

## Complexes of 1,3-Diamino-2-aminomethylpropane with Nickel(II): Equilibrium Constants and Visible Spectra

THOMAS G. SPIRO and C. J. BALLHAUSEN

*Universitetets fysisk-kemiske Institut, Copenhagen, Denmark*

From pH measurements at  $22 \pm 1^\circ\text{C}$ , in an ionic medium whose anion concentration was kept constant at 1.0 M with potassium nitrate,  $pK$  values for 1,3-diamino-2-aminomethylpropane, (pmtn) were found to be 6.90, 8.86 and 10.51 for  $\text{pmtnH}_3^{+++}$ ,  $\text{pmtnH}_2^{++}$  and  $\text{pmtnH}^+$ , respectively. Furthermore the equilibrium constants for the reactions  $\text{Ni}^{++} + \text{pmtn} = \text{Ni(pmtn)}^{++}$  and  $\text{Ni(pmtn)}^{++} + \text{H}^+ = \text{Ni(pmtn)H}^{+++}$  were found to be 9.23 and 7.18 log units, respectively. The complex,  $\text{Ni(pmtn)}_2(\text{NO}_3)_2$  has been prepared. The spectra of the various complex species and of the crystal at room temperature are in accord with the crystal field theory for octahedral nickel(II) complexes. No splittings due to the trigonal symmetry of the complex have so far been observed.

The triamine, 1,3-diamino-2-aminomethylpropane,  $\text{CH}(\text{CH}_2\text{NH}_2)_3$ , (hereafter abbreviated to pmtn), possesses a three-fold symmetry axis. If the three amino groups of a pmtn molecule occupy adjacent octahedral positions on a transition metal ion, the trigonal component of the resulting ligand field would be expected to perturb the electronic structure of the purely octahedral complex. This influence might be detectable by spectral measurement.

As a first step in the exploration of this question the solution chemistry of pmtn with nickel(II) ions has been quantitatively investigated. Formation constants for the species  $\text{Ni(pmtn)}^{++}$  and  $\text{Ni(pmtn)H}^{+++}$ , as well as the three successive dissociation constants of  $\text{pmtnH}_3^{+++}$  were determined by glass electrode titration, at room temperature,  $22 \pm 1^\circ\text{C}$ , of the triamino trihydrochloride with varying amounts of nickel(II) nitrate added. To maintain activity coefficients constant, the concentration of negatively charged counter ions (chloride plus nitrate) was kept constant at 1.0 M by addition of potassium nitrate. The formation constant for  $\text{Ni(pmtn)}_2^{++}$  could not be evaluated from pH measurements alone, but the complex was isolated by precipitation from solution. Its spectrum in the visible region was measured, both in solution and in the crystalline state. Spectra of  $\text{Ni(pmtn)}^{++}$  and  $\text{Ni(pmtn)H}^{+++}$  were also obtained.

## EXPERIMENTAL

Pure 1,3-diamino-2-methylaminopropane trihydrochloride was kindly prepared by Dr. J. Munch-Petersen of the Technical University of Denmark after the procedure of Geissman *et al.*<sup>2</sup> Microanalysis gave the following results: Found: C 22.55; H 7.34; N 19.74; Cl 49.90. Calc. for  $C_4H_{13}N_3 \cdot 3HCl$ : C 22.60; H 7.59; N 19.77; Cl 50.04.

A 1.97 M potassium nitrate stock solution was prepared from the reagent grade (Merck) chemical, and its concentration was checked by conductivity measurement. Sodium hydroxide titrant was prepared by diluting a carbonate-free concentrated stock solution to 1 M (0.1 M for titration III — see below) with distilled water and the proper amount of potassium nitrate stock solution to make the titrant 1.0 M in nitrate. The hydroxide concentration was determined by titration of standard potassium acid phthalate.

Solutions for titration were made up from weighed amounts of the amine hydrochloride and reagent grade (Analar) nickel(II) nitrate by the addition of water and potassium nitrate solution to adjust the total anion concentration to 1.0 M. In all, four different titrations were performed, with the following initial (molar) concentrations of amine and nickel.

