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The NQR and DTA Study of Metal Bromide (Metal = Hg, Cd, Zn, In, Te) Complexes

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Summary

The ^{81}Br NQR measurement of $[4\text{-}C_2H_5\text{-}C_6C_4NH_3]_2HgBr_4$ (**1**) suggested that the phase transition took place at about 170 K, although the DTA measurement of **1** showed no clear heat anomaly at around 170 K, but two heat anomalies appeared at about 250 K. Three ^{81}Br NQR lines of $[NH_3(CH_2)_2NH_3]_2[ZnBr_4]\cdot 2$ Br (**2**) were observed at temperatures between 77 and around 260 K and all NQR lines faded out above 260 K. Four ^{81}Br NQR lines of $[H_3N(CH_2)_2NH_3]ZnBr_4$ (**3**) were observed at temperatures from 77 to 335 K. One ^{81}Br NQR line of $[Mg(H_2O)_6]_3(InBr_6)_2$ (**4**) was observed at temperatures between 77 and 345 K. This observation proves that the regular $[InBr_6]$octahedra exist in this crystal. Five ^{81}Br NQR lines of $[Mg(H_2O)_6]InBr_5\cdot H_2O$ (**5**) were observed at temperatures between 77 and 305 K. This observation suggests that the $[InBr_5\cdot H_2O]^{2-}$ ions exist in this crystal. Two ^{81}Br NQR lines of $[Ca(H_2O)_6]_3(InBr_6)_2$ (**6**) were observed at temperatures from 274 to 345 K and two NQR lines disappeared below 274 K. The DTA measurement of **6** showed the heat anomalies at around 250 K. The disappearance of NQR lines is probably due to the phase transitions. One ^{81}Br NQR line of $[Mg(H_2O)_6]_2CdBr_6$ (**7**) was observed at temperatures between 89 and 300 K. One NQR line shows the strong positive coefficient of ν *vs.* T curve due to the Br···H-O hydrogen bonds. The DTA measurements of $[N(CH_3)_4]_2TeBr_6$ (**8**), Rb_2TeBr_6 (**9**) and $[Na(H_2O)_3]_2TeBr_6$ (**10**) showed that the heat anomalies probably due to phase transitions occurred in these three crystals.

Key words： NQR, DTA, Phase transition, Metal bromide complex

Introduction

Nuclear quadrupole resonance (NQR) is the sensitive method to detect even slight change of the electric field gradient (EFG) around the relevant nuclei and therefore the suitable method for detection of phase transitions and modifications. The Br NQR of title compounds was observed and the measurement of differential thermal analysis (DTA) was done in this context. As for **1**, $[4\text{-}C_2H_5\text{-}C_6C_4NH_3]_2CdBr_4$ shows a phase transition at around 190 K and in the case of $[4\text{-}C_2H_5\text{-}C_6C_4NH_3]_2ZnBr_4$ peculiar temperature dependences of NQR frequencies has been observed [1]. As for **2** and **3**, $[H_3N(CH_2)_2NH_3]_2CdBr_4 2$ Br, $[H_3N(CH_2)_2NH_3]CdBr_4$, and $[H_3N(CH_2)_2NH_3](CdBr_3)_2$ show phase transitions [2]. As for **4**, **5**, and **6**, the structures of indium bromide complexes are intriguing to in-

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vestigate and $[C_2H_5NH_3]_4InBr_7$ shows a phase transition at around 180 K [3]. As for **4**, **5**, **6**, and **7**, The hydrate ions like $[Mg(H_2O)_6]^{2+}$ are interesting as cations on the formation of metal bromide complexes. As for **8**, **9**, and **10**, the phase transitions of A_2TeBr_6 (A=NH_4, K) were reported [4,5].

Experimental

The preparation of $[4\text{-}C_2H_5\text{-}C_6H_4NH_3]_2HgBr_4$ (**1**) is as follows : 0.08 mol of 4-ethylaniline in 30 g of 48% HBr and 0.04 mol of $HgBr_2$ in 200 mL of methanol are mixed. When the solution is separated into two portions, the addition of 48% HBr is necessary. The solvent was evaporated by P_2O_5 in a vacuum dessicator. The colorless, rod-shape crystals appeared from the solution. Elemental analysis could not be done, because the crystal was very hygroscopic. The chemical formula of **1** is speculated.

