 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2211—2212 (1981)

^{14}N Nuclear Quadrupole Resonance Spectra of $K_2SrCu(NO_2)_6$, $K_2BaCu(NO_2)_6$, and $Cs_2PbCu(NO_2)_6$

Tetsuo ASAJI,* Jun ISHIKAWA, Ryuichi IKEDA, and Daiyu NAKAMURA
Department of Chemistry, Nagoya University, Chikusa-ku, Nagoya 464
(Received January 24, 1981)

Synopsis. The ^{14}N NQR frequencies of $K_2SrCu(NO_2)_6$, $K_2BaCu(NO_2)_6$, and $Cs_2PbCu(NO_2)_6$ were determined at various temperatures below about 155, 67, and 235 K, respectively. The results are discussed in referring to their crystal structure.

Recently, a number of structural studies[1–8] have been made on the compound $R_2MCu(NO_2)_6$ (R=K, Rb, Cs, NH_4, Tl and M=Pb, Ca, Sr, Ba) and it became obvious that this series of compounds can be classified into two distinct classes through the sort of the bivalent cation M. The compounds containing Pb form cubic crystals in their high-temperature phase and exhibit successive phase transitions with decreasing temperature. In their lowest-temperature commensurate phase, these crystals are thought to have a pseudotetragonal lattice with $c/a<1$.[1–6] On the other hand, the crystals containing the alkali earth metal atoms have a pseudotetragonal lattice with $c/a>1$ at room temperature[6–8] and the occurrence of phase transition has not been reported as yet.

In a preceding paper,[9] we reported the existence of at least two sets of ^{14}N nuclear quadrupole resonance (NQR) frequencies in the low-temperature phase of the former class compounds. However, there remains an unsolved problem on the assignment of the observed frequencies to nonequivalent nitrogen atoms in the crystals. Accordingly, we have undertaken the present investigation of the ^{14}N NQR of the latter compounds to clarify this point.

Experimental

The samples employed for the measurements of NQR and DTA (differential thermal analysis) were synthesized according to the method reported by Reinen *et al.*,[6] and identified by recording X-ray powder patterns. A modified Pound-Watkins type spectrometer operated in a frequency modulation mode[10] was used for the observation of ^{14}N NQR signals. The sample temperature was determined by employing the usual method already described elsewhere.[9] DTA curves were taken by means of a home-made apparatus previously described.[11]

Results and Discussion

Three NQR frequencies ν^{I}, ν^{II}, and ν^{III} defined below are usually observed for ^{14}N nuclei in compounds.

$$\left.\begin{array}{l}\nu^{I} = (3/4h)eQq(1+\eta/3),\ \nu^{II} = (3/4h)eQq(1-\eta/3) \\ \nu^{III} = (1/2h)eQq\cdot\eta.\end{array}\right\} \quad (1)$$

Here, eQq and η denote the quadrupole coupling constant and the asymmetry parameter, respectively. The ν^{I} and ν^{II} frequencies and their signal-to-noise ratios (S/N) determined at various temperatures are given in Table 1.

A single pair of ν^{I} and ν^{II} frequencies was observed for both of $K_2SrCu(NO_2)_6$ and $K_2BaCu(NO_2)_6$. For the former compound ν^{I} and ν^{II} could be detected up to about 110 and 155 K, respectively, while for the latter up to about 45 and 67 K, respectively. Both frequencies of $K_2SrCu(NO_2)_6$ decreased smoothly with increasing temperature up to respective fade-out temperatures, indicating that no phase transition takes place below 155 K. To examine the thermal properties of $K_2SrCu(NO_2)_6$, we carried out the experiment of DTA and found no thermal anomaly in the temperature range of 143—323 K. Accordingly, it can be concluded that $K_2SrCu(NO_2)_6$ retains its crystal symmetry determined at room temperature unaltered down to liquid helium temperature. For $K_2BaCu(NO_2)_6$, the resonance frequencies decreased smoothly with increasing temperature, indicating the absence of phase transition between 2 and 67 K.

The caesium salt, $Cs_2PbCu(NO_2)_6$ yielded two sets of ν^{I} and ν^{II} lines at liquid helium temperature. With increasing temperature, these ν^{I} and ν^{II} lines decreased their frequency smoothly and disappeared in the noise level at about 124 and 235 K, respectively. The latter temperature is lower by 50 K than the lowest transition temperature of the caesium salt.[12]

According to Takagi *et al.*,[8] all the complex ions $[Cu(NO_2)_6]^{4-}$ having an orthorhombic symmetry are crystallographically equivalent in the crystals of $K_2SrCu(NO_2)_6$. Therefore, three kinds of crystallographically nonequivalent nitrogen atoms exist in the crystals: one kind of axially elongated nitrogen atoms (Cu–N: 2.31 Å) and two kinds of equatorial nitrogen atoms (Cu–N: 2.04 and 2.03 Å). The fact that the Sr compound shows only one set of ^{14}N NQR frequencies suggests that only the elongated nitrogen atoms afford detectable NQR signals. The NQR signals of the other nitrogen atoms may be undiscernibly broadened owing to the magnetic disturbance of the Cu(II) unpaired electron situated near to the nitrogen atoms.

