Calculations were also carried out with $Z = 6$ and the values of ΔA obtained are about 3.5% smaller.

Within the experimental errors the values of ΔA_1 in mixtures of two nitrates (a and b) obey the linear relation[7]

$$\Delta A_1(\text{mixture}) = x_a \Delta A_1(\text{in pure a}) + x_b \Delta A_1(\text{in pure b}) \quad (6)$$

where x is the mole fraction of the nitrates. This equation was found to be followed by the Cl^- and Br^- complexes of Ag(I) in $NaNO_3$ and KNO_3 mixtures. In spite of the large difference between the ionic radii of Li^+ and K^+ this relation was used to calculate the value of ΔA_1 for the Cl^- and Br^- complexes of Ag(I) in pure $LiNO_3$ melt using the values of ΔA_1 for pure KNO_3 obtained by Manning, *et al.*,[8] and assuming that they are independent of temperature. The values found are given in Table IV together with the values for other melts. The values of $-\Delta A_1$ for the pure $LiNO_3$ melt seem large when compared with those for pure $NaNO_3$ or KNO_3. This type of anomalous behavior of the melts containing $LiNO_3$ has also been observed in the formation of $CdBr^+$ and $CdBr_2$[9] and $AgCl$[10] complexes in $LiNO_3$–KNO_3 mixtures. In these systems the values of $-\Delta A_i$ become larger as the mole fraction of $LiNO_3$ increases and the values are larger than in the corresponding $NaNO_3$–KNO_3 mixtures. These anomalous effects have been explained on the basis of a smaller effective radius of the nitrate ion in lithium-containing melts.[9-11] Thomas and Braunstein[10] have pointed out some of the difficulties of emf measurements at high lithium nitrate concentration and the solubility method reported here may be more effective for exploring high lithium systems.

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Low-Temperature Far-Infrared Spectra of Hexanitro Complex Salts[1]

BY ICHIRO NAKAGAWA,[2a] TAKEHIKO SHIMANOUCHI,[2a] AND KAZUO YAMASAKI[2b]

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Far-infrared spectra of $M_3[Co(NO_2)_6]$ (M = Na, K, Rb, and Cs) and $M'_2M''[Ni(NO_2)_6]$ (M' = K and Na; M'' = Ca and Ba) have been measured down to 50 cm^{-1} at room temperature and liquid nitrogen temperature. Lattice vibrations due to the displacements of the outer cations relative to the complex ion are observed below 200 cm^{-1}. Those frequencies change depending upon the mass of the cations and the interionic potential constants. The far-infrared bands due to the lattice vibrations and the intramolecular vibrations in the complex ion were both interpreted for $M_3[Co(NO_2)_6]$ and K_2Ca- and K_2Ba-$[Ni(NO_2)_6]$ by the normal-coordinate analysis of the crystal as a whole, on the basis of the T_h^3 structure determined by the X-ray analysis, only the interaction between the outer cations and the oxygen atoms being taken into account. $Na_3[Co(NO_2)_6]$ reveals quite a different spectrum from those for the other complex salts, in the lattice vibration region as well as in the intramolecular vibration region. This complex spectrum has been interpreted satisfactorily on the basis of the C_{3i} deformed structure.

Introduction

In a previous report we discussed the lattice vibrations of hexanitrocobalt(III) complex salts.[3] We also reported that the Na salt revealed a much more complicated spectrum than the K, Rb, and Cs salts.[3,4] From the viewpoint of the intramolecular vibrations we concluded that the $Co(NO_2)_6^{3-}$ ion in the Na salt has C_{3i} (S_6) symmetry instead of T_h symmetry.[4a]

A far-infrared spectral measurement at liquid nitrogen temperature has recently enabled us to obtain more distinct bands than those at room temperature and we have obtained well-defined far-infrared spectra in the region down to 50 cm^{-1} at low temperature as well as room temperature for a series of $M_3[Co(NO_2)_6]$ compounds (M = Na, K, Rb, and Cs). A similar measurement has been extended to the hexanitronickel(II) complex salts such as $K_2Ca[Ni(NO_2)_6]$, $K_2Ba[Ni(NO_2)_6]$, and $Na_2Ba[Ni(NO_2)_6]$.

In the present paper we give the summary of the experimental results and discuss the nature of the lattice vibrations as well as the intramolecular vibrations, on considering the frequency shifts with the lowering of temperature. A normal-coordinate analysis of $Na_3[Co(NO_2)_6]$ has been made on the basis of the structure with the space group C_{3i}, without separating the lattice vibrations and the intramolecular vibrations in the $Co(NO_2)_6^{3-}$ ion. These results yield important infor-

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mation regarding the interaction between the complex ion and the outer cations.