$[NH_3(CH_2)_2NH_3]_2[ZnBr_4]$·2 Br (**2**) was prepared by mixing 0.10 mol of $H_2N(CH_2)_2NH_2$·H_2O and 0.10 mol of $ZnBr_2$ in 40 g of 48% HBr with 100 mL water. The water solvent was evaporated by P_2O_5 in a dessicator. The colorless, rod-shape crystals appeared from the solution. On the other hand, both of white rod-shape and feather-shape crystals appeared from the solution containing only 20 g of 48% HBr. The colorless rod-shape crystals are used as NQR sample. Elemental analysis (Obsd. % / Calcd. %): C (7.03/7.18), H (2.96/3.01), N (8.16/8.37).

$[H_3N(CH_2)_2NH_3]ZnBr_4$ (**3**) appeared as square plate-like crystals from the rest solution after crystallization of **2** or from the solution consisting of 0.15 mol of anhydrous $H_2N(CH_2)_2NH_2$and 0.15 mol of $ZnBr_2$ in 65 g of 48% HBr. The compound **3** easily converted to **2** by recrystallization from dilute HBr solution. Elemental analysis (Obsd. % / Calcd. %): C (5.32/5.37), H (2.22/2.25), N (6.18/6.26).

$[Mg(H_2O)_6]_3(InBr_6)_2$ (**4**) was prepared by mixing 0.12 mol of In metal and 0.18 mol of Mg metal in 120 g of 48% HBr and the solution was concentrated to a half amount by heating. The rest of water was evaporated by P_2O_5 in a dessicator. The massive colorless crystals appeared from the solution. The crystal is hygroscopic and only Br content was determined by potentiometric titration using the standard solution of silver nitrate : Br content (Obsd. % / Calcd. %): (60.68/60.46).

$Mg(H_2O)_6InBr_5(H_2O)$ (**5**) were accidentally obtained as massive colorless prisms during the preparation of **4** and it was difficult to prepare **5** directly. Br content (Obsd. % / Calcd. %): (60.38/60.10).

$[Ca(H_2O)_6]_3(InBr_6)_2$ (**6**) was prepared by mixing 0.10 mol of In metal and 0.15 mol of $CaCO_3$ in 110 g of 48% HBr and then following the procedure of **4**. The massive colorless crystals appeared from the solution. The crystal is hygroscopic. Chemical analysis was not yet done.

$[Mg(H_2O)_6]_2CdBr_6$ (**7**) was prepared by mixing 0.20 mol of Mg metal and 0.10 mol of $CdBr_2$ in 40 g of 48% HBr and addition of extra 48% HBr to ensure that pH of solution is lower than 3. The water was evaporated by P_2O_5 in a dessicator. The massive colorless crystals appeared from the solution. The crystal is hygroscopic. Chemical analysis was not yet done.

$[N(CH_3)_4]_2TeBr_6$ (**8**) was prepared by mixing 0.08 mol of TeO_2 and 0.16 mol of $N(CH_3)_4Br$ in 55 g of 48% HBr and the wine-red powder appeared immediately. The crystallization from hot solution was repeated to obtain crystalline powder. The crystalline powder is hygroscopic. Elemental analysis (Obsd. % / Calcd. %): C(12.62/12.75), H (3.20/3.20), N (3.63/3.70).

Rb_2TeBr_6 (**9**) was prepared following Ref. [6]: by mixing 0.12 mol of TeO_2 and 0.12 mol of Rb_2CO_3 in 125 g of 48% HBr and the dark-red powder ap-

peared immediately. The crystallization from hot solution was repeated to obtain crystalline powder. The crystalline powder is hygroscopic.

$[Na(H_2O)_3]_2TeBr_6$ (**10**) was prepared following Ref. [7]: by mixing 0.12 mol of TeO_2 and 0.12 mol of Na_2CO_3 in 125 g of 48% HBr and the orange-red prisms appeared from the solution during evaporation of water by P_2O_5 in a dessicator. The crystal is hygroscopic.

The ^{79,81}Br NQR spectra were recorded by a home-made NQR spectrometer working in the super-regenerative mode, which operates at frequencies from 30 to 120 MHz. The sample temperature was measured with copper-constantan thermocouple, and the frequencies were determined by counting techniques. The observed ^{81}Br NQR frequencies at several temperatures are listed in Appendix I. DTA was measured by home-made apparatus above 100 K.

