February, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *603—607 (1987)* 603

Pressure and Temperature Effects on Octahedral-Tetrahedral Equilibria in 3-Methylpyridine Solutions of Some Cobalt(II) Halides

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(Received September 11, 1986)

The visible absorption spectra of CoX_2 (X=Cl, Br) in 3-methylpyridine (3-Me-py) solutions have been measured in the pressure range of 1 bar—3 kbar at room temperature, and in the temperature range of ≈5—≈76 °C at 1 bar. The equilibrium, $[CoX_2(3\text{-Me-py})_2]$ (tetrahedral) + 2(3-Me-py) $\rightleftarrows$ $[CoX_2(3\text{-Me-py})_4]$ (octahedral), is found to be followed over this pressure range. Higher pressures favor the octahedral species with the volume changes −18—−19 $cm^3\,mol^{-1}$ at 1 bar. On the other hand, the above equilibrium holds fairly well at temperatures up to about 40 °C. Higher temperatures favor the tetrahedral species, the heats of reaction, being 56.7 $kJ\,mol^{-1}$ (5.0—44.8 °C) and 58.6 $kJ\,mol^{-1}$ (4.8—34.2 °C) for the chloro and bromo complexes, respectively. An intense and broad band appears around 400 nm at elevated temperatures especially for the bromo complex solution. This band may be assigned to a charge-transfer band occurring in a contact ion pair of solvent molecule 3-Me-py with X^- arising from the dissociation of the tetrahedral species $[CoX_2(3\text{-Me-py})_2]$.

King et al.[1,2] and Sawada et al.[3,4] have studied in detail the configurational equilibria between the octahedral $[CoX_2(R\text{-py})_4]$ and tetrahedral $[CoX_2(R\text{-py})_2]$ complexes in nonaqueous solvents such as nitromethane and 1,2-dichloroethane, where X=Cl, Br, or I and R-py=pyridine or methylpyridines. However, the pressure and temperature effects on the equilibria have not been discussed.

In the previous papers,[5,6] the effects of pressure and temperature on the octahedral-tetrahedral equilibria in pyridine solutions of Co(II) halides have been reported. From the variations in the visible absorption spectra with pressure and temperature, the values of ΔV and ΔH, the volume and the heat of the following reaction, were obtained

$$\underset{\text{(tetrahedral)}}{[CoX_2(py)_2]} + 2py \rightleftharpoons \underset{\text{(octahedral)}}{[CoX_2(py)_4]},$$

where X=Cl, Br, or I. Higher pressures favored the octahedral species but higher temperatures did the tetrahedral species. The ΔV values were −41, −29, and −6 $cm^3\,mol^{-1}$ at 1 bar and the ΔH values were 57.3, 60.7, and 65.3 $kJ\,mol^{-1}$ for X=Cl, Br, and I, respectively.

As a part of a series of the study, the present paper describes the spectrochemical investigations of the pressure and temperature dependence of the following equilibrium

$$\underset{\text{(tetrahedral)}}{[CoX_2(3\text{-Me-py})_2]} + 2(3\text{-Me-py}) \overset{K}{\rightleftharpoons} \underset{\text{(octahedral)}}{[CoX_2(3\text{-Me-py})_4]}, \quad (1)$$

where X=Cl or Br, and K is the equilibrium constant. Moreover, the above reaction may be accompanied by another reaction and the possibility will be also discussed.

Experimental

$CoCl_2$ and $CoBr_2 \cdot 6H_2O$ were used after drying and 3-Me-py was used after drying and distillation. Sample solutions of CoX_2 in 3-Me-py were prepared just before spectroscopic measurements.

High-pressure spectra were recorded on a Hitachi 340 spectrophotometer equipped with a clamp-type optical cell[7] and high-temperature spectra on a Shimadzu MPS-2000 instrument equipped with a pair of thermostated quartz cells.

The experimental details have been described in the previous paper.[5]

Results and Discussion

Spectra at Atmospheric Pressure and Room Temperature. The changes in the absorption spectra of CoX_2 solutions in 3-Me-py with pressure and temperature are shown in Figs. 1—4. The spectra are composed of the two main bands due to d-d transitions. The one is the O-band due to the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ electronic transition of the octahedral complex $[CoX_2(3\text{-Me-py})_4]$ and the other the T-band due to the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition of the tetrahedral complex $[CoX_2(3\text{-Me-py})_2]$.

