Vibrational–Electronic Fine Structure in Tetragonally Distorted Tetrahedral Nickel(II) Compounds

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The near-i.r. electronic spectra of crystals of $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$ at 5 K are reported. Vibrational–electronic band progressions are interpreted in terms of interactions with Raman-active modes of the materials.

IN favourable cases, low-temperature electronic spectra of transition-metal ions in crystals show sharply detailed fine structure related, normally in a complex way, to vibrational effects and small electronic perturbations. In this paper we concentrate on one electronic transition of Ni^{2+} present in both $(Et_4N)_2NiCl_4$ and $(Et_4N)_2NiBr_4$, where the well resolved progressions bear a particularly simple relationship to the vibrational spectra.

The single-crystal structure of the chloride was determined by Stucky, Folkers, and Kistenmacher,[1] who also reported that the bromide and chloride were isostructural from a comparison of X-ray powder data. This common structure is one having two formula units per unit cell and in which the Ni^{II} is in the centre of a tetragonally distorted (D_{2d}) NiX_4^{2-} ion.

The electronic transitions are interpreted in terms of the point-group of the anion, since the electronic wave functions involved are mainly associated with the central metal ion, and the best form of calculation is of the ligand-field type. The peak positions of vibronic bands discussed are at 7000 and 7400 cm^{-1} for the bromide and the chloride, respectively. In the tetrahedral point-group, these bands are assignable to the $^3T_1 \rightarrow {}^3A_2$ transition. In their analysis of magnetic data on the chloride, Gerloch and Slade[2] included the effects of tetragonal distortion and spin-orbit coupling and showed that the ground state was an orbital singlet (A_2 in D_{2d}, A_1 if spin-orbit coupling is included). The next energy level is *ca.* 70 cm^{-1} higher in energy and will not be populated at 5 K. There are no comparable data for the bromide but the similarity in spectra suggests a similar interpretation. The excited state is split by spin-orbit coupling into $^3B_2$ and ^3E components separated by 10 cm^{-1} in the chloride and 8 cm^{-1} in the bromide. Couch and Smith[3] obtained very sharp polarised spectra on $NiCl_4^{2-}$ ions in Cs_3MgCl_5 and clearly observed the excited-state splitting. This band assignment is $^3A_1 \rightarrow {}^3B_2, {}^3E$, the same as ours.

Far-i.r. spectra have been previously obtained for both

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[1] G. D. Stucky, J. B. Folkers, and T. J. Kistenmacher, *Acta Cryst.*, 1967, **23**, 1064.

[2] M. Gerloch and R. C. Slade, *J. Chem. Soc.* (*A*), 1969, 1012.

[3] T. W. Couch and G. P. Smith, *J. Chem. Phys.*, 1970, **53**, 1336.

$NiCl_4^{2-}$- and $NiBr_4^{2-}$-containing species; we have obtained the Raman spectra * to complement these data. Sabatini and Sacconi[4] measured the powder spectra of both the chloride and bromide from 70 to 400 cm^{-1}, and Dunsmuir and Lane[5] have since measured the single-crystal polarised reflectance spectra of the chloride. They report the ν_3 and ν_4 modes at 284 and 100 cm^{-1} respectively at room temperature, with splittings of less than 2 cm^{-1} at 105 K. Although they carry out a factor-group analysis for this compound based on the space-group, it is best, since the electronic interpretation is for the point-group, to consider these values as the ν_3 and ν_4 modes of the tetrahedron which are slightly split in the lower symmetry point-group D_{2d}. The crystal spectrum of the bromide is not known but the powder spectrum suggests a similar interpretation, confirmed by the Raman data. The detailed interpretation of the vibronic interaction is given by Herzberg[6] and we have adopted a similar approach.