Titration	Amine	Nickel
I	0.0412	—
II	0.0313	0.0155
III	0.00368	0.0437
IV	0.0250	0.0250

Titrations were performed in the open in a room whose temperature was  $22 \pm 1^\circ C$ . The hydrogen ion concentration was measured with a Radiometer pH-meter 4 connected to a Radiometer Type G202 B glass electrode, with shielded cable, and a K100 saturated calomel electrode with a bent capillary tip liquid junction. The electrodes were calibrated using standard hydrochloric acid solutions, with potassium nitrate added to give a total anion concentration of 1.0 M.

Absorption spectra of solutions were recorded between 325 and 800  $\mu$  on a Carey Model 11 spectrophotometer, and between 800 and 1 000  $\mu$  measurements were taken pointwise on a Zeiss PMQII spectrophotometer.

## LIST OF SYMBOLS

(For simplicity charges will be omitted from chemical formulas).

A = ligand

M = central ion

H = hydrogen ion

$C_A$  = formal (analytical) concentration of A

$C_M$  = » » » » M

$C_H$  = » » » » H

(For any point in a titration:

$$C_H = 3C_A - \frac{\text{equivalents of base added}}{\text{total volume}}$$

$$K_j = \frac{(AH_j)}{ah^j}, \beta_n = \frac{(MA_n)}{ma^n}, \delta_{nj} = \frac{(MA_n H_j)}{(MA_n) n^j}, K_{MAH_j}^M = \frac{(MAH_j)}{m(AH_j)}$$

$K_w'$  = hb

$\alpha_x$  = fraction of total central ion present as the species x.

$\epsilon_x$  = optical absorptivity of the species x.

$E$  = optical absorbance per mole of total central ion per cm of path length.

## EQUILIBRIUM CONSTANTS

The acidity constants for pmtn were extracted from the data yielded in titration I, by standard methods. The mass balances representing this system are

$$C_A = \sum_{j=0} (AH_j) = a \sum_{j=0} k_j h^j$$

$$\text{and } C_H = \sum_{j=0} j(AH_j) + (H^+) - (OH^-) = a \sum_{j=0} j K_j h^j + h - \frac{K_w'}{h}$$

(The quantities  $h$  and  $K_w'/h$  are significant terms in the mass balance only at very low or very high pH. For all the titrations discussed herein they are entirely negligible, and will be dropped from the equations.)

Then

$$\frac{C_H}{C_A} = \frac{\sum_j K_j h^j}{\sum_j K_j h^j} = \bar{j}$$

Values of  $\bar{j}$  were calculated from the titration data and plotted as a function of  $\log h$ . The resulting protonation curve was analyzed graphically to determine the  $K_j$ 's. Preliminary values were obtained by comparison with a family of normalized protonation curves representing a theoretical system with  $j_{\text{maximum}} = 2^3$ , neglecting first the region  $\bar{j} > 2$  and then the region  $\bar{j} < 1$ . These values were then refined by the linear extrapolation method of Rossotti and Rossotti<sup>4</sup>, to give  $K_1 = 3.27 \times 10^{10}$ ,  $K_2 = 2.36 \times 10^{19}$ ,  $K_3 = 1.87 \times 10^{26}$ . A theoretical protonation curve calculated from these constants agrees very well with the experimental points, as can be seen the Fig. 1. Expressed in another way, these results give the following pK values for  $AH_3$ ,  $AH_2$  and  $AH$ , respectively: 6.90, 8.86, and 10.51.

Titration II was then performed and an attempt was made to construct a formation curve<sup>5</sup> for the system M, MA, and  $MA_2$ , but it became obvious that

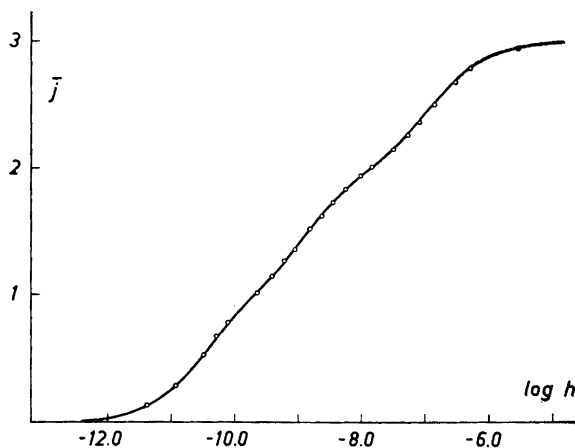


Fig. 1. Protonation curve for pmtn. The points are experimental, the curve theoretical.

the experimental points could not describe a system with only these complexes present. The distortion was thought to arise from protonated complexes, whose occurrence is common in polyamine complex systems, as shown by the studies of Prue and Schwarzenbach <sup>6</sup>.