At atmospheric pressure and room temperature, the O-band comprises the two peaks (503, 530 nm) and the shoulder (≈560 nm) for the chloro complex, and the two peaks (526, 543 nm) and shoulders (≈490, ≈570 nm) for the bromo complex. All of the peaks for both halo complexes lie in longer wavelength by 3—6 nm than those of the complexes $[CoX_2(py)_4]$ (X=Cl, Br) in pyridine solutions.[5]

Under atmospheric pressure and room temperature, the T-band comprises the three peaks (578, 613, and 640 nm) and the shoulder (≈665 nm) for the chloro complex, and the two peaks (597, 648 nm) and shoulders (≈626, ≈675 nm) for the bromo complex. All of these peaks for both halo complexes shift to longer wavelength by 3—7 nm in comparison with those of the $[CoX_2(py)_2]$ complexes in pyridine solutions.[5] This finding is in contrast to the results of Sawada et al.[3,4] They have found that the positions of the peaks for the tetrahedral complexes $[CoX_2(R\text{-py})_2]$ remain almost unchanged in 1,2-dichloroethane or in 1,2-dibromoethane regardless of pyridine and 3-Me-py. This

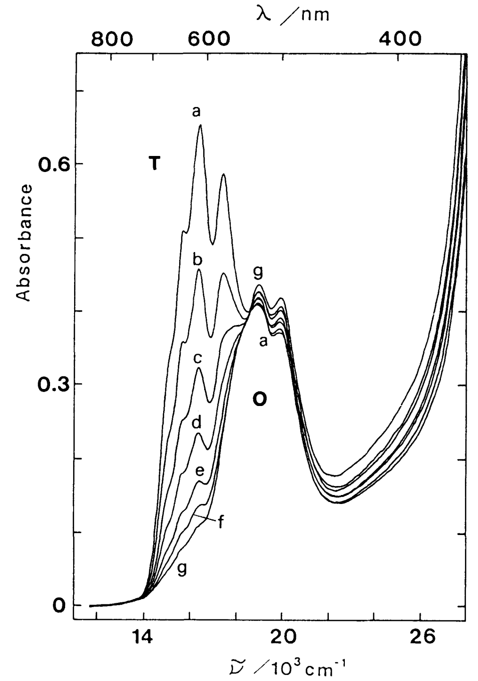

Fig. 1. Absorption spectra of $CoCl_2$ in 3-Me-py at high pressures (17.0°C), uncorrected for compression of solution. Concn: 1.38×10^{-2} mol dm^{-3}, optical path length: 1.6 cm.
a: 1 bar, b: 0.5 kbar, c: 1.0 kbar, d: 1.5 kbar, e: 2.0 kbar, f: 2.5 kbar, g: 3.0 kbar.

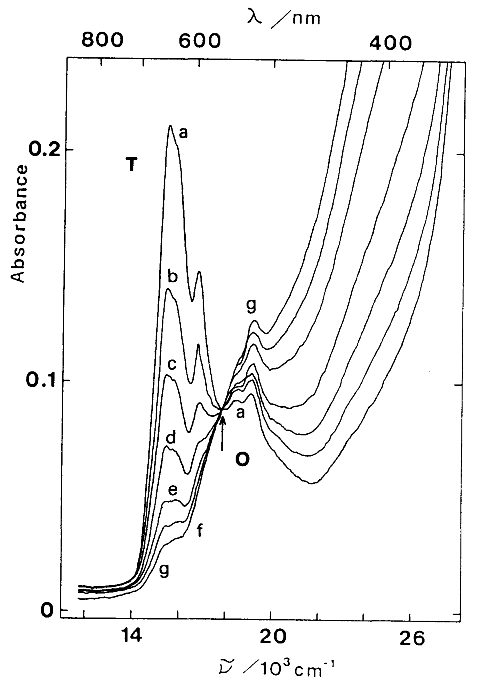

Fig. 2. Absorption spectra of $CoBr_2$ in 3-Me-py at high pressures (18.5°C), uncorrected for compression of solution. The curves d—g are drawn after shifting them along the ordinate so as to cross at a point indicated by an arrow. Concn: 2.98×10^{-3} mol dm^{-3}, optical path length: 1.6 cm.
a: 1 bar, b: 0.5 kbar, c: 1.0 kbar, d: 1.5 kbar, e: 2.0 kbar, f: 2.5 kbar, g: 3.0 kbar.

