^{113}Cd MAS NMR Study of Cadmium Halides and Their Salts

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(Received June 26, 2000; CL-000618)

^{113}Cd magic-angle spinning (MAS) NMR spectra have been measured of twenty-three kinds of Cd^{2+}-containing halide crystals with known structures to determine the isotropic chemical shifts δ_{iso}. The δ_{iso} values of halogen coordination polyhedra largely changed with the kind and the coordination number of halogen. The relationship between the δ_{iso} values and the halogen coordination environments around Cd^{2+} was revealed.

A multinuclear NMR is known to be a powerful tool to directly acquire detailed local structures around a nucleus of interest. Cadmium-113 with 12.3% natural isotopic abundance is a spin-1/2 nucleus and has a relatively high NMR sensitivity. Therefore, ^{113}Cd NMR spectroscopy has been used to examine the structures and dynamics of various inorganic, organic and biochemical substances in solid state and also in solution.

^{113}Cd chemical shifts of simple inorganic crystals such as cadmium halides CdF_2, $CdCl_2$, $CdBr_2 \cdot 4H_2O$ and CdI_2 and cadmium chalcogenides CdO, CdS, CdSe and CdTe, have been already obtained by means of ^{113}Cd NMR spectroscopy.[1–3] However, the relationship between the isotropic chemical shifts δ_{iso} and the anion coordination environments around Cd^{2+} in these crystals has not been examined.

In the present study the ^{113}Cd MAS NMR spectra are measured of twenty-three kinds of Cd^{2+}-containing halide crystals with known structures. Then the relationship between the δ_{iso} values and the anion coordination environments around Cd^{2+} is discussed.

Nineteen kinds of Cd^{2+}-containing halide crystals, except CdX_2 (X = F, Cl, Br and I), were prepared. Those crystals are given in Table 1. All the prepared crystals were identified by powder X-ray diffraction measurements.

^{113}Cd MAS NMR spectra of powdered samples were recorded on a Varian UNITY INOVA 400 MAS FT-NMR spectrometer at 88.738 MHz (9.4T) using a single pulse sequence. A pulse length of 4.0 μs, pulse delay of 10.0–120.0 s and the accumulation of 24–160 scans were adopted. Samples in a cylindrical zirconia rotor were spun at a spinning rate of about 5–6 kHz. Chemical shifts were referenced to a 1M $Cd(ClO_4)_2$ aqueous solution at 0 ppm. The experimental error in isotropic chemical shift δ_{iso} was ± 1 ppm.

All the MAS NMR spectra gave sharp peaks. The δ_{iso} values of all the crystals measured in the present study are summarized in Table 1. The δ_{iso} values of CdF_2, $CdCl_2$, $CdBr_2 \cdot 4H_2O$ and CdI_2 obtained from references 1 and 2 are also given in parentheses in the table. In order to make comparison easy these δ_{iso} values were referenced to CdI_2 at –713 ppm. The δ_{iso} values obtained in this study are considerably close to those obtained from the references. The difference in the δ_{iso} values between this study and the references may be because the δ_{iso} values from the references were obtained from static spectra. Figure 1 shows the ^{113}Cd MAS NMR spectra of the representative Cd^{2+}-containing halide crystals with different halogen coordination polyhedra of Cd^{2+}, CdF_2, $KCdF_3$, $CdCl_2$, CdBrCl, $CdBr_2$, Cs_2CdBr_4, CdI_2 and $RbCdI_3 \cdot H_2O$. The halogen coordination polyhedra of Cd^{2+} in these crystals are given in parentheses in the figure. Numerals and asterisks in the figure denote δ_{iso} values and spinning side bands, respectively.