A convenient method for studying protonated complexes containing one molecule of ligand has been given by Schwarzenbach <sup>7</sup>. It consists simply in titrating the protonated ligand in the presence of a large (10 fold) excess of central ion. Under these conditions it is clear that the concentration of complexes containing more than one ligand molecule will be negligible, and the mass balances may be written as follows

$$C_A = \sum_{i=0} (\text{MAH}_i) + \sum_{i=0} (\text{AH}_i) = a \sum_{i=0} (m\beta_1\delta_{1i} + K_i)h^i$$

$$C_H = \sum_{i=0} j(\text{MAH}_i) + \sum_{i=0} j(\text{AH}_i) = \sum_{i=0} j(m\beta_1\delta_{1i} + K_i)h^i$$

Then

$$\frac{C_H}{C_A} = \frac{\sum_j c_j h^j}{\sum c_i h^i} = \bar{j}' ; c_i = \frac{m\beta_1\delta_{1i} + k_i}{m\beta_1 + 1}$$

The quantities  $c_j$  are constants because  $m$  remains essentially constant, the central ion being present in large excess. Therefore the  $c_j$ 's may be extracted from the new protonation curve,  $\bar{j}'(\log h)$ , by the same method as described above for the amine acidity constants. Furthermore,  $\delta_{13}$  must be zero,  $A$  being a triamine; therefore  $\beta_1$  may be determined from  $c_3$  (and the known values of  $m$  and  $K_3$ ) and  $\delta_{12}$  and  $\delta_{11}$  may then be determined from  $c_2$  and  $c_1$  (together with  $K_2$  and  $K_1$ ).

Accordingly, titration III was performed and an experimental curve  $\bar{j}'$  ( $\log h$ ), was constructed. Comparison of the portion  $2 < \bar{j}' < 3$  with the normalized family of curves described above showed that, within experimental error,  $c_2 = 0$ , *i.e.*, the concentration of species containing two protons (such as  $\text{MAH}_2$ ) was negligible. At the same time, the steepness of the curve in this

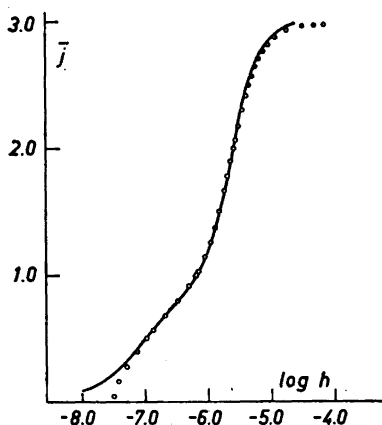


Fig. 2. Protonation curve for pmtm in the presence of excess nickel(II) ions. The points are experimental, the curve theoretical.

region allowed a reliable visual estimate of the ratio  $c_3/c_1$  as 11.22 log units. The points below  $\bar{j}' = 1$  were analyzed by the linear extrapolation method, which gave a value for  $c_1$  of  $9.87 \times 10^6$ . These two constants give a theoretical curve which adequately fits the theoretical points throughout most of the range of  $\bar{j}'$  (Fig. 2). There appears to be a slight systematic error for  $\bar{j}' > 2.8$ , and for  $\bar{j}' < 0.4$ , the points deviate from the theoretical curve due to the precipitation of nickel hydroxide. From the above values it was calculated that  $\log \beta_1 = 9.43$  and  $\log \delta_{11} = 6.99$ .