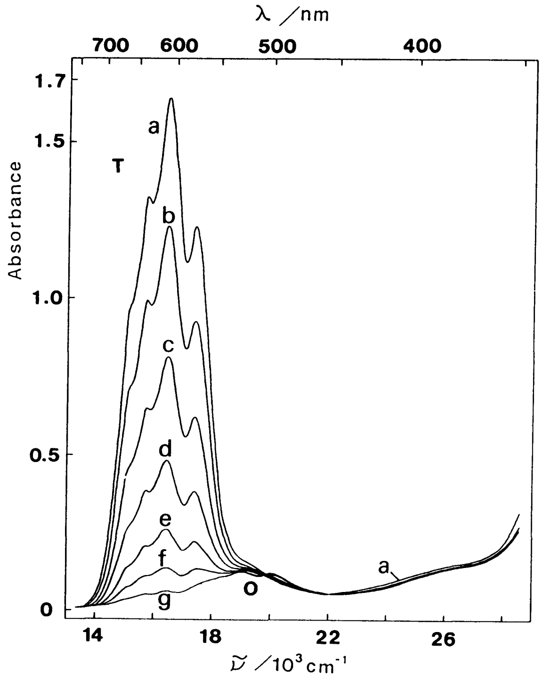

Fig. 3. Absorption spectra of $CoCl_2$ in 3-Me-py at various temperatures (1 bar), uncorrected for thermal expansion of solution. Concn: 7.01×10^{-3} mol dm^{-3}, optical path length: 0.98 cm.
a: 65.3°C, b: 55.2°C, c: 44.8°C, d: 35.0°C, e: 25.1°C, f: 16.1°C, g: 5.0°C.

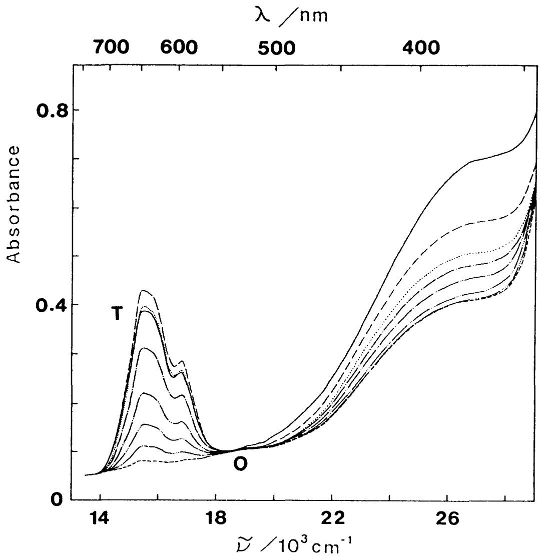

Fig. 4. Absorption spectra of $CoBr_2$ in 3-Me-py at various temperatures (1 bar), uncorrected for thermal expansion of solution. Concn: 2.33×10^{-3} mol dm^{-3}, optical path length: 0.98 cm.
——: 76.6°C, – – –: 64.8°C, ·········: 54.4°C, —·—: 44.8°C, —··—: 34.2°C, —···—: 24.4°C, —····—: 15.9°C, --------: 4.8°C.

contrast may be assumed to be caused by the solute-solvent interaction.

For both halo complexes, the intensity ratio of the T-band to the O-band is larger for the CoX_2-3-Me-py system in the present study than for the CoX_2-pyridine system[5] at atmospheric pressure and room temperature. This result suggests that the equilibrium constant of Eq. 1, K, is smaller in the 3-Me-py solutions than in the pyridine ones, being in agreement with the other results.[1-4]