Figure 2 shows the δ_{iso} for halogen coordination polyhedra, which were obtained based on the δ_{iso} values of Cd^{2+}-containing halide crystals. The δ_{iso} is –226 ppm for the CdF_8 polyhedron and in the range from –105 to –103 ppm for the CdF_6 octahedron. The δ_{iso} is in the range from 168 to 233 ppm for the $CdCl_6$ octahedron. The δ_{iso} ranges from –64 to –24 ppm for

Table 1. Isotropic chemical shifts (δ_{iso}) determined by ^{113}Cd MAS NMR at 9.4T and halogen coordination number of Cd^{2+} (N)

Crystal	δ_{iso} / ppm	N	Crystal	δ_{iso} / ppm	N	Crystal	δ_{iso} / ppm	N
CdF_2	-226 (-264)[a]	8	CdBrCl $(CdCl_6)^b$	186	6	$CdBr_2$	-24 (0)[a,c]	6
$KCdF_3$	-105	6	$(CdBrCl_5)^b$	166	6	$RbCdBr_3$	-31	6
$RbCdF_3$	-103	6	$(CdBr_2Cl_4)^b$	135	6	$CsCdBr_3$	-42	6
$CdCl_2$	183 (170)[a]	6	$(CdBr_3Cl_3)^b$	101	6	$Cd(AlBr_4)_2$	-64	6
NH_4CdCl_3	195	6	$(CdBr_4Cl_2)^b$	63	6	$(NH_4)_4CdBr_6$	-27	6
$KCdCl_3$	205	6	$(CdBr_5Cl)^b$	25	6	Cs_2CdBr_4	421	4
$RbCdCl_3$	190	6	$(CdBr_6)^b$	-21	6	CdI_2	-713 (-713)[a]	6
$CsCdCl_3$	168	6				$TlCdI_3$	-715	6
	201	6				$RbCdI_3 \cdot H_2O$	115	4
Cs_2CdCl_4	193	6				α-Cs_2CdI_4	156	4
K_4CdCl_6	233	6				γ-Ag_2CdI_4	65	4
Na_6CdCl_8	223	6						

Experimental error in δ_{iso} in this study is ±1 ppm. [a]δ_{iso} obtained from references 1 and 2. These values were referenced to CdI_2 at -713 ppm in order to make comparison easy. [b]Structural units assumed for CdBrCl crystal. [c]δ_{iso} of $CdBr_2 \cdot 4H_2O$.

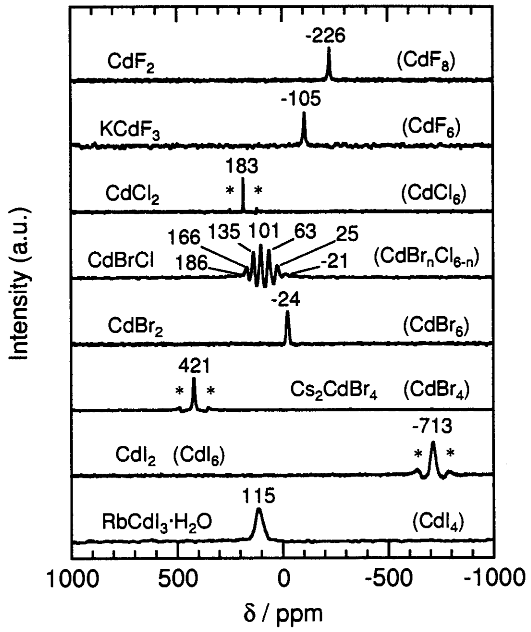

Figure 1. ^{113}Cd MAS NMR spectra of representative Cd^{2+}-containing halide crystals with different halogen coordination polyhedra of Cd^{2+}. Asterisks denote spinning side bands.

the CdBr$_6$ octahedron and is 421 ppm for the CdBr$_4$ tetrahedron. The δ_{iso} ranges from –715 to –713 ppm for the CdI$_6$ octahedron and from 65 to 156 ppm for the CdI$_4$ tetrahedron.

As clearly seen from Figure 2, halogen coordination polyhedra have quite different δ_{iso}. This means that the δ_{iso} is strongly influenced by the kind and the coordination number of halogen. In halogen coordination polyhedra with one kind of halogen, on the other hand, the δ_{iso} for the halogen coordination polyhedron has a 91 ppm width at most and smaller than the δ_{iso} difference between the halogen coordination polyhedra with the same kind of halogen.