As Schwarzenbach pointed out<sup>8</sup>, the assumption that the concentration of complexes containing more than one ligand molecule is negligible should still be valid when the ligand and central ion are present in equal concentration ( $\beta_2/\beta_1$  being appreciably lower than  $\beta_1$  for most polyamines), and an "equivalent" titration provides a useful check on the results obtained by the excess central ion method. The check can be made by simply calculating a theoretical titration curve and comparing it with the experimental one. The "degree of tetration", *i.e.*, the number of moles of base added per mole of triamine trihydrochloride, can be expressed in terms of the formal concentrations as

$$f = \frac{3C_A - C_H}{C_A}$$

There being only one protonated complex in the present system, the mass balances reduce to

$$\begin{aligned} C_M &= m + m\alpha\beta_1(1 + \delta_{11}h) \\ C_A &= m\alpha\beta_1(1 + \delta_{11}h) + ap \\ C_H &= m\alpha\beta_1\delta_{11}h + aq \end{aligned}$$

where  $p = \sum_{j=0} K_j h^j$  and  $q = \sum_{j=0} jK_j h^j$ . ( $q/p = \bar{j}$ )

Since  $C_M = C_A$ ,  $m = ap$ .

$$\text{Then, } f = \frac{m\beta_1(3 + 2\delta_{11}h) + 3 - pq}{m\beta_1(1 + \delta_{11}h) + p} = \frac{3 + 2\delta_{11}h + (3 - \bar{j})(\beta_1 a)^{-1}}{1 + \delta_{11}h + (\beta_1 a)^{-1}}$$

$\bar{j}$  can be read directly from Fig. 1, and  $a$  is best calculated by substituting  $m = ap$  into the mass balance for  $C_H$ , and solving the resulting quadratic equation. When the theoretical curve calculated in this way was compared with the experimental curve from titration IV, it was found to have the right form, but a slight systematic deviation in the latter half of the titration indicated an error in the constants used. These were therefore recalculated, using the data from titration IV, in the following manner.

In the last part of the titration curve, when the concentration of free central ion becomes negligible, the expression for  $f$  reduces to

$$f = \frac{3 + 2\delta_{11}h}{1 + \delta_{11}h}$$

from which

$$\delta_{11} = \frac{1}{h} \frac{3-f}{f-2}$$

In the first part of the curve, when the concentration of MA is negligible,

$$f = \frac{2\delta_{11}h + (3-\bar{j})(a\beta)^{-1}}{\delta_{11}h + (a\beta)^{-1}}$$

from which

$$\beta\delta_{11} = \frac{1}{ah} \frac{f + \bar{j} - 3}{2-f}$$

At the same time, the difference between  $C_H$  and  $C_A$  becomes

$$C_H - C_A = a(q-p) = ap(\bar{j}-1)$$

so that  $a$  can be calculated simply from

$$a = \frac{C_H - C_A}{p(\bar{j}-1)}$$

In this way  $\delta_{11}$  was calculated for eight points on the last part of the titration curve ( $f > 2.4$ ) and  $\beta_1\delta_{11}$  was calculated from eight points on the first part ( $f < 1.1$ ). Finally, the value for  $\delta_{11}$  was refined slightly by including the terms in  $\beta_1$ , originally neglected in the expressions for  $f$ . The resulting values,  $\log \delta_{11} = 7.18$ ,  $\log \beta_1 = 9.23$ , give a theoretical curve which is in excellent agreement with the experimental points, as can be seen in Fig. 3. These values are significantly different from those obtained from the excess central ion titration, although their product remains the same. The source of this discrepancy probably lies in the determination of  $c_1$  in the excess central ion method\*. The number of points on the protonation curve which are actually sensitive to the value of  $c_1$  (or  $\delta_{11}$ ) are very few because of the early precipitation of nickel hydroxide. Any error in  $c_1$  is reciprocated in  $c_3$ , which is calculated from the experimentally obtained ratio  $c_3/c_1$ . In the equivalent titration, on the other

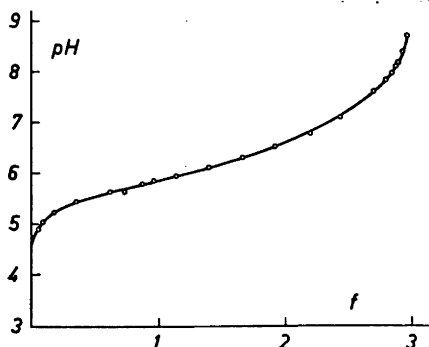


Fig. 3. "Equivalent" titration of pmtn  $H_3^{+}$  and nickel(II) ions. The points are experimental, the curve theoretical.