Pressure Effect. Figures 1 and 2 show the pressure dependence of the spectra. The intensities of the T-bands decrease with increasing pressure. Because of an enhancement of the intensities in the shorter wavelength region than about 460 nm with increasing pressure, the changes in the O-bands are more obscure in this system than in the pyridine system.[5] However, for the chloro complex the O-band intensity is found to increase slightly with pressure. This is likely for the bromo complex, judging from a comparison with the result of the $CoBr_2$-pyridine system.[5] From the facts presented above, it can be concluded that the equilibrium of Eq. 1 shifts toward the octahedral species $[CoX_2(3\text{-Me-py})_4]$ with increasing pressure.[8]

Regarding $[CoX_2(3\text{-Me-py})_4]$ as the product, the volume change, ΔV, is estimated. As shown in Ref. 5, ΔV is calculated by

$$\Delta V = -RT\frac{d}{dP}\ln(I_o/I_T), \tag{2}$$

where R is the gas constant, and I_o and I_T are the integrated intensities of the O-band and T-band, respectively.

Figure 5 shows the plots of $\ln(I_o/I_T)$ vs. pressure. These plots are fitted to the following equations by the least-squares method:

$$\ln(I_o/I_T) = -0.0960 + 0.765P + 0.125P^2,$$

for the chloro complex, and

$$\ln(I_o/I_T) = -0.463 + 0.772P, \text{ for the bromo complex.} \tag{3}$$

From Eqs. 2 and 3, the values of ΔV are estimated for the chloro complex as −18, −21, −24, −27, −29, −32, −34 $cm^3\,mol^{-1}$ in the order of pressure from 1 bar to 3.0 kbar at intervals of 0.5 kbar, and for the bromo complex as −19 $cm^3\,mol^{-1}$ over the range of 1 bar −1.5 kbar. No reliable datum is obtained for the bromo complex at high pressures above 1.5 kbar.

ΔV equals $V_{oct}-(V_{tet}+2V_{sol})$, where V_{oct}, V_{tet}, and V_{sol} are the intrinsic volumes of the octahedral species, the tetrahedral species, and the solvent molecule, respectively. Moreover, the ΔV values are always negative in the CoX_2-3-Me-py and CoX_2-pyridine systems. Therefore, the larger the value of $V_{oct}-V_{tet}$ or the smaller that of $V_{tet}+2V_{sol}$ becomes, the smaller $|\Delta V|$ is obtained. $|\Delta V|$, at 1 bar, is 18 $cm^3\,mol^{-1}$ for the chloro complex and is 19 $cm^3\,mol^{-1}$ for the bromo complex in the CoX_2-3-Me-py system. On the other hand, in the CoX_2-pyridine system, the $|\Delta V|$ values were 41 and 29 $cm^3\,mol^{-1}$ for the chloro and bromo complexes, respectively, as reported previously.[5] The values of $|\Delta V|$ for both halo complexes are found to be smaller in the CoX_2-3-Me-py system than in the CoX_2-pyridine system. This fact may imply that replacement of ligand pyridine molecules by ligand 3-Me-py ones makes the value of $V_{oct}-V_{tet}$ larger or makes the value of $V_{tet}+2V_{sol}$ smaller. For the 3-Me-py system, there is little difference in $|\Delta V|$ between the two halo complexes in contrast with the CoX_2-pyridine system. This fact may suggest that the contribution of X to V_{oct} and V_{tet} becomes relatively small in the CoX_2-3-Me-py system regardless of Cl and Br.

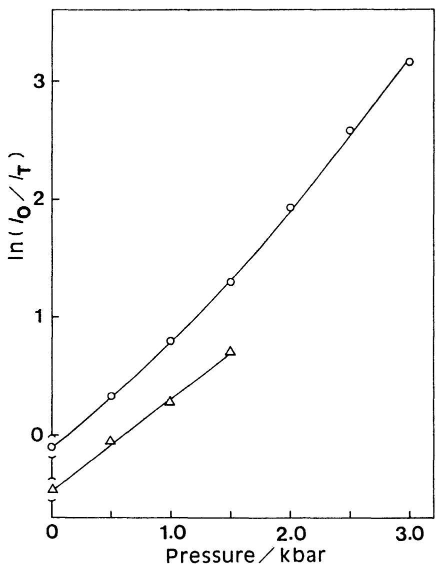

Fig. 5. Logarithm of the integrated-intensity ratio of the O-band to the T-band (I_o/I_T) vs. pressure. O: $CoCl_2$, Δ: $CoBr_2$, ——: calculated fitting lines.

