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Thermodynamic and Spectroscopic Investigation on Ni(II)–Pyridine Mixed Complexes with Iminodiacetic, Oxydiacetic and Thiodiacetic Acids in Aqueous Solution

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The stability constants ($I = 0.1$ mol dm^{-3} K[NO$_3$] and $T = 25$ °C) of the ternary complexes of Ni(II) and pyridine (py) with iminodiacetic (IDA), oxydiacetic (ODA) and thiodiacetic (TDA) acids have been determined pH metrically in aqueous solution. Electronic and PMR spectra have been carried out. In every investigated complex, the Ni(II) ion reaches the hexacoordination. A general agreement between thermodynamic and PMR data has been observed in the evaluation of the effect of the formation of pyridine mixed complexes from the simple complexes of the three investigated chelating ligands.

Introduction

The study of mixed ligand complexes has attracted the attention of many workers, on account of the biological implications of this kind of species [1].

It is still an open question what is the mutual influence of the ligands in the molecule of the complex [2]. In this connection, thermodynamic and spectroscopic investigations have been carried out extensively.

However, a structural investigation may be misleading when not knowing exactly the kind of species present. On the other hand, owing to the different sources of interactions in solutions to which the thermodynamic parameters are sensitive, thermodynamically obtained data can only be used for comparisons among strictly similar complexes.

Bearing in mind these problems, and considering that in the literature there are few works on Ni(II) dealing with both the thermodynamic and spectroscopic aspects [3], we thought it useful to study thermodynamically and spectroscopically the Ni(II) complexes with pyridine and three different potential tridentate ligands which show a structural similarity, namely iminodiacetic (IDA), oxydiacetic (ODA) and thiodiacetic (TDA) acids.

The measurements concerning the determination of the formation constants of both binary and ternary complexes, as well as of the protonation constants, were carried out potentiometrically at $I = 0.1$ mol dm^{-3} (K[NO$_3$]) and $T = 25$ °C.

Considering the short electronic relaxation time of Ni(II) in its common coordination environments, we studied these complexes using the PMR technique. Electronic spectra have also been carried out.

Experimental

Chemicals

Pyridine solutions were prepared by diluting pyridine (C. Erba RP) concentrated solutions; they were then titrated acidimetrically both to check their purity and to standardize the various stock solutions. Pyridine pK_1^H value was in agreement with the value previously determined in our laboratory [4].

The purification and the standardization of the other reagents were as previously described [5, 6].

The $Ni(NO_3)_2$ solutions were standardized by titration with EDTA using murexide as indicator, as recommended by Flaschka [7].

The ionic strength was adjusted to 0.1 mol dm^{-3} by adding KNO_3.

Grade A glassware was used throughout.

Emf Measurement

The potentiometric measurements were carried out by means of two semi-automatic potentiometers (Amel 232 and Analog Devices AD 2027B) using glass electrodes (EIL or Ingold 201NS) and single calomels (Ingold).

$E°$ and protonation constants were determined respectively by titrating 25–50 ml of HNO_3 and of ligand solution, with KOH. The stability constants of the binary and ternary systems respectively were computed from the data obtained by titrating 25–50 ml of solutions containing NiL (L =

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TABLE I. Ranges of Concentrations (mmol dm^{-3}) Used for Binary and Ternary Systems.

	Ni–L				Ni–L′–py			
	C_{Ni}	C_L	C_H		C_{Ni}	$C_{L'}$	C_{py}	C_H
IDA	3–12	6–24	12–48	IDA	3–12	6–24	20–48	32–90
ODA	3–12	9–30	18–60	ODA	3–12	9–25	15–40	33–87
IDA	3–12	8–27	16–54	TDA	3–12	8–23	15–40	31–82
py	6–12	15–40	15–40					

TABLE II. Formation Constants for Ni(II) Binary Systems at T = 25 °C and I = 0.1 mol dm^{-3} (K[NO$_3$]).

Reaction	IDA	ODA	TDA	py
$Ni + L + H \rightleftarrows NiLH$	–	–	6.0 (0.2)^a	–
	–	–	5.82^f	–
$Ni + HL \rightleftarrows NiLH$	–	–	2.15^d	–
$Ni + L \rightleftarrows NiL$	8.07 (0.05)^a	2.32 (0.03)^a	3.93 (0.02)^a	1.90 (0.05)^a
	8.13^b	3.80^c	4.20^d	1.85^e
			3.93^f	1.87^g
$Ni + 2L \rightleftarrows NiL_2$	14.23 (0.09)^a	–	6.6 (0.1)^a	3.4 (0.3)^a
	14.1^b	–	7.01^d	3.10^g
	–	–	7.03^f	–
$Ni + 3L \rightleftarrows NiL_3$	–	–	8.55^f	3.71^g

[a] This work. [b] Ref. 31. [c] Ref. 16. [d] Ref. 19. [e] Ref. 33. [f] Ref. 18. [g] Ref. 32. The figures listed in the table are the log K s of the corresponding reactions. The figures in parentheses are the range, *i.e.* the maximum deviation from the mean.

IDA, ODA or TDA) and NiLpy, with KOH. The pH values were reproducible within 0.01 units.

