H₂ND₂)₂][D₂O₂]Cl₂ [12]. The dynamic behavior of the ions in these crystals has also been investigated in the relation to the disappearance of ⁵⁹Co and ³⁵Cl NQR lines at low temperatures [13, 14]. However, there have been no studies of the ⁷⁹Br NQR about the uncoordinated Br⁻ ions in trans-[CoX₂(en)₂][H₂O₂]X₂ crystals. The present ⁷⁹Br NQR experiments have been undertaken to study the O–H···Br⁻ hydrogen bonds in the crystal and compare the results with those of the chlorine complex [8].

Experimental

A modified Dean-type superregenerative spectrometer and a chromel-alumel thermocouple with an estimated accuracy of ± 1 K were employed. X-ray powder patterns were recorded with a model 2012 diffractometer from Rigaku Denki Co. equipped with a copper anticathode.

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Trans-[CoBr₂(en)₂][H₅O₂]Br₂ was prepared in a similar way as described in [15]. The crude product was purified by recrystallization from ca. 6 M HBr solution.

Results

Trans-[CoBr₂(en)₂][H₅O₂]Br₂ was identified by analyzing the observed X-ray powder patterns with the aid of the crystal data reported [1]. A fairly broad ⁷⁹Br NQR line with a frequency of 19.954 MHz was observed at 293 K as shown in Figure 1. The line is rather broad compared with the ⁵⁹Co NQR line, v₁ (7/2−5/2) showing a frequency of 15.540 MHz at 285 K. A ⁸¹Br NQR line, which satisfies the isotope ratio of the bromine NQR frequencies was observed around 16.4 MHz. A ⁷⁹Br NQR line has been already reported at 127.33 MHz for the ligand bromine atoms [7,11]. Therefore, the observed ⁷⁹Br NQR line is to be assigned to the Br⁻ ions which do not coordinate with the central Co(III) atom. The line forms a singlet, in good agreement with the crystallographical equivalence of the Br⁻ ions [1]. The temperature dependence of the ⁷⁹Br NQR frequencies for the uncoordinated Br⁻ ions is shown in Figure 2. Upon cooling from room temperature, the frequency increased monotonously showing a fairly large temperature coefficient. The line shape remained almost unchanged down to ca. 190 K. However, it became gradually stronger below this temperature, keeping the line width almost constant. With further cooling the intensity of the line began to decrease markedly at ca. 130 K and finally disappeared at 121 K. Temperature dependencies of the ⁵⁹Co NQR frequencies v₁ (7/2−5/2), v₂ (5/2−3/2) were observed in good agreement with those already reported [11]. With decreasing temperature two lines became gradually broad and weak. The lines v₁ and v₂ disappeared at 157 and 177 K, respectively.

Discussion

Crystals of trans-[CoCl₂(en)₂][H₅O₂]Cl₂ belong to the monoclinic system, P₂₁/c, Z = 2, and a = 10.682, b = 7.883, c = 9.075 Å, β = 110.59° at room temperature [2–5]. The atomic arrangement studied by neutron diffraction [4, 5] is shown in Figure 3. The structure consists of [CoCl₂(en)₂]⁺, [H₅O₂]⁺, and Cl⁻ ions, where the [H₂O ⋅⋅⋅ H ⋅⋅⋅ OH]⁺ ion takes the trans configuration and is situated at the site of the inversion symmetry in the crystal. The Cl⁻ ions are connected through hydrogen bonds with terminal O–H hydrogen atoms in [H₅O₂]⁺ and with N–H hydrogen atoms in trans-[CoCl₂(en)₂]⁺, as shown by dotted lines in Figure 3. The shortest and the second shortest O–H distances are 2.007 and 2.047 Å between the O–H hydrogen atoms and the Cl⁻ ion. The third and fourth shortest distances are 2.329 and 2.521 Å between the N–H hydrogen atoms and the Cl⁻ ion. Although the position of the hydrogen atoms has not been determined, it has been reported that trans-[CoBr₂(en)₂][H₅O₂]Br₂ forms isomorphous crystals with the chlorine compound. The lattice constants are a = 10.98, b = 8.18, c = 9.46 Å, and β = 113.2° at room temperature [1]. It is therefore reasonable to assume that there is a strong resemblance of the proton surroundings around the halogen ions between the two complexes, however the cell is slightly larger for the bromine complex.

As shown in Fig. 1, the ⁷⁹Br NQR line is very broad and the width appears to reach almost ca. 10 kHz. The
Fig. 2. Temperature dependence of $^{79}$Br NQR frequencies $v$ observed for uncoordinated Br$^-$ ions in $\text{trans-[CoBr}_2\text{(en)}_2\text{][H}_5\text{O}_2\text{Br}_2}$. 

