

LIGAND SUBSTITUTION AND COMPLEX STRUCTURE, XV. MAGNETIC AND SPECTRAL STUDIES OF $\text{Ni}[\text{Hsal-pX.Ph}]_2$ TYPE COMPLEXES

By

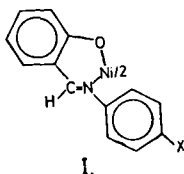
J. CSÁSZÁR

Institute of General and Physical Chemistry, Attila József University, Szeged, Hungary

(Received 6th July, 1979)

A study was made on the magnetic and spectral behaviour of $\text{Ni}[\text{Hsal-pX.Ph}]_2$ ($\text{X} = \text{N}(\text{CH}_3)_2$, OH , OCH_3 , OC_2H_5 , CH_3 , C_2H_5 , NHCOCH_3 , H , F , Cl , Br , I , CN , NO_2) type complexes and conclusions were drawn regarding their structures in the solid phase and in solution.

It is well known [1—5] that the composition, physicochemical properties and stereochemistry of metal chelates are decisively influenced by the ligand substituents. The stereochemical forms of these complexes are labile, so very often the molecular configurations in solution are different from those in the solid state, and conformational equilibria exist between different forms. This structural lability implies that the free-energy difference between the different stereochemical forms is usually small. In the present work we discuss the magnetism and spectra of the following chelate complexes (structure I).



No.	X	No.	X
I.	$\text{N}(\text{CH}_3)_2$	VIII.	H
II.	OH	IX.	F
III.	OCH_3	X.	Cl
IV.	OC_2H_5	XI.	Br
V.	CH_3	XII.	I
VI.	C_2H_5	XIII.	CN
VII.	NHCOCH_3	XIV.	NO_2

Experimental

The complexes were prepared by the known method of the reaction of bis-(salicylaldehyde)nickel(II).2 H₂O with the aniline derivatives in acetone solution; the products were purified by recrystallization from chloroform. The compositions were checked by C, N and H analyses.

The magnetic moments were determined at room temperature by the Gouy method; Hg[Co(NCS)₄] was used for the calibration. The diamagnetic correction was calculated from literature data [6].

Reflectance and solution spectra were measured with a Beckman DU and a SPECORD UV—VIS spectrophotometer, respectively; analytical grade MgO and appropriately purified [7] solvents were used as references.

Results

Magnetic moments, stereochemistry and spectral data are summarized in Table I; the visible spectra of VII and XIII are illustrated in Fig. 1 and Fig. 2.

In the solid state VII and VIII ($\sigma=0$) are diamagnetic, while the other compounds show paramagnetism with about 2.80—3.32 BM; these values are in good agreement with the data of HOLM [3]. In the case of II the low magnetism

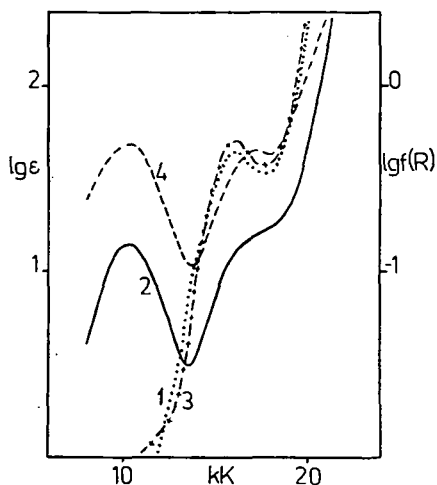


Fig. 1. Spectra of Ni[Hsal-p-NHCOCH₃.Ph]₂. 1: in CHCl₃; 2: in C₆H₅N; 3: reflection spectrum; 4: reflection spectrum of the bis-pyridine adduct.

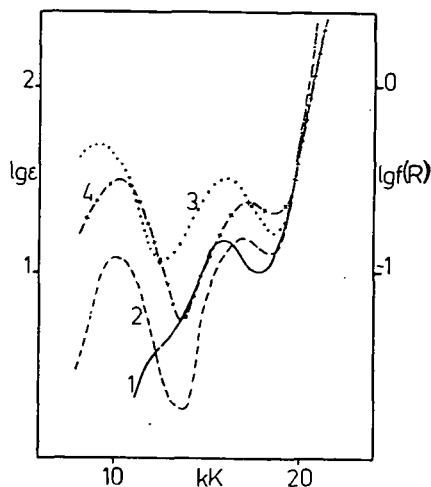


Fig. 2. Spectra of Ni[Hsal-p-CN.Ph]₂. 1: in CHCl₃; 2: in C₅H₅N; 3: reflection spectrum; 4: reflection spectrum of the bis-pyridine adduct.