Experimental Section

Samples.—$Rb_3[Co(NO_2)_6]$ and $Cs_3[Co(NO_2)_6]$ were prepared by the reaction of RbCl and CsCl with $Na_3[Co(NO_2)_6]$, respectively. The colors of these samples are lemon yellow.

$K_2Ba[Ni(NO_2)_6]$ and $K_2Ca[Ni(NO_2)_6]$ were prepared by the method given in the literature.[5,6] The former is lemon yellow and the latter is brownish yellow.

Measurement of Spectra.—A Hitachi FIS-1 vacuum far-infrared spectrophotometer (500–50 cm^{-1}) was used. The samples dispersed in a polyethylene sheet and a Nujol mull were used for the measurement of far-infrared spectra. Low-temperature measurements at liquid nitrogen temperature were made for the Nujol mull samples inserted into the two silicon plates contacted with the metal conductor in the low-temperature cell.[7] Observed low-temperature spectra are reproduced in Figures 1 and 2.

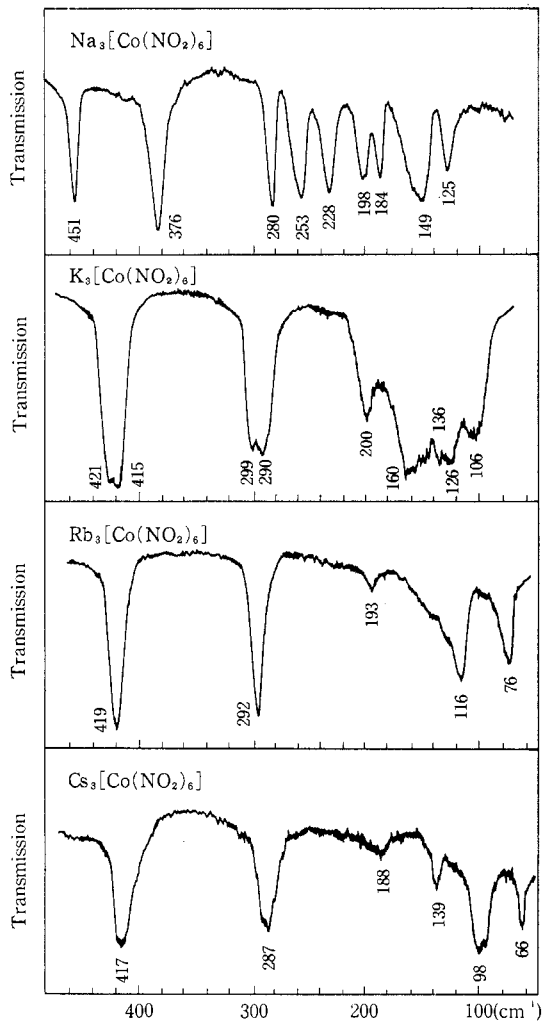

Figure 1.—Far-infrared spectra of hexanitrocobalt(III) complex salts (Nujol mull) at liquid nitrogen temperature.

Observed Frequencies.—Spectral measurements are limited to the transmittance, and throughout this study we regard the absorption frequencies obtained from the transmittance of the powder samples as ν_0's (resonance frequencies or the minimum transmission frequencies as a thickness $d \rightarrow 0$). The difference

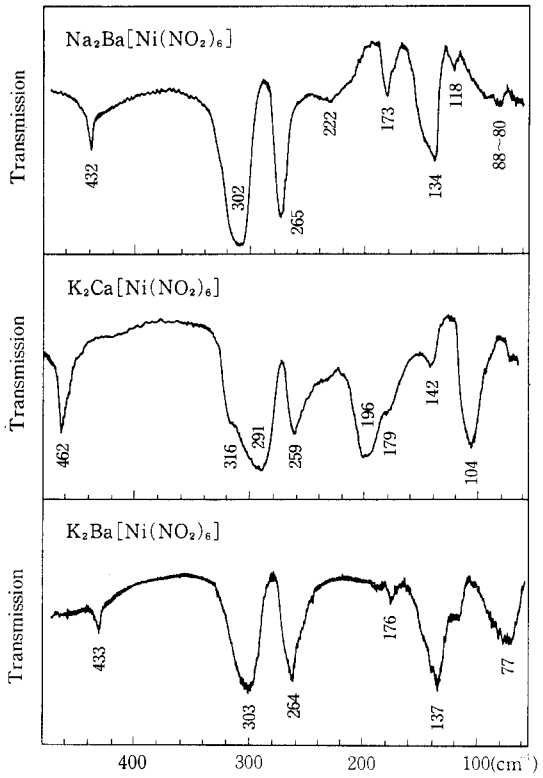

Figure 2.—Far-infrared spectra of hexanitronickel(II) complex salts (Nujol mull) at liquid nitrogen temperature.

