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On the Possible Existence of Tetrahedral Nickel(II) Complexes

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The magnetic moments and the reflection spectra of a series of apparently tetrahedral Ni(II) complexes have been measured. Comparison with corresponding data for definitively octahedral complexes seems to show that most of the complexes investigated in reality are octahedral.

The magnetic susceptibilities of several Ni(II) complexes have been measured by one of us [1]. The calculated magnetic moments are in agreement with the Pauling theory for bond type and spatial arrangement of the ligands in the complexes. Representative compounds and experimental data are given in Table 1.

It should, however, be pointed out that the distinction between tetrahedral and octahedral configurations cannot be founded upon magnetic measurements and moments alone but should principally be based upon a knowledge of the chemical properties of the ligands, in particular their usual coordination capa-

Table 1. Magnetic properties of Ni(II)complexes. Analysis.

Substance	χ_g	χ_M	$\chi_M^{corr.}$	$\mu_{eff.}$	Analysis Calc.	Analysis Found	
$Ni(NH_3)_6Br_2$	12.7	4 099	4 251	3.16	18.28	18.50	Ni
$Ni(NH_3)_4(SCN)_2$	17.6	4 286	4 418	3.23	24.15	24.01	Ni
$Nien_3(SO_4)$	12.1	4 053	4 240	3.16	17.52	17.67	Ni
$Nien_2(SCN)_2, H_2O$	12.1	3 787	3 972	3.06	18.75	18.88	Ni
$Nipy_4(SCN)_2$	9.04	4 436	4 704	3.32	11.96	11.95	Ni
$Nitren(SCN)_2$	12.88	4 135	4 325	3.19	18.28	18.38	Ni
$Nitren(SO_4), 7H_2O$	9.78	4 176	4 422	3.23	22.49	22.68	SO_4
$Nitren(SO_4)$	14.11	4 245	4 400	3.22	31.92	32.20	SO_4
$Ni(DH_2)_2Cl_2$	11.70	4 233	4 415	3.23	16.22	16.42	Ni

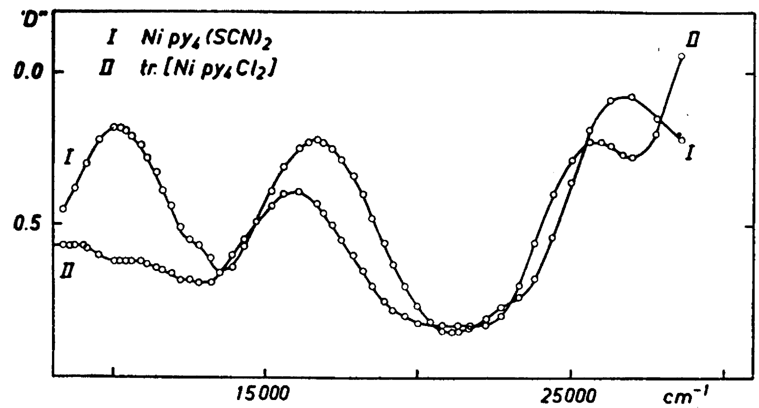

Fig. 1. Reflection spectra of $Ni(NC_5H_5)_4(SCN)_2$ and *trans* $Ni(NC_5H_5)_4Cl_2$.

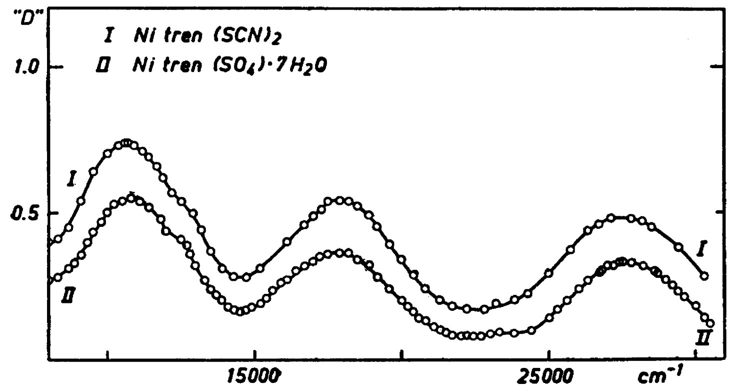

Fig. 2. Reflection spectra of $Nitren(SCN)_2$ and Nitren (SO_4) $7H_2O$.