\* An alternative explanation, that polynuclear complexes are formed, is considered highly unlikely, in view of Schwarzenbach's<sup>9</sup> finding from studies of polyamines with a variety of metal ions (including nickel(II)) that only silver(I) forms such complexes.

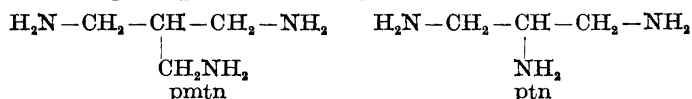
hand, nickel hydroxide does not precipitate, and points are available over the entire titration range. The constants calculated from this titration are therefore felt to be the more reliable.

In the light of these constants, another attempt was made to analyze the data for titration II (where  $C_A/C_H = 2$ ) in an effort to obtain the formation constant for  $MA_2$ . No satisfactory results were obtained however, probably because the number of chemical species present puts too much strain on pH data, taken alone. Schwarzenbach<sup>10</sup> considers it impractical to analyze pH curves when more than two complexes are formed in a given buffer region, which is certainly the case in the present system. As titration II proceeds, the solution turns from the green of aquo nickel ion, to the blue characteristic of MA (titration IV) and then on to violet, indicating the formation of di-ligand complexes. In addition to  $MA_2$ , it is quite likely that  $MA_2H$  and possibly  $MA_2H_2$  are formed. Finally, at a pH of about 8.1 there precipitated out of solution fine pink crystals, which turned out to contain the complex  $MA_2$ . It may be possible to elucidate the di-ligand complexes by augmenting the pH titration curves with measurements of the solubility of the  $MA_2$  crystals. However only a small amount of the triamine was available and the equilibrium work was not pursued further.

The precision of the determinations of the various equilibrium constants is probably about  $\pm 0.05$  log units.

#### DISCUSSION OF THE CONSTANTS

It is instructive to compare the solution chemistry of pmtn with that of the chemically similar ligand ptn, studied by Prue and Schwarzenbach<sup>11</sup>.



The constants for these two triamines are compared in Table 1. The association of the two ligands with nickel (as reflected in the values of  $\beta_1$  and  $K_{MAH}^M$ ) is seen to be practically identical, which is somewhat surprising in view of the fact that ptn can form two five membered chelate rings, while pmtn can only form six-membered rings. They do not necessarily form an exception to the general rule of increased stability for five membered rings as compared with six mem-

Table 1. Acidity constants for ptn and pmtn and their complexity constants with nickel(II)

	ptn <sup>a</sup>	pmtn <sup>b</sup>
$pK_{AH_3}$	3.72	6.90
$pK_{AH_2}$	7.95	8.86
$pK_{AH}$	9.59	10.51
$\log \beta_1$	9.3	9.23
$\log \delta_{11}$	6.3	7.18
$\log K_{MAH}^M$	6.0	5.90

<sup>a</sup> Schwarzenbach and Prue<sup>11</sup> measured at 20° in 0.1 M potassium chloride.

<sup>b</sup> This study.

bered rings<sup>12</sup>, however. It is possible that the complex  $\text{Ni}(\text{ptn})\text{H}^{+++}$  involve protonation of the middle nitrogen on ptn, leaving the end nitrogens bonded to nickel. The resulting structure would have a six-membered chelate ring. In the complexes MA, on the other hand, where all three nitrogens are presumably bonded to nickel, it is probable that the ring structure of both ligands is somewhat strained due to the fact that all three rings are joined at a single carbon atom. It is worth noting that  $\log \beta_1$  for the nickel complex of diethylenetriamine, a ligand without this steric requirement is considerably higher (10.7)<sup>13</sup> than for either ptn or pmtn.