between the resonance frequencies obtained from the reflection data of a crystal and those from the transmission data of a powder sample is less than 5% for the lattice vibrations of an ionic crystal such as $KNiF_3$ and $KMgF_3$, according to the results by Perry, *et al.*[8]

For ionic cubic crystal systems the transverse and longitudinal optical modes may be split. However, the transverse frequencies ν_t's correspond to the resonance frequencies ν_0's and accordingly the observed values here may be regarded as ν_t's which can be determined by the local restoring forces on the basis of the model of the molecular dynamics.

Results and Discussion

(1) **$M_3[Co(NO_2)_6]$ (M = K, Rb, and Cs).**—The crystal structure is cubic with the space group T_h^3 as shown in Figure 3.[9,10] The Bravais unit cell is composed of 22 atoms, $M_3[Co(NO_2)_6]$, one complex ion ($Co(NO_2)_6^{3-}$), and three outer cations (3 M^+). The result of the factor group analysis is shown in Table I, from which ten vibrations of the F_u species are expected to be observed in the infrared spectra. The spectra shown in Figure 1 in the region below 500 cm^{-1} reveal six bands for these complex salts. In the higher frequency region not shown here there are four bands, corresponding to the NO_2 symmetric and antisymmetric stretching, NO_2 scissoring, and NO_2 wagging modes; therefore, the total number of the observed infrared bands is 10 as expected in Table I. The bands for each complex become sharp and shift to the higher frequency side with lowering temperature. In the region below 150 cm^{-1} there are

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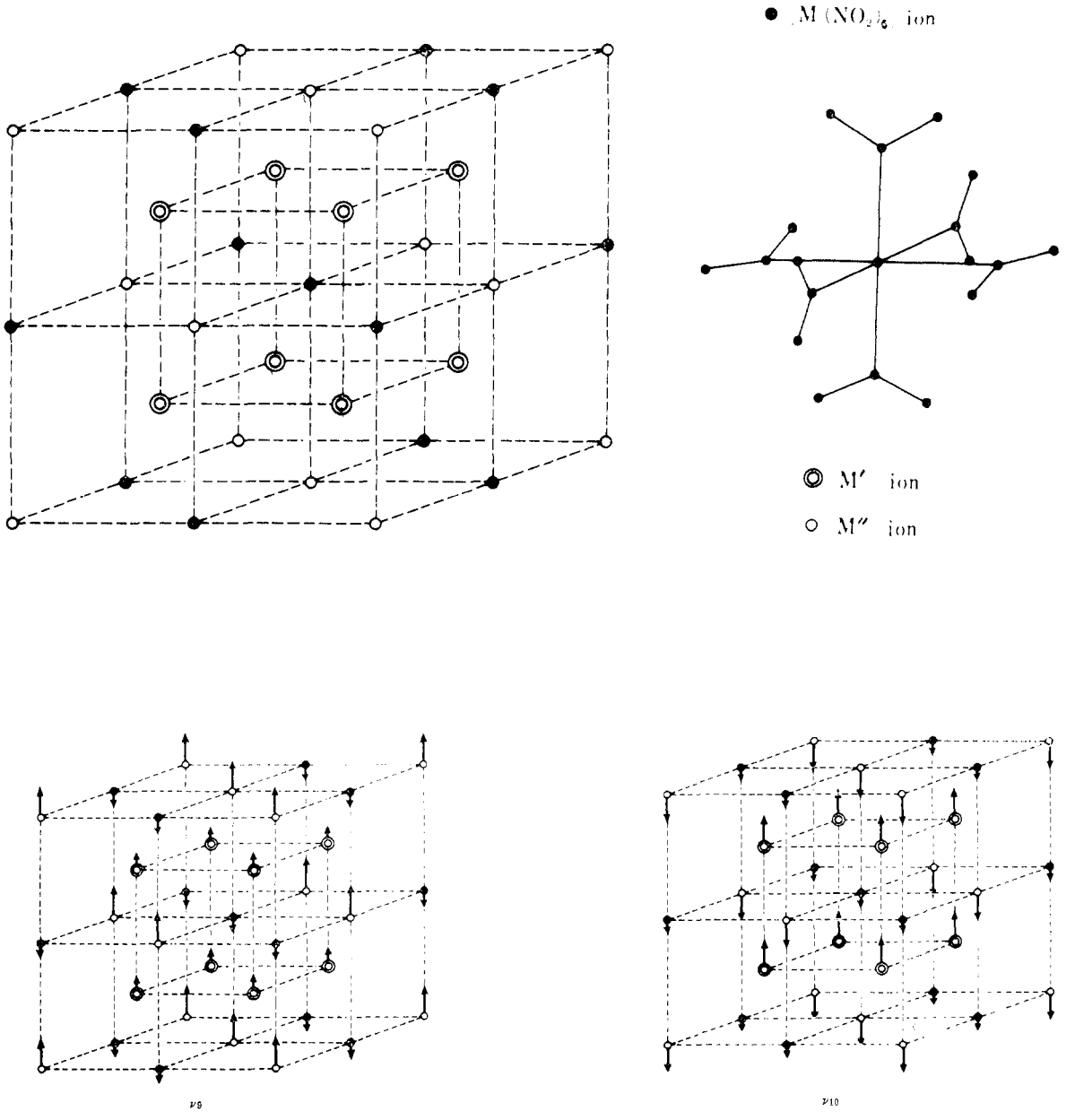