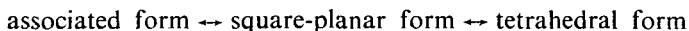
(2.42 BM) can be interpreted in terms of a polynuclear structure; this is supported by the reflectance spectral studies.

In chloroform solution all the compounds studied are paramagnetic; with the exceptions of VII and VIII, the solution magnetism is lower than the solid-phase

paramagnetism; these complexes show "anomalous magnetic behaviour". This fact shows that, at room temperature, about 69—88% of all the species are paramagnetic, with a triplet ground state.

On the basis of the magnetic moments, conclusions can be drawn regarding the stereochemistry of the chelates. In the crystalline state VII and VIII have a square-planar arrangement. The other compounds probably have a strongly distorted octahedral structure; II is polynuclear with nickel-oxygen interaction (see Table I).

The systems formed in solution are very complicated. In noncoordinating solvents (e.g. CHCl_3) three species must be taken into account: a) diamagnetic, square-planar; b) paramagnetic, distorted tetrahedral molecules; and c) paramagnetic associates. These three species give rise to the following concentration and temperature-dependent conformational equilibrium [3, 4, 8]:



This equilibrium is displaced completely towards the right with increasing temperature or with decreasing concentration. The strong temperature-dependences of the solution moments and the spectral changes confirm the presence of the species presented in Table I.

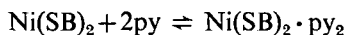
The pyridine solutions of the chelates and the solid bis-pyridine adducts have very similar magnetic moments, of about 3.10—3.25 BM; these values correspond to the moments measured for six-coordinated nickel(II) complexes.

Similar conclusions can be drawn on the basis of the spectral investigations.

The reflectance spectra of VII and VIII are characteristic of square-planar nickel(II) complexes; the bands at about 16 kK are attributed to the ${}^1B_{1g} \leftarrow {}^1A_g$ transitions [9]. The other d—d bands are covered by the absorption of the ligand itself. For the other compounds two medium-intensity bands appear at 9—10 and 16—17 kK, which can be assigned to the NiO_2N_4 chromophores.

All the complexes studied have a medium-intensity band at *ca.* 16—17 kK in chloroform solution; these spectra indicate predominantly a square-planar arrangement. The intensities of these bands change with temperature to only a small extent; a similar change can be observed for the 10 kK bands. The changes of the intensity are difficult to interpret, because the characteristic bands of the square-planar and the distorted tetrahedral species, as well as those of the distorted tetrahedral form and the associates, appear in similar spectral regions.

The absorption spectra of the complexes in pyridine solution are very similar to the reflection spectra of the corresponding $\text{Ni}(\text{SB})_2 \cdot \text{py}_2$ adducts. The bands measured at ~ 10 (ν_1^*) and ~ 17 (ν_2^*) kK can be assigned to the ${}^3B_{1g} \leftarrow {}^3B_{3g}$ and ${}^3B_{2g} \leftarrow {}^3B_{3g}$ transitions, respectively. The intensities of ν_1^* and ν_2^* show a strong temperature-dependence. With increasing temperature the equilibrium



shifts toward to the left, and the intensity of ν_1^* decreases while that of ν_2^* remains nearly unchanged. The temperature effect is enhanced if the spectra are examined in an indifferent solvent containing pyridine or pyridine derivatives. The ν_2^* band of the adducts and the ν_1^* band of the planar species can be found at very near energies.