Results and Discussion

*NQR and DTA of [4-C_2H_5-$C_6C_4NH_3$]$_2HgBr_4$ (**1**)*

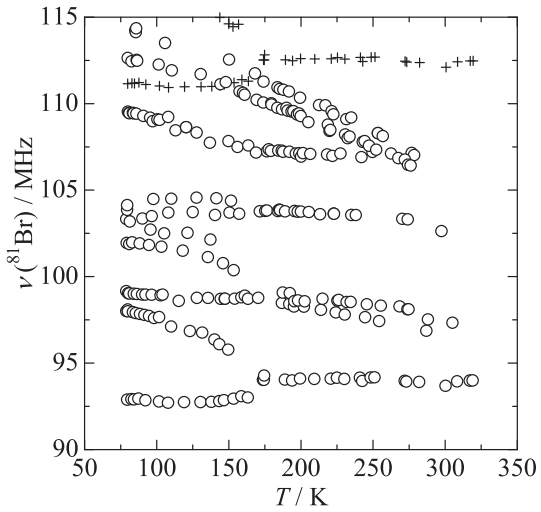

Fig.1. The temperature dependece of ^{81}Br NQR frequencies of **1**. For the simplicity only some trackable NQR lines are drawn. + indicates ^{79}Br NQR lines.

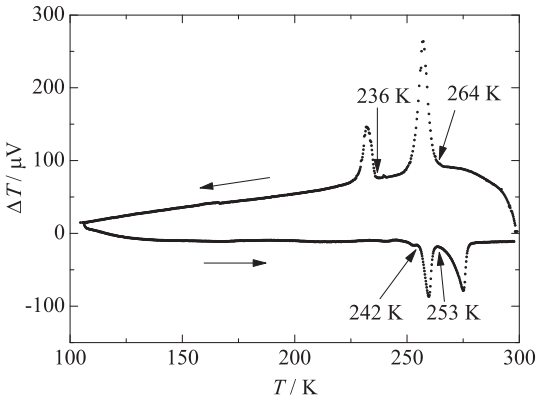

Fig.2. DTA curve of **1**. Upper curve is cooling run and lower curve is heating run.

The NQR spectra of **1** was so complicated below around 270 K as shown in Fig.1 that the number of NQR lines was not certain. There may be phase transition which takes place at around 170 K. The DTA curves at around 170 K shows no heat anomaly but heat anomalies appeared at higher temperatures than 170 K, *i.e.* at around 250 K, as shown in Fig.2. The $\nu(^{81}Br)$ *vs.* T curves shows barely a slight change at around 250 K. It is ambiguous that the phase transition occurs like cadmium bromide analogue, [4-C_2H_5-$C_6C_4NH_3$]$_2CdBr_4$ [1].

*NQR of [$NH_3(CH_2)_2NH_3$]$_2$[$ZnBr_4$]·2 Br (**2**)*

Three ^{81}Br NQR lines were observed at temperatures between 77 and around 260 K and NQR lines faded out above 265 K as shown in Fig 3. The intensity ratio of NQR lines is 1:1:2 in the order of increasing frequency. The number of NQR lines and the intensity ratio of three NQR lines agree with those of the cadmium bromide analogue, $[H_3N(CH_2)_2NH_3]_2CdBr_4$·2 Br, which has tetrahedral $CdBr_4^{2-}$ ions with C_{2v} symmetry [2]. The compound **2** must be isomorphous with $[H_3N(CH_2)_2NH_3]_2CdBr_4$·2 Br and the chemical formula of **2** is not $[H_2N(CH_2)_2NH_3]ZnBr_3$, although three ^{81}Br NQR lines can be expected in the case of $[H_2N(CH_2)_2$

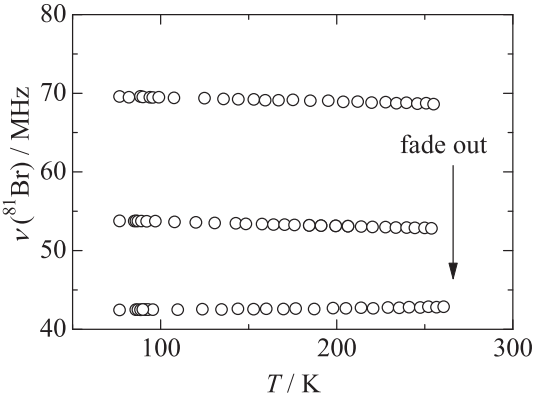

Fig.3. The temperature dependence of ^{81}Br NQR frequencies of **2**.