Figure 3.—Structure of hexanitro complex salts with the space group T_h^3 and approximate modes of lattice vibrations ν_9 and ν_{10}.

TABLE I

FACTOR GROUP ANALYSIS OF $M_3[Co(NO_2)_6]$ (K, Rb, and Cs)[a]

T_h^3	N	T	T'	R'	n	
A_g	3	0	0	0	3	R
A_u	1	0	0	0	1	ia
E_g	3	0	0	0	3	R
E_u	1	0	0	0	1	ia
F_g	7	0	1	1	5	R
F_u	11	1	2	0	8	ir

[a] Symbols: N, number of the total freedoms; T, number of the acoustical translational motions; T', number of the optical translational lattice vibrations; R', number of the rotational lattice vibrations; n, number of the intramolecular vibrations of $Co(NO_2)_6^{3-}$ ion; R, Raman active; ir, infrared active; ia, inactive.

two bands which change their frequencies considerably with the outer cations (132, 109, 94 cm^{-1} and 106, 74, 63 cm^{-1}, for K, Rb, and Cs salts, respectively). They may primarily arise from the lattice vibrations due to the interaction between the complex ion and the outer cations.

The optically active vibration frequencies of the crystal are calculated according to the procedure described in previous papers,[3,11] by using the potential function $V = V_{intra} + V_{inter}$, where V_{intra} denotes the intramolecular potential in the complex ion, which we have discussed in several of our previous papers.[4b,12-14] The values of the intramolecular force constants used in the calculation are listed in the Appendix. V_{inter} denotes the interionic interaction potential and we assume that this term arises from the interaction between the M^+ ions and the neighboring O atoms. For

