

The Magnetic Properties of the Red and Green Nickel-Compounds of the Type $[\text{Ni}(\text{PE}_3)_2\text{X}_2]$. Studies in Magnetochemistry 13*

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The red complex compound $[\text{Ni}(\text{PE}_3)_2\text{Cl}_2]$ is diamagnetic having $\chi_M = -202 \times 10^{-6}$. The transplanar molecule is in a singlet state (dsp^2 -bonds). The green compound $[\text{Ni}(\text{PE}_3)_2(\text{NO}_3)_2]$ follows the Curie-law $\chi_M^{\text{corr}} = \frac{1.194}{T}$ from 85°K to 400°K. Extrapolation to 0°K gives the Weiss correction $\Delta = 0$. The permanent magnetic moment is 3.10 Bohr magnetons. This molecule is in a triplet state (sp^3 -bonds or ion-dipole bonds).

Red complex nickel-compounds of the type $[\text{Ni}(\text{PR}_3)_2\text{X}_2]$ were prepared and described by K. A. Jensen¹. X is Cl, Br, or I and R is C_2H_5 , C_3H_7 , or C_4H_9 . The dipole moments of the compounds $[\text{Ni}(\text{PPr}_3)_2\text{Cl}_2]$ and $[\text{Ni}(\text{PE}_3)_2\text{Br}_2]$ are according to Jensen practically 0 indicating transplanar configuration of the molecules. No *cis*-forms could be isolated. However, a green nitrate $[\text{Ni}(\text{PE}_3)_2(\text{NO}_3)_2]$ could be prepared having the dipole moment 8.85 D. A corresponding red nitrate does not seem to exist. The magnetic measurements carried out by Asmussen² on Jensen's preparates show that the compounds $[\text{Ni}(\text{PE}_3)_2\text{Cl}_2]$ and $[\text{Ni}(\text{PPr}_3)_2\text{Cl}_2]$ are diamagnetic having the gram susceptibilities $-0.32_8 \times 10^{-6}$ (19° C) and $-0.34_2 \times 10^{-6}$ (20° C), respectively. The measurements of the dielectric and the magnetic susceptibilities show that we have an undoubted conformity between experiment and the magnetic criterion for planar configuration. Furthermore the magnetic measurements show that the green nitrate is paramagnetic. The effective moment was determined to 3.05 Bohr magnetons at 19° C. According to the magnetic criterion we may expect this molecule to have tetrahedral configuration (sp^3 -bonds or ion-dipole-bonds). As the dipole moment measurement cannot distinguish between *cis*-planar and tetrahedral configuration we may assume

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that these measurements and the magnetic data support each other as far as the tetrahedral configuration is concerned.

K. A. Jensen¹ observed that the solution containing nickel nitrate and alkyl-phosphine is temporarily coloured red before the green nitrate separates. K. A. Jensen suggests that this colour change originates in the transformation of the red but instable *trans*-form into the stable green nitrate. We have observed that after having been held a few degrees above the melting point and then suddenly cooled down to liquid air temperature the green nitrate contains a few red particles. Furthermore we observed that solutions of the green nitrate in methyl- or ethylalcohol are decomposed slowly but the colour changes to red when the solutions are cooled in carbon dioxide-acetone. If a few crystals of the green compound are placed in water they are rapidly dissolved and decomposed but in a zone near the crystal surface a red colour is observed even at room temperature. Solutions in benzene are rather stable and their green colour is preserved at low temperature. In view of these observations we considered it of interest to prepare the compounds again and study their magnetic properties, in particular the temperature dependence of the susceptibility in order to decide whether a transformation between the two magnetically different forms occurs. The temperature dependence of the susceptibilities has not been studied before.

We prepared the red $[\text{Ni}(\text{PE}_3)_2\text{Cl}_2]$ and the green $[\text{Ni}(\text{PE}_3)_2(\text{NO}_3)_2]$ following the methods of K. A. Jensen¹. The compounds were recrystallized and analysed. Nickel was determined cyanometrically. The melting points were 112–113° and 130–131° C, respectively. The results of the analysis together with room temperature measurements of the susceptibilities of these compounds at different values of the field strength are given in Table 1. The magnetic measurements were carried out as reported in earlier papers³.

Table 1. Field strength dependence of the susceptibility. Analysis.

$[\text{Ni}(\text{PE}_3)_2\text{Cl}_2]$, red. 297°K			$[\text{Ni}(\text{PE}_3)_2(\text{NO}_3)_2]$, green. 296°K		
H (Ørstedes)	$-\chi_g \times 10^6$	$-\chi_M \times 10^6$	H (Ørstedes)	$\chi_g \times 10^6$	$\chi_M \times 10^6$
6 226	0.549	201	2 657	9.195	3 853
7 021	0.554	203	3 346	9.146	3 832
7 635	0.556	203	3 822	9.177	3 845
Mean value	0.553	202	Mean value	9.172	3 843
Analysis Ni %	Calc. 16.04 % Found 16.14 %, 16.08 %		Analysis Ni %	Calc. 14.01 % Found 14.07 %	

The susceptibilities for the two salts are independent of the field strength; their analytical and magnetical purity is secured. Table 2 gives the measurement of the temperature dependence of the susceptibility of the red compound from liquid air temperature to room temperature.