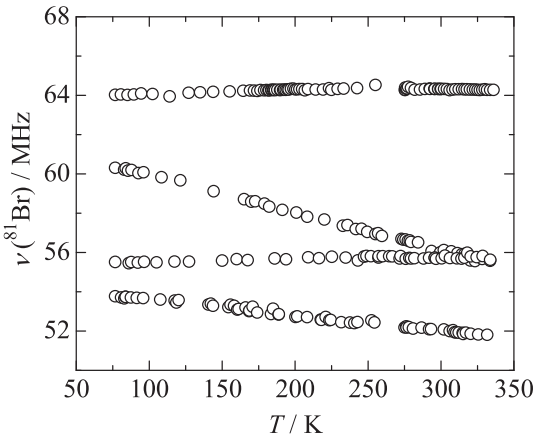

Fig.4. The temperature dependence of ^{81}Br NQR frequencies of **3**.

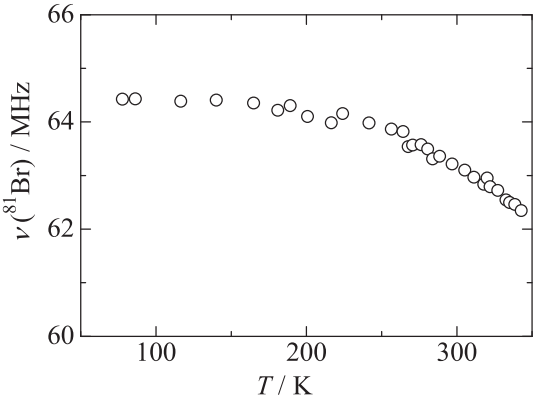

Fig.5. Temperature dependence of ^{81}Br NQR frequencies of **4**.

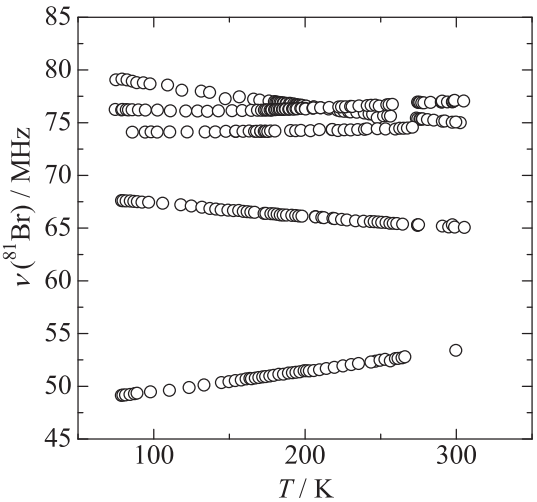

Fig.6. The temperature dependence of ^{81}Br NQR frequencies of **5**.

$NH_3]ZnBr_3$.

*NQR of $[H_3N(CH_2)_2NH_3]ZnBr_4$ (**3**)*

The four ^{81}Br NQR lines with equal intensity of **3** were observed at temperatures from 77 to 335 K as shown in Fig 4. The cadmium bromide analogue, $[H_3N(CH_2)_2NH_3]CdBr_4$ shows three ^{81}Br NQR lines at 77 K and a phase transition at about 340 K[2].Therefore, compound **3** is not isomorphous with $[H_3N(CH_2)_2NH_3]CdBr_4$, but $ZnBr_4$ anions probably exist in the crystal of **3**. The averaged NQR frequencies of **3** at 77 K of about 58 MHz are comparable to the averaged frequencies of 59 MHz for the compounds with tetrahedral $ZnBr_4$ anions which we have observed previously [8,9].

*NQR of $[Mg(H_2O)_6]_3(InBr_6)_2$ (**4**)*

The one ^{81}Br NQR line of **4** was observed at temperatures between at 77 and 345 K as shown in Fig.5. This suggests that regular octahedral $[InBr_6]^{3-}$ ions with O_h symmetry exist in the crystal of **4**. The existence of $[Mg(H_2O)_6]^{2+}$ ion is well known in $[Mg(H_2O)_6]\cdot Br_2$ [10], $[Mg(H_2O)_6]Zn_2Br_6$ [11], and $[Mg(H_2O)_6]_2CdBr_6$ (**7**) [12]. Therefore, the chemical formula of **4** can be speculated taking account of the Br content.

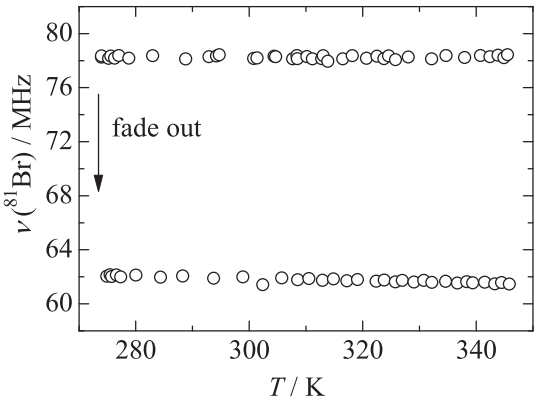

Fig.7. The temperature dependence of ^{81}Br NQR frequencies of **6**.