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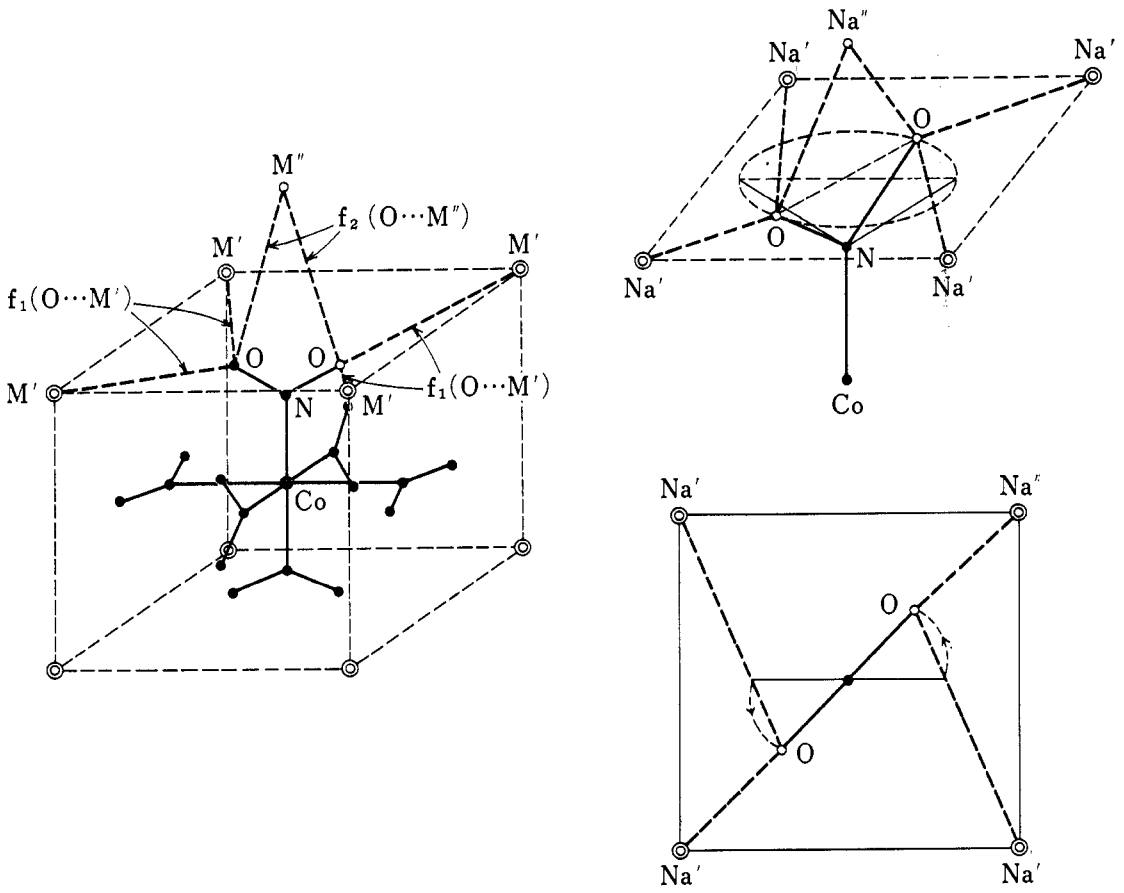

Figure 4.—Positions of oxygen atoms and outer cations for $M_3[Co(NO_2)_6]$ (M = K, Rb, and Cs) and $Na_3[Co(NO_2)_6]$.

these complex salts the nearest and the second nearest $M^+\cdots O$ distances are 2.80–3.15 Å ($q_2(M''\cdots O)$) and 3.05–3.30 Å ($q_1(M'\cdots O)$), respectively (see Figure 4 and Table II). The interaction between the atoms whose distances are longer than 3.5 Å is not taken into consideration.

The calculated frequencies and the interionic potential constants are shown in Table II, where only the vibration frequencies of the F_u species are given to save space. We can see that the observed bands for this series of complex salts are explained satisfactorily by the above potential function and by the use of the interionic potential constants $f(M^+\cdots O)$ of *ca.* 0.1 mdyn/Å which change slightly depending upon the interatomic distances.

The displacement of each atom is obtained from the elements of the $\mathbf{L}_x$ matrix (the eigenvector of the $\mathbf{M}^{-1}\mathbf{F}_x$ matrix and the transformation matrix between the Cartesian displacement coordinates $\mathbf{X}$ and the normal coordinates $\mathbf{Q}$, $\mathbf{X} = \mathbf{L}_x\mathbf{Q}$).[2] We can see from this calculation that M′ and M″ displace in the same direction for the ν_9 mode and in the opposite direction for the ν_{10} mode, though in the ν_9 vibration for the K and Rb salts the lattice modes are coupled appreciably with the intramolecular modes. A sketch of the approximate motion is given in Figure 3.

(2) **$Na_3[Co(NO_2)_6]$**.—No structural analysis has been made for this complex salt. As shown in Figures 1 and 2 the spectrum of the Na salt is quite different from those for the K, Rb, and Cs salts. In the previous note we attributed this remarkable difference in the spectrum to the lowering of the symmetry of the $Co(NO_2)_6^{3-}$ ion from T_h to C_{3i} (S_6) through the analysis of