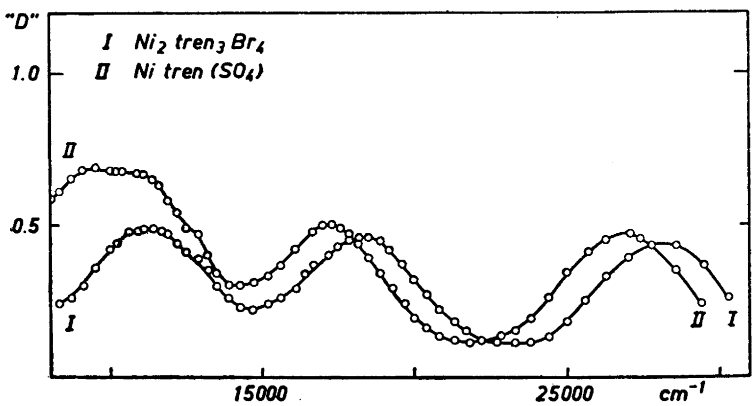

Fig. 3. Reflection spectra of $Ni_2tren_3Br_4$ and $Nitren(SO_4)$.

Table 2. Reflection spectra of some Ni(II) complexes. σ_1, σ_2 and σ_3 are the wavenumbers in cm^{-1} of the three main bands. The wavenumbers for some small bands are also given. The ratio σ_2/σ_1 has been discussed by Ballhausen [10].

Substance	σ_1	σ_2	σ_3	Small bands	Δ	15 B	σ_2/σ_1
$NiSO_4 . 7H_2O$	8 500	14 700	25 700	15 500 19 000 22 000	8 500	14 900	1.73
$Nipy_4Cl_2$	9 500	15 900	25 700	11 000	9 500	13 100	1.67
$Nitren(SO_4)$	10 000	17 200	26 800	12 500	10 000	14 000	1.72
$Nien_2(SCN)_2 . H_2O$	10 000	17 900	28 000	12 000	10 000	15 900	1.79
$Nipy_4(SCN)_2$	10 200	16 600	26 700	14 000	10 200	12 700	1.63
$Ni(NH_3)_6Br_2$	10 800	17 500	28 200		10 800	13 500	1.62
$Nitren(SO_4) . 7H_2O$	10 800	17 800	27 600	13 000	10 800	13 000	1.65
$Nitren(SCN)_2$	10 800	17 800	27 800	12 500	10 800	13 200	1.65
$Nien_3(SO_4)$	11 300	18 500	29 000	12 800	11 300	13 600	1.64
$Ni_2tren_3Br_4$	11 400	18 400	28 200		11 400	12 400	1.61
$Ni\ ptn_2\ SO_4$	12 100	19 300	29 500		12 100	12 500	1.59
$Ni(DH_2)_2Cl_2$	10 900	17 100		12 900	10 900		1.57

city. This means, *e.g.*, that a complex as $Nitren(SCN)_2$ can either be considered as $[Nitren(SCN)_2]$ or as $[Nitren]\ (SCN)_2$, both structures are in agreement with the magnetic moment found.

Magnetic measurements on paramagnetic Ni(II) complexes show that the orbital magnetic moment contributes in higher or lesser degree to the total moment. The Penney-Schlapp approximation makes it probable that the orbital contribution will be smaller in octahedral complexes than in tetrahedral [2]. According to Table 1 we may consider some of these complexes, which hitherto have been formulated as tetrahedral, as octahedral.

Our study of the reflection spectra of some of the tabulated apparently tetrahedral complexes has shown that in all cases three bands approximately situated as the three bands in undoubtedly octahedral Ni(II) complexes and reasonable values for the parameters Δ and 15 B can be found. Table 2 gives a summary of our results. Some examples of the measured reflection spectra are given in Figs. 1—3.