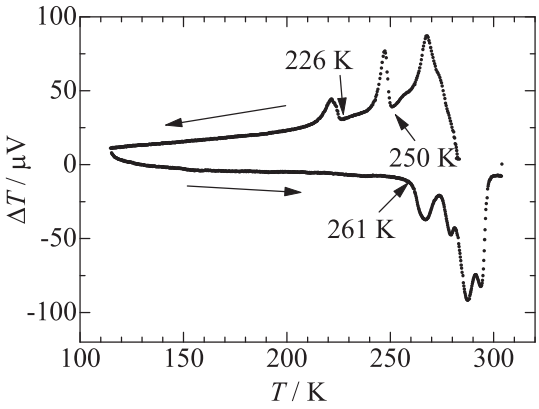

Fig.8. DTA curve of **6**. Upper curve is cooling run and lower curve is heating run.

*NQR of $[Mg(H_2O)_6]InBr_5{\cdot}H_2O$ (**5**)*

The five ^{81}Br NQR lines with equal intensity of **5** were observed between at 77 and 305 K as shown in Fig.6 and this observation suggests that the $[InBr_5H_2O]^{2-}$ ions exist in the crystal of **5**. The existence of $[InBr_5H_2O]^{2-}$ ion is known in a series of $A_2[InBr_5{\cdot}H_2O]$ (A=K, NH_4, Rb, Cs) [13,14]. Therefore, the chemical formula of **5** can be speculated in consideration of the Br content.

*NQR and DTA of $[Ca(H_2O)_6]_3(InBr_6)_2$ (**6**)*

Two ^{81}Br NQR lines of **6** with equal intensity were observed at temperatures from 274 to 345 K and two NQR lines disappeared below 274 K as shown in Fig 7. DTA measurement of **6** shows that exothermic peaks appear at 250 and 226 K as shown in Fig.8. This is probably due to phase transitions. On heating run, DTA curve above 261 K are complicated. These heat anomalies are not due to dehydration, because NQR lines can be observed at temperatures above 274 K.

*NQR of $[Mg(H_2O)_6]_2CdBr_6$ (**7**)*

One ^{81}Br NQR line of **7** was observed at between 89 and 300 K as shown in Fig.9. This observation agrees with the report by Krishnan [15], although the preparation of a sample is different

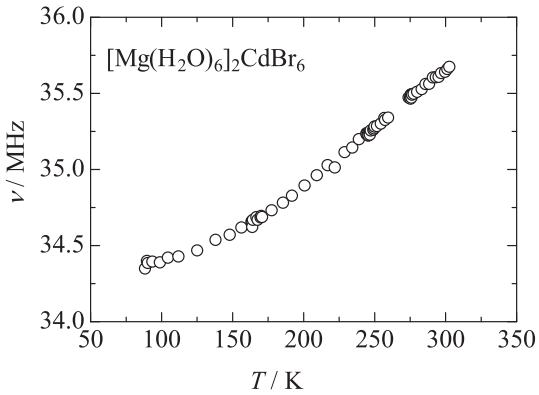

Fig.9. The temperature dependence of ^{81}Br NQR frequencies of **7**.

from ours. The crystal structure of **7** is reported by Duhlev *et al*. One nonequivalent Br atom exists in the crystal, and the Cd-Br bond distance is 2.788 Å [9]. The relation of between ν(^{81}Br) and Cd-Br bond distance is well known [2]. The ^{81}Br NQR frequency expected from the Cd-Br bond distance may be lower than 35 MHz in consideration of the minus charge of $[CdBr_6]^{4-}$. The observed NQR frequency is almost comparable to the expected one. In addition, one observed NQR line shows strong positive coefficient of ν *vs.* T curve which is apparently due to short Br···H-O hydrogen bonds (2.58~2.85 Å) [9]. The hydrogen bond becomes weak owing to thermal vibration with increasing temperature and thus relevant Cd-Br bond becomes strong. Therefore, Br NQR frequency in-