TABLE II

Observed and Calculated Frequencies (cm^{-1}) of $M_3[Co(NO_2)_6]$ Salts

T_h^3 F_u	$K_3[Co(NO_2)_6]$ Obsd	Calcd	$Rb_3[Co(NO_2)_6]$ Obsd	Calcd	$Cs_3[Co(NO_2)_6]$ Obsd	Calcd	Vib modes
ν_1	1386	1393	1399	1393	1400	1393	NO_2 antisym str
ν_2	1332	1325	1327	1325	1326	1325	NO_2 sym str
ν_3	827	818	827	818	832	817	NO_2 scissor
ν_4	637	619	633	619	630	618	NO_2 wag
ν_5	416	421	413	421	409	420	Co–N str
ν_6	293	293	287	288	281	286	NO_2 rock and skel def
ν_7	195	201	191	181	186	170	Skel def and M′ lattice
ν_8	154	157	141	149	136	141	Skel def, NO_2 rock, and M″ lattice
ν_9	132	162	109	117	94	95	M″ and M′ lattice
ν_{10}	106	106	74	76	63	59	M′ and M″ lattice

Interionic Potential Constants and Interatomic Distances of $M_3[Co(NO_2)_6]$ Salts

	$K^+\cdots O$	$Rb^+\cdots O$	$Cs^+\cdots O$
f_1, mdyn/Å	0.11	0.10	0.08
q_1, Å	3.05	3.15	3.30
f_2, mdyn/Å	0.14	0.12	0.10
q_2, Å	2.83	2.95	3.15

the intramolecular vibrations (see Figure 1 of ref 4a). This C_{3i} structure where the NO_2 plane rotates about the Co–N axis may be understood by the smaller ionic radius of the Na^+ ion, since for the T_h structure four interatomic distances, $q_1(Na'\cdots O)$ in Figure 4, are too large to form a stable crystal. When the $Co(NO_2)_6^{3-}$ ion takes a C_{3i} structure, two of the $q_1(Na'\cdots O)$ distances become shorter and a stable crystal may be formed (see Figure 4). In order to see whether this C_{3i} structure may explain the lattice frequencies as well as the intramolecular vibration frequencies for the Na salt, we made a calculation of optically active vibrational frequencies of crystal as a whole. In our assumed structure, Na^+ cations and Co atoms are located at the lattice points as shown in Figure 3 as in the case of a cubic crystal. However, owing to the twisting of the NO_2 plane, the crystal structure is no longer cubic. On the basis of the C_{3i} structure with a twisting angle of 30° and a = 10.00 Å, the interatomic distances $q(Na\cdots O)$ are calculated as: $q_1(Na'\cdots O)$ = 2.55 Å, $q_1'(Na'\cdots O)$ = 3.42 Å, and $q_2(Na''\cdots O)$ = 2.62 Å (see Figure 4).

The result of the factor group analysis is shown in Table III, from which both A_u and E_u vibrations are expected to appear in the infrared spectrum. In the A_u and E_u species two NO_2 twisting modes are included, whose intensities may be very weak. The calculated frequencies are given in Table IV, together with the interionic potential constants, where those for the A_g and E_g species are not included to save space. In this calculation the intramolecular force constants are the same as those for the K, Rb, and Cs salts (see Appendix). We can see in Table IV that the calculated frequencies for the C_{3i} crystal structure correspond with the observed frequencies.

TABLE III

FACTOR GROUP ANALYSIS OF $Na_3[Co(NO_2)_6]$[a]

C_{3i}	N	T	T'	R'	n	
A_g	10	0	1	1	8	R
A_u	12	1	2	0	9	ir
E_g	10	0	1	1	8	R
E_u	12	1	2	0	9	ir

[a] See Table I for the meanings of N, T, T', R', n, R, and ir.

In the spectrum of $Na_3[Co(NO_2)_6]$, each band shifts by 2–5 cm^{-1} to the higher frequency side with a lowering of temperature. Among them we see a remarkable frequency shift and an intensity enhancement for the band at 214 cm^{-1}. The reason for this feature is not certain. According to the calculation shown in Table IV, this band is assigned to the lattice vibration where the Na^+ ion displaces primarily.

(3) $K_2Ca[Ni(NO_2)_6]$, $K_2Ba[Ni(NO_2)_6]$, and $Na_2Ba[Ni(NO_2)_6]$.—For these complex salts we have two kinds of outer ions M'^+ and M''^{2+}. However, the crystal structure of $K_2Ca[Ni(NO_2)_6]$ and $K_2Ba[Ni(NO_2)_6]$ is cubic (a = 10.34 and 10.67 Å, respectively), with the space group T_h^3,[9] as in the case of $M_3[Co(NO_2)_6]$ (M = K, Rb, and Cs). No structural analysis has been made for $Na_2Ba[Ni(NO_2)_6]$.