For the concentrations investigated see Table I. Other details were as previously described [8–11].

Electronic Absorption Spectra

These were recorded on an Optica CF4NI double-beam spectrophotometer, using 1 cm quartz cells.

PMR Spectra

These were obtained at 80 MHz on a Bruker WP-80 spectrometer at room temperature in the Fourier transform mode. The concentrations of the solutions, in D_2O, were 10–20 mmol dm^{-3} in Ni(II) and in the chelating ligands. Owing to the broadness of the paramagnetic peak (especially of the *o*-proton of pyridine) when compared with the sharpness and strength of HDO peak, it was necessary to use the block-averaging technique to obtain the spectra [12].

Calculations

All calculations concerning the calibration of the electrode system, the purity of the ligands (checked by acidimetric titrations) and the protonation constants were performed by using the computer program ACBA [13] which refines the parameters of an acid–base titration by using a non-linear least squares method minimizing the function $U = \Sigma(v - v_{calcd})^2$. MINIQUAD 76A [14] was used to handle the binary and ternary systems data. MINIQUAD minimizes the function $U = \Sigma(T_i - T_{i,calcd})^2$, where T is the analytical concentration of the i-th component, in our case i = 1, ..., 4 (at most four components, *i.e.* nickel, L, py, and the proton).

The residuals ($v - v_{calcd}$, $T - T_{calcd}$) were analyzed statistically according to a method proposed by Vacca *et al.* [14].

However the validity of the statistical analysis depends on two additional factors, *i.e.*: i) independdence and ii) wide range of experimental conditions. As to the first point we used different equipment and different standard solutions throughout in order to make the experiments as independent as possible from one another; as regards the second point we tried to vary as much as possible the analytical concentrations of the reagents as well as the delivery interval of the burettes.

The distribution diagrams were obtained by means of the computer program DISDI [15].

TABLE III. Formation Constants for Ni(II) Ternary Complexes at T = 25 °C and I = 0.1 mol dm^{-3} (K[NO$_3$]).

Reaction	IDA	ODA	TDA
Ni + L + py $\rightleftarrows$ NiLpy	10.07 (0.09)^a	5.05 (0.05)^a	6.40 (0.06)^a
	10.10^b	–	–
Ni + L + 2py $\rightleftarrows$ NiLpy$_2$	11.4 (0.2)^a	6.10 (0.09)^a	–
	10.9^b	–	–
Ni + L + 3py $\rightleftarrows$ NiLpy$_3$	11.27^b	–	–

^{a}This work. ^{b}Ref. 20. The figures listed in the table are the logK's of the corresponding reactions. The figures in parentheses are the range, *i.e.* the maximum deviation from the mean.

Results

Potentiometry

The formation constants of binary and ternary complexes are reported in Tables II and III respectively, where we have also reported some literature values for comparison. As can be seen, a good agreement is generally observed. For [Ni(ODA)], under similar experimental conditions a significantly higher value has been reported [16]. This value is very close to the value of the corresponding copper(II) complex [17], and this is in contradiction with the known trend.

For the Ni–TDA system, a 1:3 species has been reported [18], in contradiction with our and other authors' [19] results. Owing to the high charge of this hypothetical species, and to the fact that TDA which has three potential donor atoms should behave as a bidentate ligand, the existence of the 1:3 complex seems unlikely.

As regards ternary systems, only the Ni–IDA–py system has already been investigated, by Fridman *et al.* [20] who reported a 1:1:3 species. It must be pointed out that the above authors used pyridine/IDA ratios much higher than the highest used in our measurements.