When the values of V_{oct} and V_{tet} are obtained, the quantitative interpretation upon ΔV can be formulated.

Temperature Effect. The variations in the spectra with temperature are shown in Figs. 3 and 4. The intensities of the T-bands increase steeply with increasing temperature. Although the changes in the O-bands with temperature are obscured due to the intense T-bands, the equilibrium of Eq. 1 probably shifts toward the tetrahedral species $[CoX_2(3\text{-Me-py})_2]$ with increasing temperature contrary to the pressure effect described above. This tendency is very similar to the CoX_2-pyridine system.[5]

However, a marked difference between the two systems should be pointed out here, that is, absorption bands at about 400 nm are observed only in the CoX_2-3-Me-py system. These bands show the following features: (i) They can be observed even at low temperatures. Those peak positions are not clear, but can be estimated at about 390 nm in the chloro complex solution and at about 400 nm in the bromo complex solution. Another peak seems to lie around 430 nm in the latter. Anyway, there is little difference in the peak positions between these two halo complex systems. (ii) For the bromo complex system, the intensity of the 400-nm band increases markedly with increasing temperature simultaneously with suppression of the enhancement of the T-band intensity. The intensity of the T-band becomes smaller at 76.6 °C than at 64.8 °C. Even if the bromo complex solution heated to 76.6 °C is cooled to room temperature, the 400-nm band intensity remains almost unchanged, but the T-band intensity is reduced to a value slightly smaller than that at room temperature before heat of the solution (not shown); the variation in the intensity of the 400-nm band as a function of temperature is irreversible, but that of the T-band is almost reversible. For the chloro complex system, the similar trend for the spectral changes with temperature is observed but not significantly. These facts suggest that the 400-nm band occurs more easily for the bromo complex system than for the chloro complex one and that this band is the more strengthened, the T-band is the more suppressed. (iii) In relation to the 400-nm band, a weak and broad absorption is observed in the region of ≈350—≈440 nm in each of the spectrum of the 3-Me-py solution of KBr, $N(CH_3)_4Br$, $ZnBr_2$, or $NiBr_2$.[9]

By the way, Cabral et al.[2] have concluded that for the tetrahedral complex $[CoBr_2(3\text{-Me-py})_2]$ in nitromethane in the presence of an excess of 3-Me-py, the reaction of exchanging Br^- by 3-Me-py occurs at room temperature. Therefore, from the results of this investigation in addition to the conclusion of Cabral et al.,[2] besides the main reaction of Eq. 1, the following dissociation reaction of the tetrahedral complex occurs in the 3-Me-py solutions and shifts toward a new octahedral species with increasing temperature

$$\underset{\text{(tetrahedral)}}{[CoX_2(3\text{-Me-py})_2]} + (4-x)(3\text{-Me-py}) \longrightarrow \underset{\text{(octahedral)}}{[CoX_x(3\text{-Me-py})_{6-x}]^{(2-x)+}} + (2-x)X^-, \quad (4)$$

where x=0 or 1. The reaction of Eq. 4 is greatly dependent on the temperature for the bromo complex system, but is little for the chloro complex system.

Although any spectral evidence for the presence of the octahedral $[CoX_x(3\text{-Me-py})_{6-x}]^{(2-x)+}$ complex can not be obtained, a free X^- ion in 3-Me-py solutions is probably related to the appearance of the 400-nm band. That is, from the facts (i)—(iii) described above, the 400-nm band may be assigned to a charge-transfer band occurring in a contact ion pair of X^- with a solvent molecule of 3-Me-py.

To our knowledge, there have been some reports on the charge-transfer spectra of ion pairs between halide ions and another ions or molecules the absorption maxima of which lie in relatively long wavelength such as 400 nm. Briegleb et al.[10] have reported that in the interaction of halides e.g. LiI or LiBr (electron donor is I^- or Br^-) with trinitrobenzene in different kinds of solvents, the absorption maximum lies in 385—476 nm for the iodo complex and in 294—370 nm for the bromo complex. Dwivedi and Rao[11] have found that for the $(C_7H_{15})_4N^+X^-$-trinitrobenzene systems in CCl_4, $CHCl_3$, or CH_2Cl_2, the charge-transfer bands appear at 323 nm for X=Cl, at 371—383 nm for X=Br, and at 450—475 nm for X=I. In comparison with these authors' results, the assignment of the 400-nm band in the present study may be reasonable.

