

Spectroscopy at Very High Pressures. Part IX. Far-i.r. Spectra of some Hexa-ammine Complexes of Ni(II) and Co(III)

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Introduction

The hexa-ammine complexes $[M(NH_3)_6]^{n+}$ ($n = 2$ or 3), have been studied often by i.r. and Raman spectroscopy and most features of the vibrational assignment are not in doubt. Interest in these materials has recently revived with the recognition that at very low temperatures they may show non-magnetic phase changes associated with removal of rotational freedom from NH_3 groups.^{1,2} We report here the results of experiments designed to discover whether or not such phase changes could be induced by an increase of pressure.

Experimental

The complexes were prepared by standard methods.³ Far-i.r. spectra at high pressure were obtained using an ungasketed diamond anvil cell (DAC) in a Beckman-RIIC FS-720 interferometer.⁴ Low temperature spectra were obtained for Nujol mulls in a CTI-20 closed-circuit cryostat.

Results and Discussion

The series $[Ni(NH_3)_6]X_2$ ($X = Cl, Br, I$), are all said to have the (cubic) fluorite structure.⁵ As is well known, selection rules then predict that the far-i.r. spectrum should show three T_{1u} modes due to ν_3, ν_4 of the cation, and ν_L (a lattice mode) respectively. In agreement with earlier work we find three bands in the $[Ni(NH_3)_6]I_2$ spectrum (Table I): what is new is that upon cooling to 77K, in addition to the usual band sharpening, an entirely new feature appears *ca.* 150 cm^{-1} in the form of a broad, intense absorption (Figure 1). ν_3 shows no sign of splitting and neither do ν_4 and ν_L insofar as they can be seen. The position of the new absorption is consistent with its origin as a torsional mode associated with NH_3 ^{6,7} although we find it at a temperature well in excess of the known phase transition temperature of 20K. The behaviour of ν_3, ν_4 , and ν_L support the observation¹ that there is no phase transition down to this

temperature. A similar result was obtained for the bromide but the new absorption overlapped ν_4 to the extent that neither could be measured accurately; ν_3 remained sharp and single but ν_L was broadened.

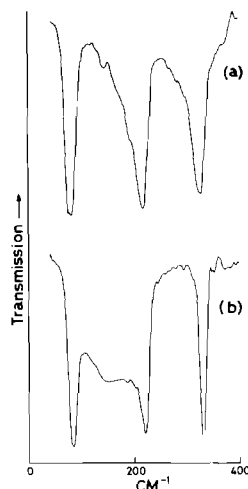


Figure 1. Far-i.r. absorption spectrum of $[Ni(NH_3)_6]I_2$ at (a) 290K; (b) 77K.

The effects of pressure were quite different from those due to lowering the temperature, and plainly indicate a phase change with lowering of symmetry for all three compounds $[Ni(NH_3)_6]X_2$. ν_3 and ν_4 either split or broaden significantly in each case; no splitting was resolved for ν_L although there was usually some broadening which may be due to band splitting, or to the effects of the known non-hydrostatic pressure distribution in the DAC when used in the non-gasketed mode.⁴ The above results are consistent with a structural change to a rhombohedral factor group such as D_3 or D_{3d} , both of which would accommodate the observed splitting of T_{1u} modes. Due to the increased breadth and complexity of bands in the high-pressure spectra it is not clear whether or not $\tau(NH_3)$ modes contribute to the absorption, or whether this is accounted for solely by changes in the selection rules applicable to skeletal modes, although on balance it seems probable that they do.

$[Co(NH_3)_6]I_3$ has the symmetry $Fm\bar{3}m (O_h^5)$, with a unimolecular primitive cell.^{5,8} The result of a factor group analysis for the optic branch modes is:

$$\begin{array}{ll} \Gamma(\text{CoN}_6 \text{ vibrations}) & A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u} \\ \Gamma(\text{rotatory lattice modes}) & T_{1g} \\ \Gamma(\text{translatory lattice modes}) & T_{2g} + 2T_{1u} \end{array}$$

TABLE I. Infrared Vibrational Wavenumbers/cm⁻¹ for some Hexa-ammine Complexes at Various Temperatures and Pressures.

		0.001 kbar; 77K			0.001 kbar; 290K			40 kbar; 290K		
		ν_3	ν_4	ν_L	ν_3	ν_4	ν_L	ν_3	ν_4	ν_L
[Ni(NH ₃) ₆]X ₂	X = Cl	344	219 ^a	120	335	216	115	342,370	226	138
	X = Br	—	—	—	329	218	91	334, 368	225, 265	107
	X = I	329	219	83 ^b	322	215	82	332	258,217	100
[Co(NH ₃) ₆]X ₃	X = Cl	—	269,335	94,156	—	332	148	—	341	175
	X = Br	—	—	—	—	320	118	—	325	144
	X = I	—	320	88, 109 ^c	—	318	101 ^d	—	330	112,140

^a Approximate value only; see text.^b There is also a strong, very broad, band *ca.* 150 cm⁻¹ attributed to $\tau(\text{NH}_3)$.very broad, absorption *ca.* 200 cm⁻¹ probably due to $\tau(\text{NH}_3)$.^c Weak,^d Doublet with unresolved components *ca.* 86,106 cm⁻¹

where only T_{1u} modes are i.r.-active. Thus, the selection rules for skeletal modes are the commonly accepted ones, but *two* lattice modes are expected in the far-i.r. We found two such lattice modes at 77K: Le Postelloc⁹ found bands at 104 and 55 cm⁻¹ at room temperature but did not comment on the fact. At 77K there is a definite increase in absorption in a broad region centred *ca.* 200 cm⁻¹ in the i.r. spectrum of [Co(NH₃)₆]I₃ and which we attribute to $\tau(\text{NH}_3)$ motion. However, under an average pressure (force/area value) of 40 kbar no such increase was observed, although ν_4 and ν_L both showed substantial shifts to higher energy. Equivalent experiments were performed on [Co(NH₃)₆]X₃ (X = Cl, Br), with much the same results, although there were complications due to the much lower symmetry of these materials.

Conclusion

Preliminary i.r. studies have located a new high-pressure phase in each of the compounds [Ni(NH₃)₆]X₂, and have revealed some new low-temperature features both in these spectra and in those of the cobalt(III) hexa-ammines. These systems warrant more detailed investigation at high pressures

under hydrostatic conditions, using both Raman and i.r. techniques over a range of temperatures: we plan to undertake this work shortly.

Acknowledgment

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