EXPERIMENTAL

The crystal preparation and growth were carried out using similar techniques to those reported previously.[1,7] Raman spectra were obtained using a Coderg helium-neon laser. The ν_1 vibrational modes were clearly established at 271 and 168 cm^{-1} for the chloride and bromide respectively. Higher resolution spectra closer to the exciting line reveal weaker bands at about 100 (ν_3) and 88 cm^{-1} (ν_2) in the chloride and at 73 cm^{-1} (ν_2) in the bromide. Far-i.r. spectra between 5 and 80 cm^{-1} were obtained, using a Beckmann RIIC Lamelar grating spectrometer and FTC 100 computer. A broad, featureless peak was found at *ca.* 48 cm^{-1} for the chloride and *ca.* 40 cm^{-1} for the bromide. Near-i.r. spectra were taken with a Hilger and Watts D400 Monospek spectrometer with a 600 lines/in grating; using a tungsten lamp source and a fast-vacuum thermopile detector. The samples were studied as thin sections ground from single crystals mounted in an Oxford Instruments cryostat, which was placed in the exit beam of the spectrometer. The cryostat is a cold finger type with liquid-helium and liquid-nitrogen shields and double silica windows. The sample block temperature was at 5 K.

RESULTS AND DISCUSSION

The interpretation is simplified by the fact that we expect only one electronic origin in the spectra. When the low-symmetry field and spin-orbit coupling perturbations are included in the calculation, the ground state is found to be an orbital singlet and the next highest level is 100 cm^{-1} or higher in energy so that it will not be appreciably populated at 5 K. The excited state is split by spin-orbit coupling only and although second-order effects may alter this slightly, the overall splitting should be of the order of 8—10 cm^{-1}, about the limit of resolution of the spectral bands. The electronic-state symmetries are already so low that the Jahn-Teller effect which should be small in any case, will not be operative. However, since there are two molecules per unit cell, Davydov splittings are possible; they should be small and we see no positive evidence of them in the spectra.

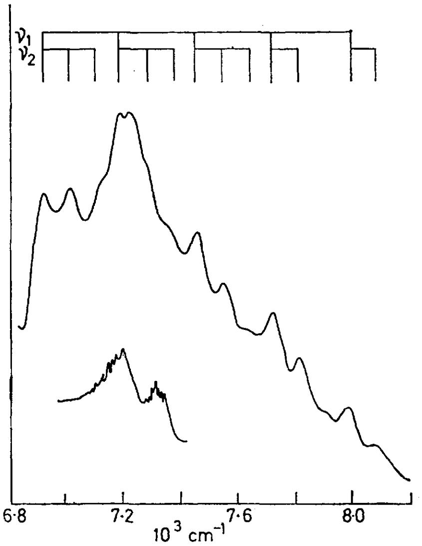

FIGURE 1 $^3A_1 \rightarrow {}^3B_2, {}^3E$ band of $(Et_4N)_2NiCl_4$ crystal at 5 K

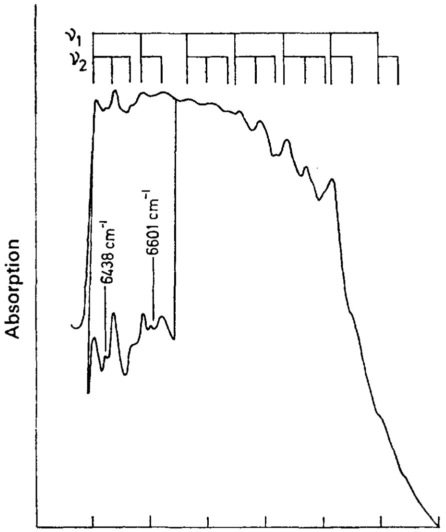

FIGURE 2 $^3A_1 \rightarrow {}^3B_2, {}^3E$ band of $(Et_4N)_2NiBr_4$ crystal at 5 K

The Raman powder spectra do not show splittings due to the lower symmetry D_{2d} point-group and the single-crystal i.r. splittings are only 1—2 cm^{-1}, which are much smaller than the available resolution for the electronic

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* We thank Dr. D. Adams of Leicester University and Miss J. Gardner for running the Raman spectra of these samples for us.

