

## Characterization of two Forms of the Ion $[\text{Nien}_2(\text{OH}_2)_2]^{2+}$

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DURING the course of work on the formation of solvent adducts of  $[\text{Nien}_2]\text{X}_2$ , where X is either of the anions of low co-ordinating ability perchlorate

or tetraphenylborate,<sup>1</sup> two forms of the ion  $[\text{Nien}_2(\text{OH}_2)_2]^{2+}$  have been prepared.

The two salts  $[\text{Nien}_2(\text{OH}_2)_2](\text{ClO}_4)_2$  and  $[\text{Nien}_2-$

<sup>1</sup> M. E. Farago, J. M. James, and V. C. G. Trew, to be published.

(OH<sub>2</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> might be expected to contain the same complex cation.<sup>2</sup> However, there are marked differences in the properties of the two compounds and it is concluded that the perchlorate contains the cation in the *trans*-configuration while the tetraphenylborate contains that of the *cis*-configuration.

The visible absorption spectra of the compounds together with other relevant data from the literature are shown in the Table. The spectra fall into two types: those with and those without splitting of band I.

TABLE  
Bands (cm.<sup>-1</sup> × 10<sup>-3</sup>) in the visible spectra of some Ni<sup>II</sup> complexes.

Complex	State	Bands <sup>a</sup>			
		I	II	III	IV
[Nien <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	.. .. . solid	9·8, 13·7	12·6	18·4	29·0
[Nien <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	.. .. . H <sub>2</sub> O soln.	10·6	—	17·4	28·1
[Nien <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	.. .. . solid	11·0	12·8	18·0	—
[Nien <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	.. .. . solid	8·8, 14·6	—	18·1	27·4
[Nien <sub>2</sub> (ONO <sub>2</sub> ) <sub>2</sub> ] <sup>b</sup>	.. .. . solid	8·7, 14·1	—	18·4	27·9
[Nitren(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> c..	.. .. . H <sub>2</sub> O soln.	10·5	12·8	17·8	27·8
[Nien <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	.. .. . solid	11·3	12·5	18·4	29·0

<sup>a</sup> Bands may be assigned as follows: I, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>; II, <sup>3</sup>A<sub>2g</sub> → <sup>1</sup>E(D); III, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F); IV, <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P);  
<sup>b</sup> data from reference 5; <sup>c</sup> data from reference 3.

Jørgensen<sup>3</sup> has already assigned the *cis*-configuration to the [Nien<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> ion in solution on the basis that the spectrum is very similar to that of [Nitren(OH<sub>2</sub>)<sub>2</sub>]<sup>2+</sup> which like [Nitren(NCS)<sub>2</sub>] must have a *cis*-structure.<sup>4</sup> The spectra of these compounds show no splitting of band I and are like those of octahedral complexes, *e.g.* [Nien<sub>3</sub>]<sup>2+</sup>. The spectrum of the tetraphenylborate salt is very similar to these, and the complex cation is therefore assigned the *cis*-configuration.

The spectrum of the perchlorate salt shows a marked splitting of band I and is similar to those of [Nien<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> and [Nien<sub>2</sub>(ONO<sub>2</sub>)<sub>2</sub>] recently reported by Curtis.<sup>5</sup> It was suggested that both these compounds have *trans*-tetragonal structures, with four nitrogens in-plane and two oxygens axially co-ordinated. Thus the perchlorate

salt may also be assigned a *trans*-tetragonal structure. The spectrum of this salt in solution, however, shows that on dissolution it reverts to the more stable *cis*-configuration.

These assignments of *cis*- and *trans*-configurations are supported by the positions of the NH<sub>2</sub> rocking frequencies in the infrared spectra of the two compounds, which appear at 676 cm.<sup>-1</sup> in the perchlorate and at 644 cm.<sup>-1</sup> in the tetraphenylborate. It has been found that the NH<sub>2</sub> rocking frequencies in a series of compounds decrease

with increasing strength of the axial field in relation to that of the in-plane field. Thus the strongly tetragonally distorted *trans*-complex shows a higher NH<sub>2</sub> rocking frequency than the octahedral *cis*-complex.

It seems likely that in order to stabilize the *trans*-diaquo-complex in the solid state some form of interaction in the crystal between the water and the oxyanion is needed. When this is absent, as for example in the tetraphenylborate, the more usual *cis*-form is obtained.

It is interesting to note that whereas water is lost very easily from both [Nien<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Nien<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> it is impossible to remove the water molecules from [Nien<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> by heating *in vacuo*.

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<sup>2</sup> Infrared spectrum shows ionic perchlorate.

<sup>3</sup> C. K. Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 887.

<sup>4</sup> S. E. Rasmussen, *Acta Chem. Scand.*, 1959, **13**, 2009.

<sup>5</sup> N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.