TABLE IV

Calculated and Observed Frequencies (cm^{-1}) of $Na_3[Co(NO_2)_6]$

A_u	Calcd	Vib modes	E_u	Calcd	Vib modes	Obsd
ν_1	1389	NO_2 antisym str	ν_1'	1391	NO_2 antisym str	1425
ν_2	1324	NO_2 sym str	ν_2'	1324	NO_2 sym str	1333
ν_3	802	NO_2 scissor	ν_3'	801	NO_2 scissor	845, 831
ν_4	662	NO_2 wag	ν_4'	630	NO_2 wag	623
ν_5	382	Co–N str	ν_5'	441	Co–N str	449, 372
ν_6	270	NO_2 rock and skel def	ν_6'	283	NO_2 rock and Na'' lattice	276, 249
ν_7	219	Na'' lattice	ν_7'	237	Na' and Na'' lattice	214
ν_8	179	Skel def and Na' and Na'' lattice	ν_8'	194	Na'' lattice and NO_2 rock	195, 183
ν_9	163	Skel def and Na' and Na'' lattice	ν_9'	158	Skel def and Na' and Na'' lattice	147
ν_{10}	109	Na' lattice and skel def	ν_{10}'	133	Skel def	123
ν_{11}	94	NO_2 twist	ν_{11}'	94	NO_2 twist	...

Interionic Potential Constants and Interatomic Distances ($Na^+\cdots O$)

Constant	Value, mdyn/Å	Distance	Value, Å
f_1	0.15	q_1	2.55
f_1'	0.05	q_1'	3.42
f_2	0.15	q_2	2.62

The result of the factor group analysis given in Table I can be applied to the case of $K_2Ca[Ni(NO_2)_6]$ and $K_2Ba[Ni(NO_2)_6]$. The spectra shown in Figure 2 in the region below 500 cm^{-1} reveal seven bands for these complex salts and we have three bands (NO_2 stretching and scissoring vibrations) in the higher frequency region. Therefore, the infrared spectra of these complex salts are consistent with the cubic structure T_h^3. The calculated frequencies of $K_2Ca[Ni(NO_2)_6]$ and $K_2Ba[Ni(NO_2)_6]$ are given in Table V, together with the interionic potential constants. For $K_2Ca[Ni(NO_2)_6]$ the vibrations below 200 cm^{-1} show very complicated modes in which lattice modes of K^+ and Ca^{2+} ions and intramolecular deformation modes are mixed in a com-

TABLE V

Observed and Calculated Frequencies (cm^{-1}) of $K_2Ca[Ni(NO_2)_6]$ and $K_2Ba[Ni(NO_2)_6]$

T_h^3	$K_2Ca[Ni(NO_2)_6]$			$K_2Ba[Ni(NO_2)_6]$		
F_u	Obsd	Calcd	Vib modes	Obsd	Calcd	Vib modes
ν_1	1355	1388	NO_2 antisym str	1343	1387	NO_2 antisym str
ν_2	1325	1325	NO_2 sym str	1306	1325	NO_2 sym str
ν_3	834	838	NO_2 scissor	838 (813)	837	NO_2 scissor
ν_4	458	461	NO_2 wag	433	460	NO_2 wag
ν_5	284	306	Ni–N str and NO_2 rock and wag	291	304	Ni–N str and NO_2 rock and wag
ν_6	255	244	NO_2 rock and Ca lattice	255	230	NO_2 rock and skel def
ν_7	192	196	K lattice and skel def	173	180	K lattice and skel def
ν_8	176	154	Ca lattice and skel def	130	132	Skel def and K lattice
ν_9	135	140	Skel def and NO_2 rock	(130)	107	Skel def and NO_2 rock
ν_{10}	105	94	Ca and K lattice and skel def	80	73	Ba lattice

Interionic Potential Constants and Interatomic Distances

	$K_2Ca[Ni(NO_2)_6]$		$K_2Ba[Ni(NO_2)_6]$	
	$K^+\cdots O$	$Ca^{2+}\cdots O$	$K^+\cdots O$	$Ba^{2+}\cdots O$
f_1, mdyn/Å	0.12		0.10	
q_1, Å	3.01		3.13	
f_2, mdyn/Å		0.15		0.12
q_2, Å		2.77		2.93

plex manner. This may be due to the fact that the intrinsic intramolecular vibration frequencies of $Ni(NO_2)_6^{4-}$ are lower than those of $Co(NO_2)_6^{3-}$.