The species involving pmtn appear to be somewhat stronger bases than the corresponding ones involving ptn, though part of this effect may be due to the stronger ionic medium of this study as compared with that used by Prue and Schwarzenbach. (However, the  $\text{p}K$  for  $\text{H}_3\text{A}$  is over three units higher for pmtn than for ptn, a remarkably large difference. Possibly the five membered rings which could be formed by internal hydrogen bonding in  $\text{ptnH}_2^{++}$  are more stable than the six-membered rings to be expected in  $\text{pmtnH}_2^{++}$ ).

The values of  $K_{\text{MAH}}^{\text{M}}$ , representing the association of HA with nickel ion, presumably through two of the three nitrogen atoms, are, for both ligands, smaller than the value of  $\log \beta_1$ , 7.66<sup>5</sup>, for the nickel-ethylenediamine complex, as would be expected from the charge repulsion present in the protonated triamine complexes. On the other hand, the values of  $\beta_1$  for the two triamines are considerably greater than  $\beta_1$  for ethylenediamine, implying that all three nitrogens are indeed bonded to nickel in the complexes MA.

#### SPECTRA OF MAH AND MA

The spectra of MAH and MA were obtained<sup>5</sup> from two solutions containing equal formal concentrations of ligand and central ion (0.025 M), adjusted to different pH values by addition of sodium hydroxide. The anion concentration was again kept at 1.0 M with potassium nitrate. For such solutions we have, from the results of the above equilibrium study, and from Beer's law, that

$$E = \epsilon_{\text{M}}\alpha_{\text{M}} + \epsilon_{\text{MAH}}\alpha_{\text{MAH}} + \epsilon_{\text{MA}}\alpha_{\text{MA}}$$

The values of  $\alpha_x$  are calculated with the aid of the equilibrium constants, and  $\epsilon_{\text{M}}$  can be determined independently (from the spectrum of aquo nickel(II) ion). The result is an equation in two unknowns ( $\epsilon_{\text{MAH}}$  and  $\epsilon_{\text{MA}}$ ) which can be determined from two sets of value of  $E$  and the fractions  $\alpha_x$ . For the two pH values selected, 6.84 and 7.90, the following distributions of the complexes were calculated

pH	$\alpha_{\text{M}}$	$\alpha_{\text{MAH}}$	$\alpha_{\text{MA}}$
6.84	0.089	0.626	0.285
7.90	0.009	0.158	0.833

The spectra of MAH and MA, calculated from the spectra of these solutions are shown in Fig. 4. The spectrum of MAH is nearly identical with that of the first ethylenediamine complex of nickel<sup>14</sup>, while the peaks in the MA spectrum are shifted definitely to higher frequencies. Thus the spectra support the



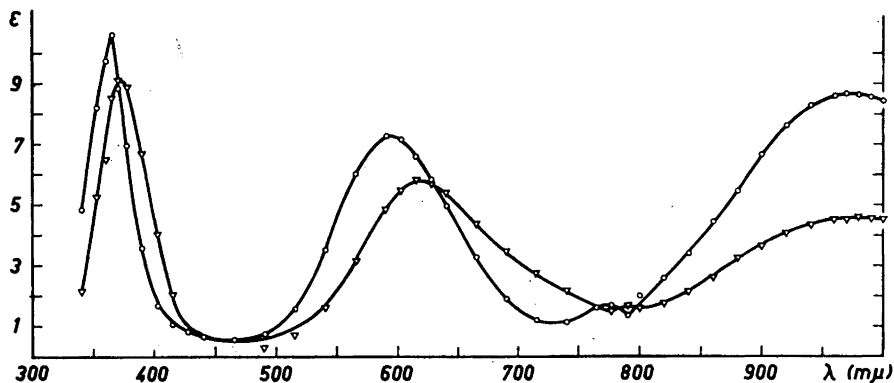


Fig. 4. Solution spectra of NiA (circles) and NiAH (triangles).

impression gained from the equilibrium constants that in MAH two nitrogens are bonded to nickel, while in MA, all three nitrogen atoms are bonded.