Table 2. $[\text{Ni}(\text{PE}_3)_2\text{Cl}_2]$. Temperature dependence of χ .

$^{\circ}\text{K}$	$-\chi_g \times 10^6$	$-\chi_M \times 10^6$
297	0.553	202.0
195	0.546	199.8
85	0.539	197.8
Mean value	0.546	199.7

The susceptibility is independent of the temperature. The slight decrease in χ_g when the temperature increases is not significant. The mean value -0.55×10^{-6} differs rather much from the earlier value. However, discre-

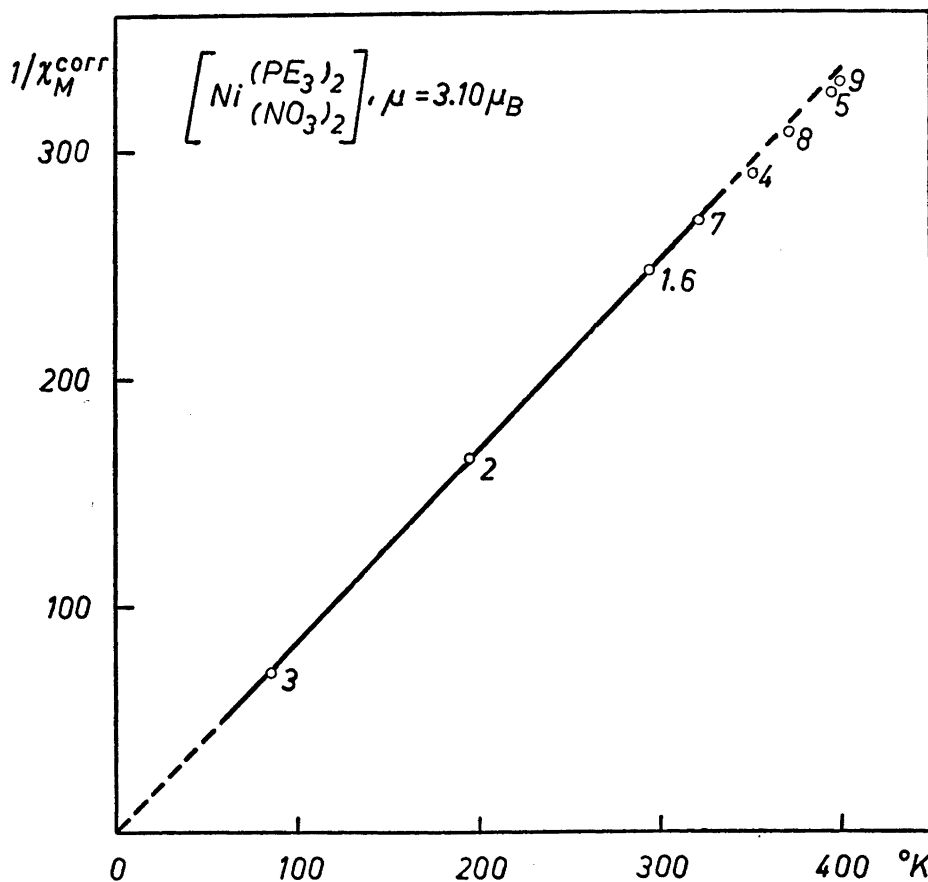


Fig. 1. $[\text{Ni}(\text{PE}_3)_2(\text{NO}_3)_2]$. Reciprocal corrected molar susceptibility plotted against the abs. temperature ($^{\circ}\text{K}$).

pancies of this order of size in the case of diamagnetic compounds are not unusual for different specimens of the same compound (different origin). We did not consider the effect important enough to recrystallize the salt until the diamagnetic susceptibility was constant. The original sample was not available; it might have contained a paramagnetic nickelcomplex. The new value, -0.55×10^{-6} , is considered to be the most probable.

The temperature-susceptibility measurements for the green nitrate are given in Fig. 1 where the reciprocal corrected molar susceptibilities are plotted against the temperature. We applied the molar diamagnetic susceptibility (room temperature) of the red chloride to correct the molar susceptibility of the green nitrate for diamagnetism. The total molar diamagnetic correction is $-\chi \times 10^6 = 202 - 42 + 38 = 198$, using the values -21×10^{-6} and -19×10^{-6} for the gramionic susceptibilities for the ions Cl^- and NO_3^- , respectively (compare Asmussen ²).

The green nitrate follows the Curie-law exactly; the Weiss correction is 0. The equation for the straight line is

$$\chi_M^{\text{corr}} = \frac{1.194}{T}$$

The magnetic moment calculated by means of the Curie-constant measured is = 3.10 Bohr magnetons. The earlier determination of the effective moment is in good agreement with this value; the deviation is not greater than that to be expected for specimens of different origin. The points in Fig. 1 are numbered, the measurements were carried out in the succession indicated by these numbers. It will be seen that points above 325°K are situated a little below the Curie-line. The reason is that the green nitrate gives off a slight amount of phosphine, which is condensed as small droplets in the measuring tube; the tube was evacuated at room temperature and sealed off. The series of measurements show, however, that the reaction is reversible.

The general conclusions of the measurements here reported are: The *trans*-planar molecule is in a singlet state and the tetrahedral molecule is in a triplet state. No significant indications of magnetically observable reactions in the solid state have been found. The colour changes in solution may be attributed to chemical reactions in the liquid.

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