An X-ray investigation carried out by Cox and Webster [3] showed that $Nitren(SCN)_2$ either has the tetrahedral structure $[Nitren]\ (SCN)_2$ or the *cis*-octahedral $[Nitren(SCN)_2]$. Our measurements of magnetism and reflection spectrum seem to indicate the latter possibility. If the compound $Nitren(SO_4)$, 7 H_2O has octahedral structure (*cis*) then it is either an aquo or a sulphato complex. Since two of the seven water molecules in $Nitren(SO_4)$, 7 H_2O are

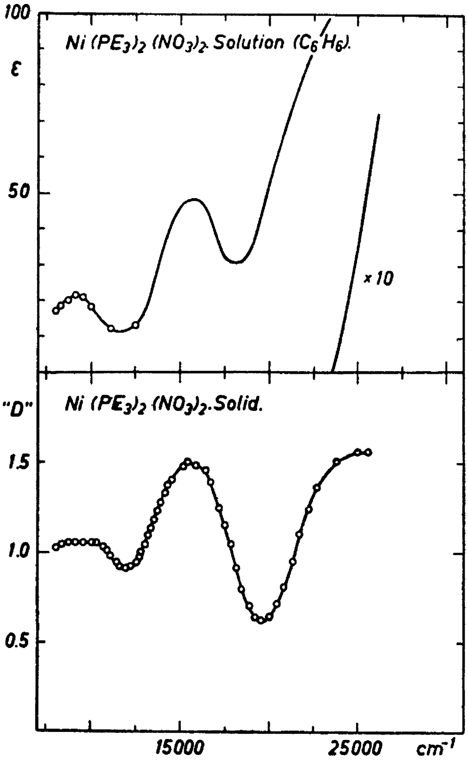

Fig. 4. Absorption spectrum and reflection spectrum of $[Ni(P(C_2H_5)_3)_2(NO_3)_2]$

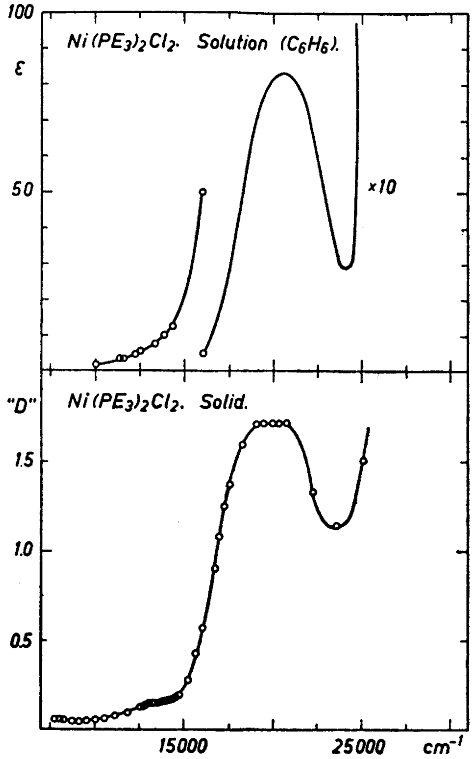

Fig. 5. Absorption spectrum and reflection spectrum of $[Ni(P(C_2H_5)_3)_2Cl_2]$

stronger bound than the others [4], and since the absorption bands are situated at the same places as in the aqueous solution of equivalent amounts of tren and $Ni(NO_3)_2$ investigated by Ballhausen and Klixbüll Jørgensen [5] it is reasonable to consider the heptahydrat as a *cis* diaquo complex. It is, however, difficult for the authors to imagine the anhydrous complex Nitren(SO_4) with octahedral configuration since as far as we know it has never been verified that SO_4^{-2} can act as a ligand with the coordination capacity 2. However, the experimental data indicate nothing unique with the properties of this compound.