The large line width is, however, not attributable only to the lattice defects which cause the inhomogeneity in the EFG, because the $^{59}$Co NQR line which arises from the same sample is sharp enough. The phenomenon can be considered to have its origin in the local magnetic field at the $^{79}$Br$^-$ nuclei, which is induced by the surrounding protons. The local field produced by a proton at a distance $r$ is given by $H_{\text{loc}} = \mu/r^3$, where $\mu$ represents the proton magnetic moment. The H $\cdots$ Br$^-$ distances have not been determined for $\text{trans-[CoBr}_2\text{(en)}_2\text{][H}_5\text{O}_2\text{Br}_2}$. However, the shortest O $\cdots$ Br$^-$ distance has been determined to be 3.24 Å [1]. If we assume the same O $-$ H bond length and the same atomic arrangement for the bromine and chlorine complexes, the H $\cdots$ Br$^-$ distance can be estimated to be 2.25 Å. This leads to $H_{\text{loc}} \sim 1.24$ G at the Br$^-$ nucleus. The value itself corresponds to a broadening of ca. 1.3 kHz in the $^{79}$Br NQR line, which appears to be too small to explain the observed line width. The local field, however, can point to various directions and cause further broadening of the line. Furthermore, there are at least four protons which can contribute to the broadening, as can be seen in Figure 3. Therefore the observed large line width is well explained by the local field induced by protons.

The $^{79}$Br NQR frequencies for the uncoordinated Br$^-$ ions in $\text{trans-[CoBr}_2\text{(en)}_2\text{][H}_5\text{O}_2\text{Br}_2}$ yielded a marked temperature dependence as shown in Figure 2. The temperature coefficient of the frequency, $(1/v)(\partial v/\partial T)$ at 300 K amounts to $-2.536 \times 10^{-4}$ deg$^{-1}$. This is larger by more than one and two order magnitudes of the temperature coefficients for the ligand Br and Cl atoms, respectively, in $\text{trans-[CoX}_2\text{(en)}_2\text{][H}_5\text{O}_2\text{X}_2}\ (X = \text{Cl, Br})$ [11, 12] and suggests a large amplitude of the thermal motion of the atoms. The observed larger temperature coefficients for the uncoordinated Br$^-$ ions than for the ligand halogen atoms agrees with the fact that the thermal parameters determined by structural analysis for Cl$^-$ ions are larger than for ligand Cl atoms in $\text{trans-[CoCl}_2\text{(en)}_2\text{][H}_5\text{O}_2\text{Cl}_2}$ [5]. The restricted motion of the ligand halogen atoms is due to the formation of
coordination bonds, while the easy motion of the uncoordinated halogen ions shows that they are suspended in the crystals only through hydrogen bonds. The easy movement does not, however, imply that the hydrogen bonds are weak. The hydrogen bonded O–H⋯Cl" and N–H⋯Cl" distances are 3.0 and 3.3 Å, respectively in trans-[CoCl₂(en)₂][H₂O₂]Cl₂ [5]. These lengths belong to the group of rather short distances in the present type of hydrogen bond systems [16].

The reported ³⁵Cl NQR frequency for the uncoordinated Cl" ions in the chlorine complex is 2.843 MHz at room temperature [8]. The corresponding ⁷⁹Br NQR frequency in the bromine complex is 19.594 MHz and the ratio of the frequencies divided by the respective nuclear quadrupole moments to 0.61. On assuming equal values of η for the halogen nuclei in the respective crystals, the ratio can be interpreted as an experimentally obtained relative magnitude of EFG at the nuclei. As earlier mentioned, the shortest H⋯Cl" and H⋯Br" distances are 2.01 and 2.25 Å, respectively. The field gradient produced by a point charge at a distance r depends inversely on r³. If one disregards the effect of the closed electron shells on the EFG, the value 2.01⁻³/2.25⁻³ = 1.40 can be interpreted as the ratio of the EFG's at the Cl" and Br" nuclei produced by the nearest proton in each crystal. In ionic crystals, the EFG at the nucleus is seriously affected by the distortions of the electron shells. By introducing Sternheimer's antishielding factors as 56.6 for Cl" and 123.0 for Br" ions [17], the above mentioned ratio 1.40 reduces to 0.65, which shows a remarkable agreement with the observed EFG ratio, 0.61.

A charge of +0.25 on the terminal O–H proton considered above produces an EFG at the uncoordinated Cl" nucleus of e\text{q} = 0.2976 \times 10^{14} \text{esu cm}^{-3}. This value is much smaller than the experimental value e\text{q}_{\text{exp}} = 8.812 \times 10^{14} \text{esu cm}^{-3}. If the Sternheimer's antishielding factor for Cl" is introduced, the induced EFG gives rise to a value of (1 – γ) e\text{q} = 17.14 \times 10^{14} \text{esu cm}^{-3}, showing the same
order of magnitude as $e \eta_{eq}$ exp. However, the observed $\eta$ amounts to 0.904 [8], and a single point charge on the proton cannot yield any account for this large value of $\eta$. Therefore, we have tried a point charge model calculation for the Cl complex to confirm the considerations above. The EFG at the centering Cl$^-$ nucleus, which is produced by the atoms within a sphere of radius 10 Å has been calculated. In the sphere there are 408 atoms. Reported values for the atomic charges, Co(+0.60), ligand Cl(−0.50), N(−0.35), C(−0.35), N−H(+0.34), C−H(+0.18), have been used for the complex cation [9]. For the $[\text{H}_5\text{O}_2]^+$ ion, a charge of +0.25 on the terminal protons has been assumed. The calculated values are $e \eta_{cal} = 0.2316 \times 10^{14}$ esu cm$^{-3}$ and $\eta = 0.828$. Introduction of the antishielding factor yields $(1 - \gamma_{eq}) e \eta_{cal} = 13.34 \times 10^{14}$ esu cm$^{-3}$. The results of the calculation indicate that the principal axis of the EFG reasonably points to the O−H terminal proton situated at the shortest distance of 2.007 Å from the Cl$^-$ ion.

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