[4] A. S. Sabatini and L. Sacconi, *J. Amer. Chem. Soc.*, 1964, **86**, 17.

[5] J. Dunsmuir and A. Lane, *J. Chem. Soc.* (*A*), 1971, 2781.

[6] G. Herzberg, 'Spectra of Polyatomic Molecules,' Van Nostrand, New York, 1966.

[7] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

spectra, so that tetrahedral assignments are used throughout for vibrational spectra. The electronic data, however, are sensitive to the tetragonal distortion and the magnetic data indicate that the effective ground state is $^3A_1$. The vibronic selection rules worked out in D_{2d} symmetry show that at least one component derived from each of the ν_1–ν_4 tetrahedral vibrations may couple with the electronic wave functions. Both i.r.-active vibrations of a tetrahedron (ν_3 and ν_4) involve a change in the point-group symmetry of the nickel(II) ion during the vibration, so that coupling should be mainly with the Raman-active modes ν_1 and ν_2. The spectra obtained are shown in Figures 1 and 2, and a table of frequencies given in the Table. For the chloride, the transition studied is on top of a vibrational overtone of water vapour; in consequence, the band profile is distorted. For comparison the background spectrum of the instrument is plotted on the same scale as the observed spectrum in Figure 1. In both cases a major progression is observed and the interval corresponds to the ν_1 vibration of the NiX_4^{2-} ion (observed average values are 268 and 167 cm^{-1} compared to 271 and 168 cm^{-1} for the room-temperature Raman bands of the chloride and bromide respectively).

$^3A_1 \rightarrow {}^3B_2, {}^3E$ vibronic transitions; band frequencies and differences

$(Et_4N)_2NiCl_4$				$(Et_4N)_2NiBr_4$			
A_1 (cm^{-1})	Difference	E (cm^{-1})	Difference	A_1 (cm^{-1})	Difference	E (cm^{-1})	Difference
6916	261	7011	95	6399	169	6465	66
7177	271	7092sh	81	6568	156	6536sh	71
7448	268	7280sh	87	6724	172	6637	69
7716	271	7367sh	93	6896	171	6795	71
7987		7541	91	7067	158	6862	67
		7632sh	84	7225	160	6963	67
		7800	77	7385sh		7022sh	59
		7911sh				7133	66
		8064				7200sh	67
						7288sh	63
						7452	67

sh = Shoulder.

A second vibrational progression originating on each of the ν_1 bands has an interval of 87 ($NiCl_4^{2-}$) and 67 cm^{-1} ($NiBr_4^{2-}$) corresponding to observed values for ν_2 of *ca.* 88 and *ca.* 73 cm^{-1}. While the vibrational spectra were obtained at 300 K and the electronic spectra at 5 K, in general internal-mode vibrations in crystals are little affected by a lowering of temperature in the range 300—77 K so that neglect of temperature should not be serious.

The shapes of both bands show that the lowest-energy transitions are the most intense, suggesting that the potential curves for the two states lie directly above each other. The success of our analysis depends on the observed decrease of intensity with increasing energy, otherwise complete sets of ν_2 progressions, each originating upon a transition to ν_1, would overlap and destroy the fine structure away from the band edge. In the bromide spectrum there is some loss of resolution, due to this effect, in the middle of the overall band. The first interval in the ν_1 progression of the bromide shows some additional fine structure (inset in Figure 2). We observed a lattice mode at *ca.* 40 cm^{-1} in the far-i.r. spectrum of the bromide which could couple. A similar effect, much better resolved, was observed for Ni^{II}-doped in Cs_3MgCl_5 by Couch and Smith. At this stage we cannot exclude the alternative possibility that we may have fortuitously observed a splitting due to the excited electronic level. We observe that fine structure appears in other electronic bands of the complexes presently discussed. The interpretation of these data is not clear to us at present but may perhaps be resolved by studies of liquid He Raman and far-i.r. transitions of the complexes discussed.

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