The NQR parameters, eQq/h and η obtained at 4.2 K are given in Table 2 with those of $R_2PbCu(NO_2)_6$ for comparison. The $R_2PbCu(NO_2)_6$ type complexes except for $(NH_4)_2PbCu(NO_2)_6$ yield two sets of the parameters.[9] The ammonium salt shows an additional structural phase transition at 94.5 K, above which temperature the salt also yields two sets of the parameters. On the X-ray and neutron diffraction studies of $K_2PbCu(NO_2)_6$, Noda *et al.*[1] interpreted their experimental results in terms of a structural model proposed by Reinen *et al.*[6] In this model, local tetragonal elongation of a complex ion takes place and the axis of the elongation alternates between the a- and b-axis of the pseudotetragonal crystal. Taking into account of the configuration of oxygen atoms, this indicates that there exist two crystallographically different elongated complex ions. Accordingly, there are two nonequivalent nitrogen atoms

Table 1. ^{14}N NQR frequencies (±0.1 kHz) and their signal-to-noise ratios (S/N) of $K_2SrCu(NO_2)_6$, $K_2BaCu(NO_2)_6$, and $Cs_2PbCu(NO_2)_6$ determined at various temperatures

Compound	Temp/K	ν^{I}/kHz	(S/N)	ν^{II}/kHz	(S/N)
$K_2SrCu(NO_2)_6$	2	4555.8	(≈200)	3527.9	(≈400)
	18	4555.8	(8)	3527.9	(35)
	77	4547.0	(≈4)	3525.3	(≈7)
	109	4536.7	(3)	3521.2	(5)
	155	—		3511.7	(5)
$K_2BaCu(NO_2)_6$	2	4572.8	(60)	3541.1	(170)
	20	4572.1	(4)	3540.9	(10)
	45	4566.5	(2)	3539.7	(5)
	67	—		3537.9	(3)
$Cs_2PbCu(NO_2)_6$	2	4496.2	(150)	3508.1	(200)
		4495.4	(150)	3512.1	(230)
	22	4496.0	(7)	3508.0	(6)
		4495.2	(7)	3512.0	(6)
	77	4490.5	(≈5)	3504.5	(≈4)
		4489.7	(≈5)	3508.5	(≈4)
	124	4478.2	(3)	3495.5	(3)
		4477.6	(3)	3499.7	(3)
	235	—		3458.4	(2)
		—		3463.2	(2)

Table 2. ^{14}N NQR parameters of $R_2MCu(NO_2)_6$ type complexes determined at 4.2 K

$R_2MCu(NO_2)_6$		Ref.	Quadrupole parameter	
R	M		(eQq/h)/kHz	η
K	Ba	this work	5409.3	0.3815
K	Sr	this work	5389.3	0.3815
K	Pb	9	5363.5	0.3752
			5360.5	0.3737
NH_4	Pb	9	5357.5	0.3744
Rb	Pb	9	5348.3	0.3743
			5345.5	0.3722
Cs	Pb	this work	5336.1	0.3703
			5338.3	0.3684
Tl	Pb	9	5296.1	0.3510
			5293.7	0.3498

having longer Cu–N distances and it is considered that these nitrogen atoms afford detectable NQR signals.[9,13)]

References

1) Y. Noda, M. Mori, and Y. Yamada, *J. Phys. Soc. Jpn.*, **45**, 954 (1978).

2) B. V. Harrowfield and J. R. Pilbrow, *J. Phys. C*, **6**, 755 (1973).

3) S. Takagi, M. D. Joesten, and P. G. Lenhert, *Acta Crystallogr., Sect. B*, **32**, 1278 (1976).

4) D. Mullen, G. Heger, and D. Reinen, *Solid State Commun.*, **17**, 1249 (1975).

5) B. V. Harrowfield, A. J. Dempster, T. E. Freeman, and J. R. Pilbrow, *J. Phys. C*, **6**, 2058 (1973).

6) D. Reinen, C. Friebel, and K. P. Reetz, *J. Solid State Chem.*, **4**, 103 (1972).

7) S. Takagi, P. G. Lenhert, and M. D. Joesten, *J. Am. Chem. Soc.*, **96**, 6606 (1974).

8) S. Takagi, M. D. Joesten, and P. G. Lenhert, *Acta Crystallogr., Sect. B*, **32**, 2524 (1976); *ibid.*, **31**, 596 (1975).

9) T. Asaji, R. Ikeda, and D. Nakamura, *Z. Naturforsch., B*, **34**, 1722 (1979).

10) R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **70**, 3626 (1966).

11) Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.*, **33**, 331 (1979).

12) M. Mori, Y. Noda, and Y. Yamada, *Solid State Commun.*, **27**, 735 (1978).

13) H. Chihara and N. Nakamura, "Advances in Nuclear Quadrupole Resonance," ed by J. A. S. Smith, Heyden, London (1980), Vol. 4, p. 62.