Table I
Magnetic and Spectral Data on the Complexes

No.	μ_{BM}		p % ^{2*}	Stereochem. ^{3*}		ν_{max}^{4*}		ν_{max}^{4*}	
	solid	CHCl ₃ soln.		solid	CHCl ₃ soln.	refl.	CHCl ₃ soln.	refl. of py-add.	py soln. of chelate
I	3.28	3.06	86	q0	P+dT+A	10.20; 16.90	16.85	~16.50; 10.22	10.30
II	2.42	*	?	q0+A	?	~9.00; ~17.00	~16.90	18.00 ^{5*}	10.50; 16.00
III	3.28	3.02	84	q0	P+dT+A	10.60; 16.80	16.70	10.30; 17.10	10.10; ~16.50
IV	3.24	3.10	88	q0	P+dT+A	10.40; 16.60	16.60	10.40; 17.30	10.20; 17.20
V	3.30	3.03	84	q0	P+dT+A	10.00; 16.90	16.40	10.08; 17.00	10.20; 17.20
VI	3.25	2.97	81	q0	P+dT+A	10.00; 16.80	16.60	10.00; 17.00	10.00; 17.10
VII	0	2.75	69	P	P+A	16.00	16.10	10.20; 17.10	10.20; 17.20
VIII	0	2.96	80	P	P+A	16.30	16.35	10.20; 17.30	10.20; 17.20
IX	3.27	2.93	79	q0	P+dT+A	9.90; 16.30	16.40	10.50; 17.30	10.22; 17.10
X	3.32	2.95	80	q0	P+dT+A	9.80; 17.00	16.10	10.30; 17.10	10.20; 17.30
XI	2.80	2.88	76	q0	P+dT+A	9.70; 16.60	16.20	10.35; 17.10	10.15; 17.20
XII	3.30	3.07	87	q0	P+dT+A	10.20; 16.70	16.30	10.40; 17.10	10.40; 16.90
XIII	3.18	3.04	85	q0	P+dT+A	~9.30; 16.10	15.80	10.20; 17.20	10.05; 17.00
XIV	3.26	*	?	q0	?	9.40; 16.40	~16.60	10.80; 17.70	10.30; ~16.80

* insoluble;

^{2*} p% = 100 ($\mu_{BM}^2/3,3^2$);

^{3*} P: square-planar, A: associates, q0: quasi-octahedral, dT: distorted tetrahedral;

^{4*} in kK;

^{5*} broad, indistinct band

From these data a great decrease of symmetry can be deduced; this is also suggested by the very high values of the RACAH parameters; the octahedral energy functions cannot be used.

The chemical behaviour and stereochemistry of the nickel(II) chelates are governed by the electronic (electronegativity of Ni(II) and L; ligand field strength; nature of Ni—L bond) and steric factors (shape of ligand, crystal packing effect). In the case of the complexes studied in this work, the nature and position of X are the determining factors in the stereochemistry of the complexes, probably only through an electronic effect.

References

- [1] Yamada, S. *et al.*: *Coord. Chem. Rev.*, **3**, 247 (1968); **1**, 415 (1966) (and references therein).
- [2] Yamada, S. *et al.*: *Bull. Chem. Soc. Japan*, **36**, 755 (1963); **40**, 1864 (1967); **39**, 994 (1966).
- [3] Holm, R. H.: *Advances in the Chemistry of the Coordination Compounds.*, Ed. S. Kirschner, McMillan Co., New York, 1961.
- [4] Sacconi, L.: *Transition Metal Chemistry. A Series of Advances.*, Ed. R. L. Carlin; M. Dekker Inc., New York, 1968. p. 341 (and references therein).
- [5] Császár, J., *et al.*: *Acta Chim. Hung.*, **86**, 9 (1975); **78**, 17 (1973); **86**, 3 (1975).
- [6] Lewis, L., R. G. Wilkins: *Modern Coordination Chemistry.*, Intersci. Publ. Co., New York, 1960.
- [7] *Technique of Organic Chemistry*, VII. Organic Solvents, 2nd Ed., Intersci. Publ. Co., No. 4., 1955.
- [8] Sacconi, L., M. Ciampolini: *J. Amer. Chem. Soc.*, **85**, 1750 (1963).
- [9] Maki, G.: *J. Chem. Phys.*, **28**, 651 (1958); **29**, 1129 (1959).
- [10] Kannan, T. S., A. Chakravorty: *Inorg. Chem.*, **9**, 1153 (1970).

ИССЛЕДОВАНИЯ ВЛИЯНИЯ ЗАМЕСТИТЕЛЕЙ В ЛИГАНДАХ НА СТРУКТУРУ КОМПЛЕКСОВ, XV. ИЗУЧЕНИЕ МАГНИТНЫХ И СПЕКТРАЛЬНЫХ СВОЙСТВ КОМПЛЕКСОВ ТИПА $\text{Ni}[\text{Hsal-pX.Ph}]_2$

Й. Часап

Изучены магнитные и спектральные свойства комплексов $\text{Ni}[\text{Hsal-pX.Ph}]_2$ ($\text{X} = \text{N}(\text{CH}_3)_2$, OH, OCH₃, OC₂H₅, CH₃, C₂H₅, NHCOCH₃, H, F, Cl, Br, I, CN, NO₂) и сделаны заключения относительно их структуры в твердой фазе и растворах.