Particular interest is connected with the paramagnetic green compound $Ni(P(C_2H_5)_3)_2(NO_3)_2$. The absorption spectrum in solution (benzene) and the reflection spectra are shown in Fig. 4. In Fig. 5 we give the spectra for the diamagnetic red chloro-compound [6]. The similarity between the spectra in Fig. 4 indicates that a monomer is also present in the crystal. The magnetic moment [6] is 3.10 μ_B which may be interpreted as corresponding with an octahedral structure. This assumption requires the ligand NO_3^- to be bidendate;

this seems to be rather unprobable although the isoster ion CO_3^{-2} can have the coordination capacity two, *e.g.* in $[Co(NH_3)_4(CO_3)]^{+1}$. Furthermore we do not observe 3 bands in the spectra and are forced to postulate that the band corresponding to $^3F(\Gamma_4)$ is masked of the high electron-transfer band in ultraviolet. The octahedral structure thus involves 2 unproven assumptions. However, it must be admitted that the 2 bands observed occur nearly at the wavenumbers required for an octahedral Ni(II)-complex. The possibility of the tetrahedral configuration cannot be ruled out, but we want in this connection to point out that the absorption curves for $Ni(P(C_2H_5)_3)_2(NO_3)_2$ and for $[Ni(OH_2)_6]^{+2}$ differ less than the corresponding curves for $[Co(OH_2)_6]^{+2}$ and $[CoCl_4]^{-2}$. The last ion has after all experimental evidences tetrahedral structure. The last possibility for the structure of $Ni(P(C_2H_5)_3)_2(NO_3)_2$ is the *cis*-planar configuration. As for the present we have no knowledge of how far it is possible that the action of this asymmetric field may result in such splittings that the configuration will allow for the observed magnetic moment, we are of the opinion that the lack of theoretical and experimental evidence makes it impossible to solve this problem with security. We consider an X-ray structure analysis to be more conclusive than the conclusions drawn from the spectra and magnetic moments alone.

EXPERIMENTAL

The solid samples were prepared according to the methods previously described [1,6]. The following abbreviations are used:

tren = β,β',β''-triaminotriethylamin
ptn = 1,2,3-triaminopropane
DH_2 = dimethylglyoxime

The magnetic measurements were carried out by means of the Guoy method described in earlier papers [9].

The reflection spectra were measured by means of a Beckman DU spectrophotometer equipped with a photomultiplier. In order to estimate the accuracy of the apparatus we measured the reflection spectrum of $NiSO_4$, $7H_2O$ and compared it with the known absorption curves for $[Ni(OH_2)_6]^{+2}$-solutions. These results will be published elsewhere [7] but it is worth while to note that all the bands known from solutions [8] were found in the reflection spectrum.

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REFERENCES

1. Asmussen, R. W. *Studies in the Magnetochemistry of Inorg. Complex Compounds* (in Danish), Copenhagen 1944.
2. Nyholm, R. S. *Quart. Rews.* **53** (1953) 263.
3. Cox, E. G. and Webster, K. C. *Z. Krist.* **92** (1935) 478.
4. Mann, F. G. and Pope, W. J. *J. Chem. Soc.* **1926** 482.
5. Jørgensen, C. Klixbüll *Acta Chem. Scand.* **10** (1956) 887.
6. Asmussen, R. W., Jensen, A. and Soling, H. *Acta Chem. Scand.* **9** (1955) 1391.

7. Bostrup, O. and Jørgensen, C. Klixbüll, *Acta Chem. Scand.* **11** (1957) 1223.
8. Orgel, L. E. *J. Chem. Phys.* **23** (1955) 1004.
9. Christiansen, J. A. and Asmussen, R. W. *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.* **12** (1934) No. 10.
Asmussen, R. W. and Soling, H. *Acta Chem. Scand.* **8** (1954) 558; *Wilhelm Klemm-Festschrift, Z. anorg. Chem.* **283** (1956) 3.
10. Ballhausen, C. J. *Rec. trav. chim.* **75** (1956) 665.

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