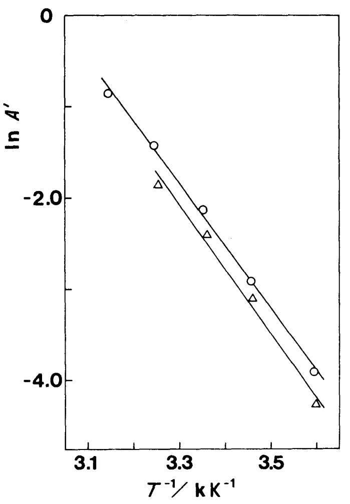

Fig. 6. Logarithm of the corrected absorbance A' vs. reciprocal of absolute temperature.
○: $CoCl_2$, △: $CoBr_2$, ——: calculated fitting lines.

The heat of reaction, ΔH, is estimated in the lower-temperature range (the tetrahedral $[CoX_2(3\text{-Me-py})_2]$ species is regarded as the product). As described in Ref. 5, the change in the equilibrium constant with temperature can be followed by the absorbance change of the 665-nm shoulder for the chloro complex and the 648-nm peak for the bromo complex. In Fig. 6, the logarithm of the corrected absorbance A' is plotted against the reciprocal of absolute temperature. As the thermal expansion coefficient of 3-Me-py has never been estimated, the corresponding value of pyridine (0.001 K^{-1})[12] is used as the approximate value for 3-Me-py over the temperature range in order to obtain the corrected absorbance A'.

As shown in Fig. 6, the plots are fitted to straight lines, indicating that ΔH is constant for each of the halo complex reaction of Eq. 1 over the lower-temperature range. From the slopes of the lines, ΔH is estimated for the chloro complex as 56.7 kJ mol^{-1} over the range of 5.0—44.8 °C and for the bromo complex as 58.6 kJ mol^{-1} between 4.8 and 34.2 °C.

The value of 56.7 kJ mol^{-1} for the chloro complex is compatible with 56.1 kJ mol^{-1} of Cabral et al.[2] Like the CoX_2-pyridine system,[5] ΔH is also larger for the bromo complex (58.6 kJ mol^{-1}) than for the chloro complex (56.7 kJ mol^{-1}) in this CoX_2-3-Me-py system.

This tendency is consistent with the proposal of King et al.[1] that ΔH is a measure of Co(II)-pyridine base dative π-bonding which increases with decrease in the electronegativity of X. For the chloro complexes, ΔH is larger for the pyridine system (57.3 kJ mol^{-1}) than for the 3-Me-py one (56.7 kJ mol^{-1}). The similar relation can be found between the two bromo complexes (60.7 and 58.6 kJ mol^{-1}). This tendency may be accounted for by the result of Cabral et al.[2] that ligand pyridine is a better π-accepter compared with ligand 3-Me-py.

The author would like to express his sincere thanks to Professor Jiro Matsuda of Ritsumeikan University for valuable discussions, critical reading of the manuscript, and continuous encouragements. The author also wishes to thank Professor Ikuji Tsujikawa of Kyoto University for his encouragements. Thanks are due to Mr. Masao Yoshikawa for his support in the experiment. This work was partially supported by a Grant-in-Aid for Scientific Research No. 59470038 from the Ministry of Education, Science and Culture.

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8) As will be described below in the temperature effect, an appearance of a 400-nm band is probably related to the existence of another kind of reaction besides the equilibrium of Eq. 1. However, it is observed that the 400-nm band scarcely changes with pressure and is also not the cause of the enhancement of the intensity below about 460 nm described above. Therefore, it is thought to be reasonable that only the equilibrium of Eq. 1 is influenced by pressure.

9) The experiment has been done as follows: The four kinds of bromide were dried under reduced pressure at about 105 °C to constant weight. After dried with anhydrous $CaSO_4$, 3-Me-py was distilled. Each salt was sealed with 3-Me-py into a glass tube, and then kept for a month at about 70 °C in a drying box. The spectra were recorded at room temperature. If the experiment for the salts of chloride is done, similar results with the bromide will be expected.

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