#### PREPARATION AND SPECTRA OF $\text{Ni}(\text{pmtn})_2(\text{NO}_3)_2$

A portion of the triamine trihydrochloride was converted to the nitrate salt by dissolving it in a small quantity of water, adding a stoichiometric amount of silver nitrate, and filtering off the resulting silver chloride precipitate. One half the equivalent amount of nickel(II) nitrate was then added to the nitrate solution and sodium hydroxide was dripped in slowly until the precipitate observed in titration II appeared. This was filtered and recrystallized from water as fine, pink hexagonal plates. Microanalysis gave the following results: Found: C 24.30; N 28.55; H 6.61. Calc. for  $\text{Ni}(\text{C}_4\text{N}_3\text{H}_{13})_2(\text{NO}_3)_2$ : C 24.70; N 28.81; H 6.74.

A saturated solution of the complex in 1.0 M potassium nitrate, and a more concentrated one in water, were prepared and their visible spectra were recorded. Subsequent analysis of the solutions by dimethylglyoxime precipitation of nickel gave the following concentrations for the water and potassium nitrate solutions respectively:  $C_M = 2.71 \times 10^{-3}$  and  $9.03 \times 10^{-3}$  M. It was also possible to grow a sizable crystal (about 1 mm per hexagonal edge) of the complex, which was then mounted on a microscope stage, and its absorption spectrum was recorded after focusing the microscope image on the slit of a Beckman D.U. spectrophotometer.

The spectra are shown in Fig. 5. The peaks are shifted considerably to higher frequencies relative to those of MA. On the other hand, the three spectra are also shifted relative to one another, the crystal peaks having the highest frequencies and those in the potassium nitrate having the lowest. These shifts may be due to dissociation and/or hydrolysis of  $\text{MA}_2$ , the degree of which cannot be reliably estimated as the relevant equilibrium constants are not known.

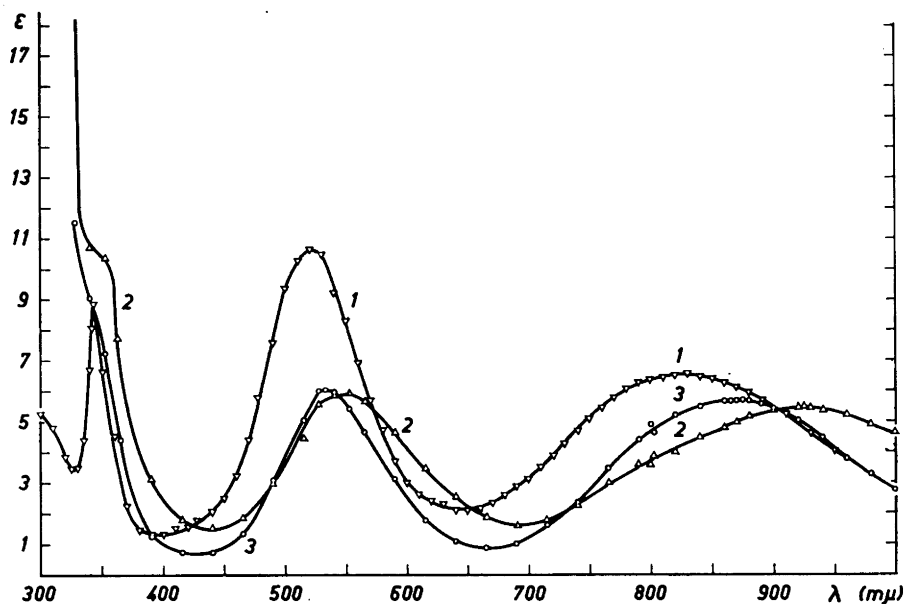


Fig. 5. Absorption spectra of (1)  $\text{NiA}_2(\text{NO}_3)_2$  crystal (arbitrary absorbance units), (2)  $\text{NiA}_2$  in 1.0 M  $\text{KNO}_3$  and (3)  $\text{NiA}_2$  in water.

