Nuclear Quadrupole Resonance of Chlorine-35 in Molybdenum(V) and Rhenium(III) Chlorides. Evidence for the Crystal Modifications of $MoCl_5$

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Synopsis. The ^{35}Cl NQR frequencies were determined for molybdenum(V) and rhenium(III) chlorides at various temperatures. Two crystal modifications, showing two and three ^{35}Cl NQR frequencies, were found for the former compound. The three resonance frequencies observed for the latter compound are attributable to three chemically different chlorine atoms in the crystal.

Molybdenum(V) and rhenium(III) chlorides are known to form crystals in which polymeric units, Mo_2Cl_{10} and Re_3Cl_9, respectively, are discernible.[1,2] It is interesting to examine the temperature dependence of ^{35}Cl NQR frequencies for both compounds, because there exist both terminal and bridging chlorine atoms, which usually yield temperature dependences considerably different from each other.

Experimental

Molybdenum(V) chloride $MoCl_5$ was procured from commercial sources and was purified by means of a sublimation method similar to that described in the literature.[3] Commercial $MoCl_5$ was placed in the end of a Pyrex bulb train, and the sublimation system including the train was evacuated. When the bulb containing crude $MoCl_5$ was heated to about 130 °C, dark purple crystals were deposited in the next-neighboring bulb. The temperature of this bulb was maintained at a lower temperature than about 40 °C. After the sublimation process had finished, the bulb was sealed off at each side, with great care being taken not to heat the deposited crystals. The sample thus prepared is called $MoCl_5$ (I). When the bulb containing $MoCl_5$ (I) was heated very rapidly by a flame to the melting point of $MoCl_5$, the deposited crystals were melted without breaking the Pyrex bulb. The melted $MoCl_5$ was cooled very slowly, and black crystals with a bluish gloss were obtained. The sample obtained after melting is called $MoCl_5$ (II). Since the X-ray analysis of $MoCl_5$ was carried out with the sample prepared by melting,[1] $MoCl_5$ (II) is considered to have a dimeric structure. Commercial rhenium(III) chloride $ReCl_3$ was purified by use of a similar sublimation method. The chloride was sublimed at a temperature of about 450 °C under reduced pressure.

Chlorine NQR was observed by means of a modified Dean-type spectrometer in a frequency-modulation mode.[4]

Results and Discussion

Table 1 shows the NQR frequencies of ^{35}Cl in $MoCl_5$ and $ReCl_3$ at room, Dry Ice, and liquid-nitrogen temperatures.

The sample $MoCl_5$ (I) yielded four rather closely separated resonance frequencies at various temperatures observed. The second-highest frequency line was broad and weak, whereas other lines were moderately strong and had a relatively narrow line-width. The relative intensity of the second-highest line to that of other lines varied depending on the samples, which were different from each other in the deposit temperature in the sublimation purification process. The sample deposited at a lower temperature gave a weaker second-highest line. Furthermore, the resonance frequencies of the second-highest line determined at various temperatures agree with those reported by Brown and Kent[5] for Mo_2Cl_{10}. The sample $MoCl_5$ (II), prepared by melting, showed two widely separated broad resonance lines at liquid N_2 temperature, the higher-frequency line of which yielded a resonance frequency identical with that of the second-highest line of $MoCl_5$ (I). The lower-frequency line of the doublet, which escaped detection in the study of Brown and Kent,[5] was weaker. With increasing the tem-

TABLE 1. NQR FREQUENCIES OF ^{35}Cl IN MOLYBDENUM(V) AND RHENIUM(III) CHLORIDES

Compound	NQR frequency ν/MHz		
	27 °C	−78 °C	−196 °C
$MoCl_5$ (I)	14.224±0.01	14.346±0.01	14.471±0.01
	14.036±0.01	14.114±0.01	14.206±0.01
	13.904±0.01	13.977±0.01	14.063±0.01
$MoCl_5$ (II)	14.10 ±0.02	14.19 ±0.02	14.27 ±0.02
	(fade-out at −50 °C)	12.22 ±0.02	12.18 ±0.02
$ReCl_3$	21.772±0·003	21.843±0.003	21.921±0.003
	16.475±0.003	16.481±0.003	16.494±0.003
	15.040±0.003	15.058±0.003	15.074±0.003