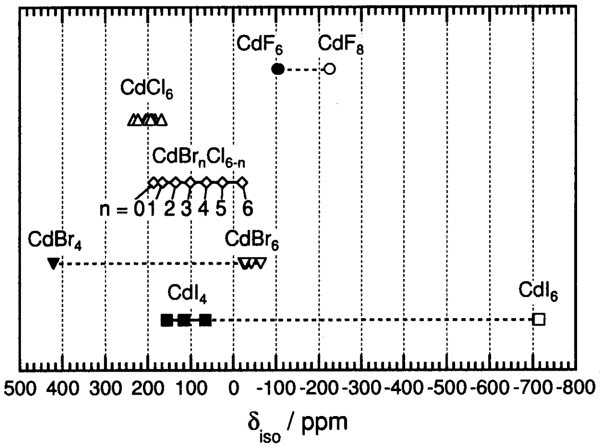

Figure 2. δ_{iso} for halogen coordination polyhedra determined from ^{113}Cd MAS NMR of Cd^{2+}-containing halide crystals.

The following two relations were found in the δ_{iso}: (i) The δ_{iso} increases with decreasing coordination number, that is, CdF$_6$ > CdF$_8$, CdBr$_4$ > CdBr$_6$, and CdI$_4$ > CdI$_6$. This is because a decrease in coordination number leads to a decrease in shielding of the Cd nucleus. (ii) In halogen coordination polyhedra with the same coordination number the δ_{iso} increases in order of I, F, Br and Cl, namely, CdCl$_6$ > CdBr$_6$ > CdF$_6$ > CdI$_6$, and CdBr$_4$ > CdI$_4$. These tendencies are consistent with that previously reported for the chemical shifts of CdF$_2$, CdCl$_2$, CdBr$_2$·4H$_2$O and CdI$_2$.[2] In order to give an explanation about the above tendencies it will be necessary to examine the electronic states around Cd nucleus by means of an MO calculation.

Based on the δ_{iso} values of CdBr$_2$ and CdCl$_2$, seven δ_{iso} values observed in the MAS spectra of CdBrCl, –21, 25, 63, 101, 135, 166 and 186 ppm, can be assigned to CdBr$_6$, CdBr$_5$Cl, CdBr$_4$Cl$_2$, CdBr$_3$Cl$_3$, CdBr$_2$Cl$_4$, CdBrCl$_5$ and CdCl$_6$, respectively. Although CdBrCl is a solid solution between CdBr$_2$ and CdCl$_2$ and is isomorphous with CdCl$_2$,[4] detailed local structure around Cd^{2+} has not been examined yet. The ^{113}Cd MAS NMR spectrum of CdBrCl in the present study revealed the presence of seven types of halogen coordination octahedra CdBr$_n$Cl$_{6-n}$ (n = 0–6). Assuming that the Br and Cl atoms in CdBrCl randomly occupy chlorine sites in CdCl$_2$ structure, a peak intensity ratio of CdBr$_n$Cl$_{6-n}$ octahedra is 1 (for n = 0 and 6) : 6 (for n = 1 and 5) : 15 (for n = 2 and 4) : 20 (for n = 3). The peak intensity ratio of CdBr$_n$Cl$_{6-n}$ octahedra was roughly estimated from the CdBrCl spectrum in Figure 1. The estimated ratio was 1 (n = 0) : 4 (n = 1) : 11 (n = 2) : 17 (n = 3) : 15 (n = 4) : 6 (n = 5) : 1.4 (n = 6). This ratio is close to the assumed ratio, suggesting that Br and Cl atoms in CdBrCl randomly occupy chlorine sites in CdCl$_2$ structure.

In closing, the following three facts may be summarized. (1) The δ_{iso} for halogen coordination polyhedra of Cd^{2+} in cadmium halides and their salts are largely changed with the kind and the coordination number of halogen. Accordingly, discrimination between halogen coordination polyhedra of Cd^{2+} is easily possible on the basis of the δ_{iso} values. (2) The δ_{iso} values for the halogen coordination polyhedra composed of only one kind of halogen are (i) CdF$_6$ > CdF$_8$, CdBr$_4$ > CdBr$_6$, and CdI$_4$ > CdI$_6$. (ii) CdCl$_6$ > CdBr$_6$ > CdF$_6$ > CdI$_6$, and CdBr$_4$ > CdI$_4$. (3) In a CdBrCl crystal the Br and Cl atoms randomly occupy chlorine sites in the CdCl$_2$ structure and seven types of halogen coordination octahedra CdBr$_n$Cl$_{6-n}$ (n = 0–6) are present.

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