In the spectrum of $Na_2Ba[Ni(NO_2)_6]$ shown in Figure 2, the band around 200 cm^{-1} shifts considerably with a lowering of temperature. Such a frequency shift was also seen for the band at 214 cm^{-1} of $Na_3[Co(NO_2)_6]$. Therefore, the band around 200 cm^{-1} of $Na_2Ba[Ni(NO_2)_6]$ may be assigned to the lattice mode related to the Na^+ ion. The lowest band around 80 cm^{-1} which also exists in the spectrum of $K_2Ba[Ni(NO_2)_6]$ is assigned to the lattice mode related to the Ba^{2+} ion.

Conclusion

The far-infrared bands due to the lattice vibrations and the intramolecular vibrations of the hexanitro complex salts were both interpreted by the normal-coordinate analysis of the crystal as a whole, only the interaction between the outer cations and the oxygen atoms being taken into consideration. Low-temperature spectra yield useful information on the interpretation of the observed bands.

Lattice vibrations due to the displacements of the outer cations relative to the complex ion are observed below 200 cm^{-1}. Those frequencies change depending upon the mass of the cations and the interionic force constants. In order to establish the characteristic frequencies of the lattice vibrations arising from the outer cations, further investigations on the far-infrared spectra of various types of complex salts are in progress.

Appendix

For the intramolecular potential, V_{intra}, the modified Urey–Bradley force field (MUBFF) has been used and the use of this type of potential in the vibrational analysis of the complex ions has been fully discussed in several previous papers.[4b,12-14] Force constants used in the present study are summarized in Table VI, where

TABLE VI
INTRAMOLECULAR POTENTIAL CONSTANTS (MDYN/Å) FOR $Co(NO_2)_6^{3-}$ AND $Ni(NO_2)_6^{4-}$ [a]

	$Co(NO_2)_6^{3-}$	$Ni(NO_2)_6^{4-}$
F_{dia}(MN str)	1.50	0.80
F_{dia}(NO str)	9.30	9.30
F_{dia}(NMN def)	1.10	0.60
F_{dia}(ONO def)	1.78	2.00
F_{dia}(MNO def)	0.50	0.40
	0.30 (Na salt)	
F_{dia}(NO_2 wag)	0.55	0.32
F_{dia}(NO_2 twist)	0.03 (assumed)	0.03
F(N···N)	0.05	0.20[b]
F(O···O)	3.00	3.00
F(M···O)	0.20	0.10
p(NO,NO)	0.50	0.50

[a] In the Urey–Bradley approach, diagonal elements of the **F** matrix corresponding to the bond stretching modes include F as well as K and those for angle deformation modes include F as well as H. The off-diagonal elements are expressed in terms of F. [b] Taking into account the appreciable interaction between the Ni–N stretching and NMN deformation modes, the effective value of F(N···N) was assumed to be large.[4b,12]

K, H, and F denote the bond stretching, the angle deformation, and the repulsion between nonbonded atoms, respectively. F_{dia} means the diagonal element of the **F** matrix (potential energy matrix) for the corresponding mode. p(NO,NO) is the resonance interaction constant. The value of p(MN,MN) cannot be determined unless the frequencies of the g species are available.

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Rare Earth Orthogallates

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Single crystals of the rare earth orthogallates, $REGaO_3$ with RE = Sm–Lu, have been synthesized by the decomposition of the respective garnets at high pressure in the presence of a flux. Previously reported crystals of $LaGaO_3$, $PrGaO_3$, and $NdGaO_3$ have been prepared by the flux method at atmospheric pressure. The rare earth orthogallates are isostructural with the rare earth orthoferrites; namely, they have the orthorhombic perovskite-like structure. Their lattice parameters have been calculated by the least-squares method. The parameters a and c increase smoothly in going from Lu to La. However, the lattice parameter b goes through a maximum. It seems that this anomalous variation of the b parameter can be explained in terms of a variation of the coordination number of the rare earth cation.

Introduction

In a recent note[1] we reported the synthesis and the crystal structure of $GdGaO_3$, $YbGaO_3$, and $YGaO_3$. They were synthesized by decomposition at high pressure and high temperature of the respective garnets. The new orthogallates are isostructural with the respective orthoferrites; namely, they have the orthorhombic perovskite-like structure. An interesting feature is that the rare earth orthoferrites can be synthesized at atmospheric pressure, whereas a pressure greater than 45 kbars is needed to synthesize $GdGaO_3$, $YbGaO_3$, and $YGaO_3$. This was explained in terms of

(1) M. Marezio, J. P. Remeika, and P. D. Dernier, *Mater. Res. Bull.*, **1**, 247 (1966).