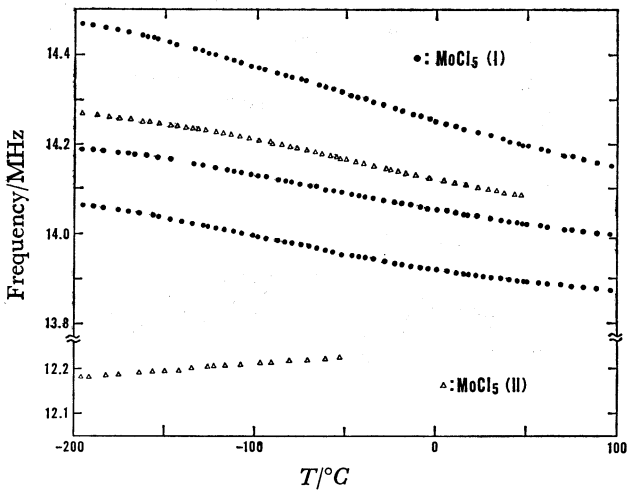

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in $MoCl_5$ (I) prepared by sublimation and $MoCl_5$ (II) obtained by once melting $MoCl_5$ (I).

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perature from liquid N_2 temperature, this line showed a positive temperature coefficient, as shown in Fig. 1; it gradually became weaker until it faded out at about −50 °C. These experimental facts indicate that molybdenum(V) chloride directly crystallized by sublimation gives three ^{35}Cl NQR frequencies at various temperatures, whereas the compound once melted yields two widely separated lines. Accordingly, it is concluded that there exist two crystalline modifications in molybdenum(V) chloride: one, the crystal directly deposited from its vapor, has at least three nonequivalent chlorine atoms in the crystal, while the other is the crystal once melted and contains at least two chemically different chlorine atoms.

Three widely separated ^{35}Cl NQR frequencies were observed for rhenium(III) chloride at various temperatures studied. This indicates that there exist three chemically nonequivalent chlorine atoms in the crystal. According to the X-ray crystal analysis by Cotton and Mague,[2] crystallographically equivalent trimer units, Re_3Cl_9, exist in the crystal. In a trimer unit, there are three chemically nonequivalent chlorine atoms: terminal chlorine, **a**, asymmetric bridging chlorine, **b**, and symmetric bridging chlorine, **c**. Consequently, the present NQR results agree well with those of the X-ray analysis.

The highest-frequency line of the triplet is greatly separated from the remaining two lines. By referring to the NQR results of dimeric IIIB metal halides,[6,7] this line can be assigned to the terminal chlorine, **a**, and the lower-frequency lines, to the bridging chlorine atoms, **b** and **c**. Since the asymmetric bridging chlorine **b** forms a weak bridge bond with rhenium in the neighboring trimer, the chlorine atom may have a character of terminal chlorine to some extent. Accordingly, the middle-frequency and the lowest-frequency lines can be assigned to the bridging chlorine atoms, **b** and **c**, respectively.

The temperature coefficients, $|d\nu/dT|$, of the middle-frequency and lowest-frequency lines were very small (0.09 and 0.15 kHz K^{-1}, respectively, in the temperature range of −196—27 °C). Since bridging chlorine is usually bound more tightly than terminal chlorine, the thermally excited vibrational amplitude of the former chlorine atom is smaller than that of the latter. According to the simple Bayer-Kushida theory,[8,9] the coefficient, $|d\nu/dT|$, is proportional to the vibrational amplitude. This fact supports the above assignments of the observed resonance frequencies.

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