

INFRARED SPECTRA OF PARTIALLY DEUTERATED ANALOGUES  
OF SOME AMMINE COMPLEXES

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The results of an approximate normal-coordinate calculation, based on a simple  $M-N(H,D)_3$  model, were used as an aid in assigning the bands observed in the infrared spectra of partially deuterated analogues of hexaaminenickel(II) bromide, hexaammincobalt(III) chloride and bromopentaamminechromium(III) bromide.

The ammine complexes of various metals have been subject to numerous investigations, including much spectroscopic work (cf., for example, [1,2] and references given therein). In the majority of the reported studies, however, either only the protiated forms were investigated or, in addition to that, fully deuterated analogues were used. As far as we know, there has been no systematic study of the spectra of partially deuterated ammine complexes, although (as the experience with water [3] and other species has shown) valuable structural information can be extracted from such investigations. As a first step towards such a goal (continuing, besides, our previous work on various ammine complexes [4]), we now report the results of our study of the infrared spectra of the partially deuterated analogues of hexaaminenickel(II) bromide (HANB), hexaammincobalt(III) chloride (HACC) and bromopentaamminechromium(III) bromide (BPACHB). Of these, by far the best quality had the spectra of the nickel compound (HANB). The spectra were recorded, at room and liquid-nitrogen temperature (RT and LNT) on a Perkin-Elmer 580 spectrophotometer.

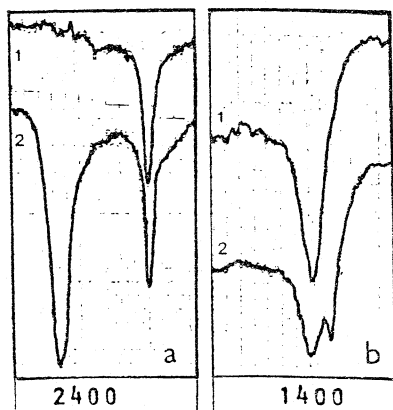


Fig. 1. The stretching (a) and bending ND region in the spectra of the protiated (1) and slightly deuterated (2) HANB

#### RESULTS AND DISCUSSION

The ND stretching and bending regions in the spectra of protiated and slightly deuterated HANB are shown in Fig. 1. As can be seen, when the deuterium content is low, in each of these regions there is just a single new band (at 2430 and 1385  $\text{cm}^{-1}$  respectively), attributable to vibrations of the isotopically isolated  $\text{NH}_2\text{D}$  groups. This would, then, imply that all the protons in this case are equivalent (crystallographically or effectively) with a further inference that the symmetry of the unit cell must also be high (again either strictly speaking or effectively).

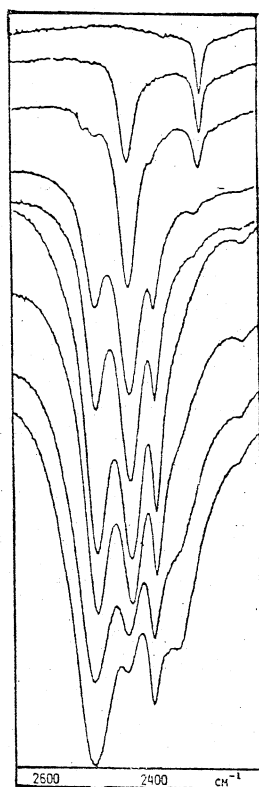


Fig. 2. The ND stretching region in the spectra of the series of partially deuterated analogues of HANB

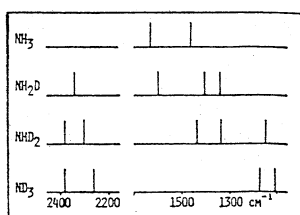


Fig. 3. Schematic representation of the frequencies of various  $N(H,D)_3$  isotopomers

As seen in Fig. 2 (here the ND stretching region is shown for the whole series of partially deuterated analogues of HANB, the deuterium content in the samples increasing on going downwards from the top of that figure), bands appear both at the high- and the low-frequency side of that which is due to the ND stretching of  $NH_2D$ . The position of these bands (and of those appearing in the ND bending region) can easily be understood if the results from a rather crude normal-coordinate calculation (performed on a simple  $M-N(H,D)_3$  model) are taken into account. As shown in Fig. 3, namely, the calculated frequencies of the consecutively formed  $NHD_2$  and  $ND_3$  species have values which show trends in agreement with the experimentally determined ones (not only in the stretching, but also in the bending ND region). It should be pointed out that the agreement is only qualitative since no attempt was made to optimize the force field used in the course of the calculations.

The situation is less clear in the case of the two other studied compounds since in the ND stretching region bands which are much broader than that in HANB are found. Some splitting is, nevertheless, seen and it can thus be concluded that in both of them there are non-equivalent protons, implying a symmetry lower than for  $[Ni(NH_3)_6]Br_2$ .

#### REFERENCES

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