### CRYSTAL FIELD CONSIDERATIONS

In general outline, the spectra of the three species measured are adequately explained by the usual crystal field model for octahedral complexes of nickel(II)<sup>14</sup>. The major peaks clearly represent those transitions which have been assigned as  ${}^3A_{2g} \rightarrow {}^3T_{2g}$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  in order of increasing frequency. The value of  $Dq$  is some 1 200  $\text{cm}^{-1}$ , or about the value found for  $\text{Ni}(\text{en})_3$ . In addition, the MA and MAH spectra also show a minor peak, between

Table 2. Octahedral transition frequencies ( $\text{cm}^{-1}$ ) for pmtn complexes of nickel(II).

Transition	$\text{MA}_2$ (crystal)		MA		MAH	
	Exptl.	Theoret. <sup>a</sup>	Exptl.	Theoret. <sup>a</sup>	Exptl.	Theoret. <sup>a</sup>
${}^3A_{2g} \rightarrow {}^3T_{2g}$	12 050	12 000	10 300	10 000	10 200	10 000
		-12 500		-10 800		-10 500
${}^3A_{2g} \rightarrow {}^1E_g$	—	12 700	12 900(?)	12 500	12 650(?)	12 500
${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	19 250	18 800	16 800	16 200	16 100	15 800
		-19 500		-17 210		-16 900
${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	29 250	29 700	27 400	27 000	27 000	26 600
		-30 300		-27 400		-27 000

<sup>a</sup> Taken from the energy level diagram of Liehr and Ballhausen<sup>15</sup>. The ranges are a reflection of splittings due to spin orbit coupling.

the first two major ones, which has about the right frequency for the spinforbidden  ${}^3A_{2g} \rightarrow {}^1E_g$  transition. The experimental and theoretical frequencies (taken from the energy level diagram of Liehr and Ballhausen<sup>15</sup>) for the three complexes are compared in Table 2.

The application of a trigonal perturbation to the octahedral field should produce a splitting of all three excited triplet states, and therefore the three major peaks of MA and MA<sub>2</sub> should all be split. Evidently the splitting is too small to be observed in solution, nor is it apparent in the crystal spectrum of MA<sub>2</sub>. The latter was obtained with a rather crude setup, however, and the resulting uncertainty in the absorbance values might be enough to obscure any fine structure. Conceivably a more careful measurement of the spectrum at low temperatures might show the trigonal splitting. Also the trigonal symmetry of the complex should give rise to dichroism in the crystal, which could be measured if a crystal could be grown large enough to present more than one face to an incident light beam. Work on these aspects of the problem are currently underway in this laboratory.

*Acknowledgements.* One of us (T.G.S.) is indebted to the *Fulbright Foundation* for a study grant which made possible his study in Copenhagen. Both of us want to thank Dr. Jon Munch-Petersen of the Technical University of Denmark for having prepared our supply of the ligand, and Professor J. Bjerrum for an instructive discussion.

## REFERENCES

1. Biedermann, G. and Sillén, L. G. *Arkiv Kemi* **5** (1953) 425.
2. Geissman, T. A., Schlatter, M. J. and Webb, I. A. *J. Org. Chem.* **11** (1946) 736.
3. Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 194.
4. Rossotti, F. J. C. and Rossotti, H. S. *Acta Chem. Scand.* **9** (1955) 1166.
5. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution* P. Haase, Copenhagen 1941.
6. Prue, J. E. and Schwarzenbach, G. *Helv. Chim. Acta* **33** (1950) 963.
7. Schwarzenbach, G. *Ibid.* **33** (1950) 954.
8. Schwarzenbach, G. *Ibid.* **33** (1950) 958.
9. Schwarzenbach, G. *Ibid.* **33** (1950) 956.
10. Schwarzenbach, G. *Ibid.* **33** (1950) 960.
11. Prue, J. E. and Schwarzenbach, G. *Ibid.* **33** (1950) 995.
12. Irving, H., Williams, R. J. P., Ferret, D. J. and Williams, A. E. *J. Chem. Soc.* **1954** 3494.
13. Prue, J. E. and Schwarzenbach, G. *Helv. Chim. Acta.* **33** (1950) 992.
14. Ballhausen, C. J. *Kgl. Danske Vidskab. Selskab. Mat. Fys. Medd.* **29** (1955) No. 8.
15. Liehr, A. D. and Ballhausen, C. J. *Ann. Phys.* **6** (1959) 146.

Received June 8, 1961.