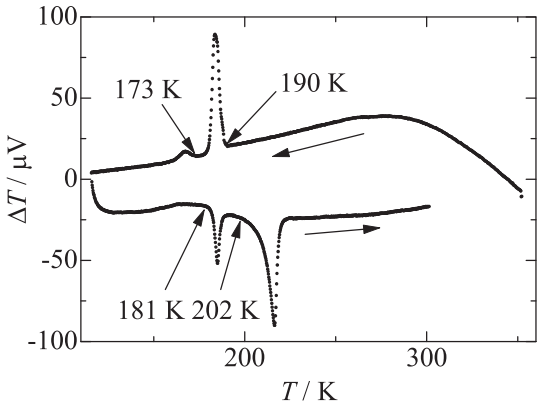

Fig.10. DTA curve of **8**. Upper curve is cooling run and lower curve is heating run.

creases with increasing temperature [16].

*DTA of $[N(CH_3)_4]_2TeBr_6$ (**8**), Rb_2TeBr_6 (**9**), and $[Na(H_2O)_3]_2TeBr_6$ (**10**)*

The phase transitions of A_2TeBr_6 (A=NH_4, K) with K_2PtCl_6 type structure were reported [4,5]. DTA curves of **8**, **9**, and **10** are shown in Figs.10, 11, and 12, respectively.

One ^{79}Br NQR line of **8** was reported at 289, 203 K, and liquid N_2 temperature [17] and the NQR frequency is 142.58 MHz at liquid N_2 temperature. It means that one NQR line do not split into multiple lines below 190 or 173 K at which shows heat anomalies on DTA curve of **8**, as shown in Fig.10.

Compound **9** shows heat anomalies on DTA curve as shown in Fig.11, although Abriel reported that the crystal structure of **9** retained by cooling from 298 to 160 K (cubic system, space group $Fm\,3\,m$) [9]. On heating run of DTA measurement, a strange peak appeared at 168 K accompanying with exothermic peak.

Compound **10** shows complicated heat anomalies on DTA curve as shown in Fig.12. In regard to phase transitions, the further investigation of these bromotellurate complexes of **9**, **10**, and **11** is necessary.

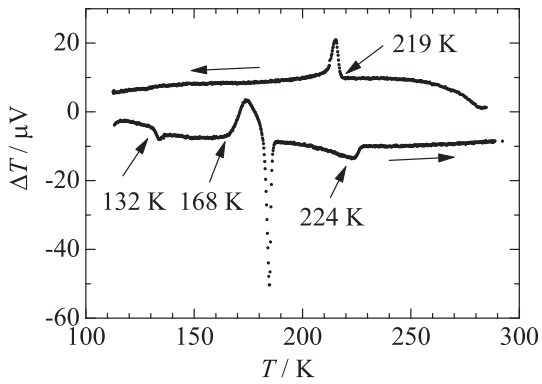

Fig.11. DTA curve of **9**. Upper curve is cooling run and lower curve is heating run.

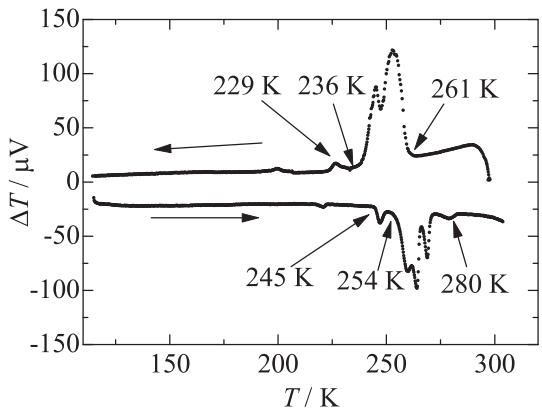

Fig.12. DTA curve of **10**. Upper curve is cooling run and lower curve is heating run.

Acknoledgement

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Appendix

I. The ^{81}Br NQR frequencies of the title compounds at several temperatures.

Compound	ν/MHz (T/K)	
1	–	93.94(300) 97.40(300) 102.54(300) 105.98(300)
2	42.38(77) 53.71(77) 69.53(77)	42.80(250) 52.82(250) 68.55(250)
3	53.75(77) 55.49(77) 60.29(77) 64.00(77)	52.06(300) 55.68(300) 55.98(300) 64.30(300)
4	64.42(77)	63.20(297)
5	49.09(77) 67.56(77) 74.05(86) 76.20(77) 79.01(77)	53.36(300) 65.05(300) 75.01(300) 75.00(300) 77.06(300)
6	62.00(274) 78.22(274)	61.56(340) 78.33(340)
7	34.35(89)	35.47(275)