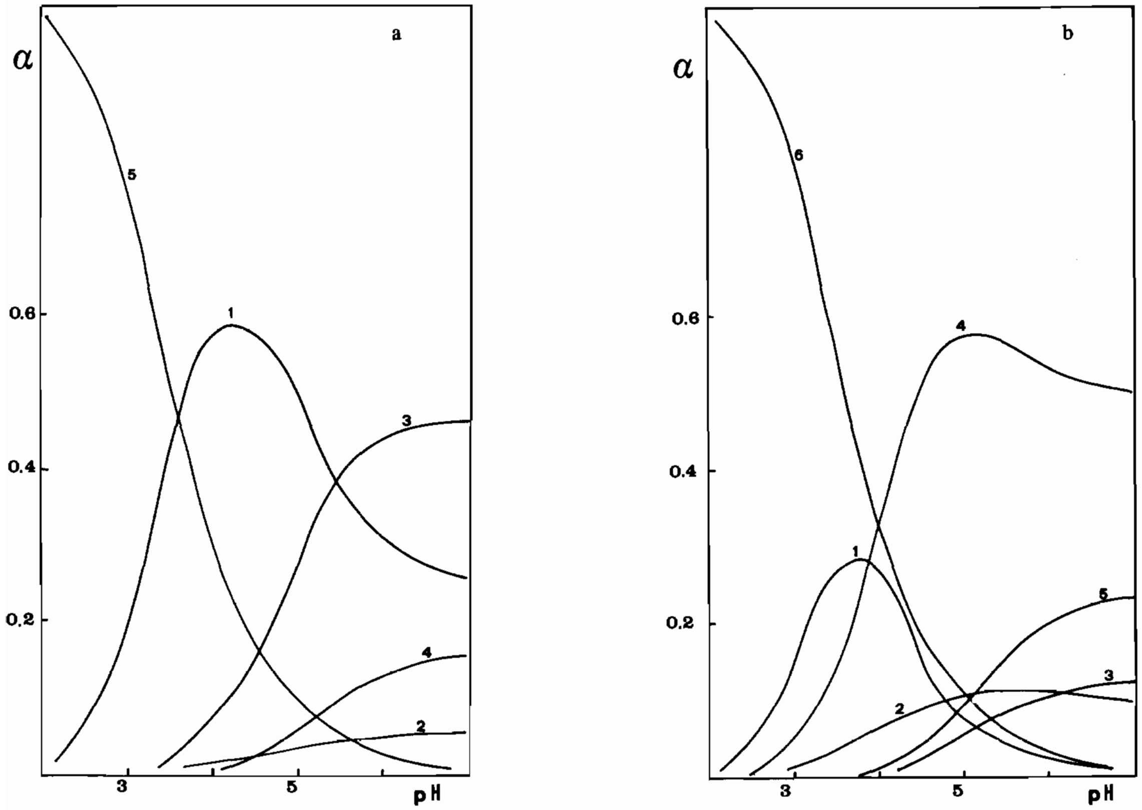

Fig. 1. See overleaf for full legend.

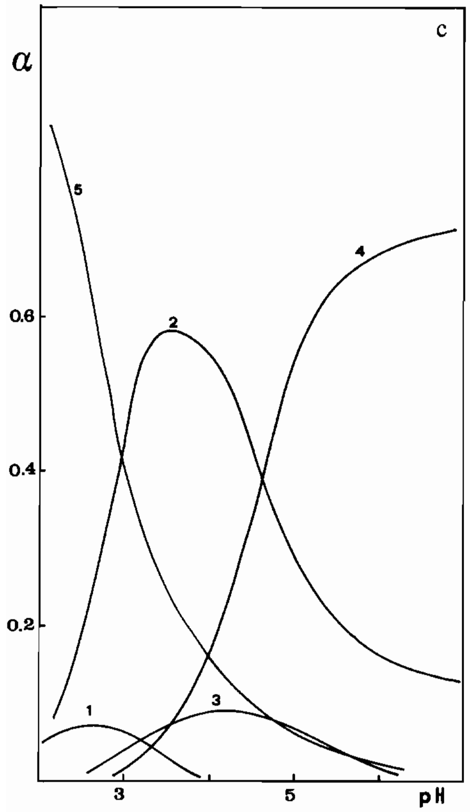

Fig. 1. Distribution diagrams. The degree of formation refers to Ni(II). Concentrations are expressed in mmol dm^{-3}. a) Ni–IDA– py system: C_{Ni} = 10; C_{IDA} = 10; C_{py} = 25. 1. Ni(IDA); 2. Ni(IDA)$_2$; 3. Ni(IDA)(py); 4. Ni(IDA)(py)$_2$; 5. Free Ni(II) ion. b) Ni–ODA–py system: C_{Ni} = 10; C_{ODA} = 10; C_{py} = 40. 1. Ni(ODA); 2. Ni(py); 3. Ni(py)$_2$; 4. Ni(ODA)(py); 5. Ni(ODA)(py)$_2$; 6. Free Ni(II) ion. c) Ni–TDA–py system: C_{Ni} = 10; C_{TDA} = 10; C_{py} = 25. 1. Ni(TDA)H; 2. Ni(TDA); 3. Ni(TDA)$_2$; 4. Ni(TDA)(py); 5. Free Ni(II) ion.

Typical distribution diagrams, reported in Fig. 1, show that in the Ni–IDA–py system there is a competition between simple and mixed complexes all over the investigated pH range, whereas in the Ni–ODA–py and Ni–TDA–py systems, at higher pH values, the 1:1:1 species are by far the most relevant.

Electronic Spectra

In the investigated wavelength range, we observe the presence of the two peaks due to d – d transitions, namely $^3T_{1g} \leftarrow {}^3A_{2g}$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, while the third transition ($^3T_{2g} \leftarrow {}^3A_{2g}$) can be guessed from the increase of absorbance on going towards higher wavelengths.

The low values of absorbance show that, in every investigated complex, hexacoordination is achieved through the coordination of the required number of water molecules. This behaviour is different from that observed in the corresponding complexes of Cu(II), where a change in coordination number occurs on going from one complex to another [21, 22].

PMR Spectra

In Fig. 2 a scheme is reported showing the downfield isotropic shifts for the different complexes, referred to the corresponding diamagnetic peak of the free ligand. The spectra in Fig. 2 are all new, apart from [Ni(IDA)] [23], reported for comparison.

The analytical concentrations at which the spectra were carried out were chosen in such a way as to have the predominance of one species; this could be done through the *a priori* simulation of the titration using the stability constants obtained potentiometrically.

The assignment of the peaks to the corresponding protons has been made supposing, as is likely, that no

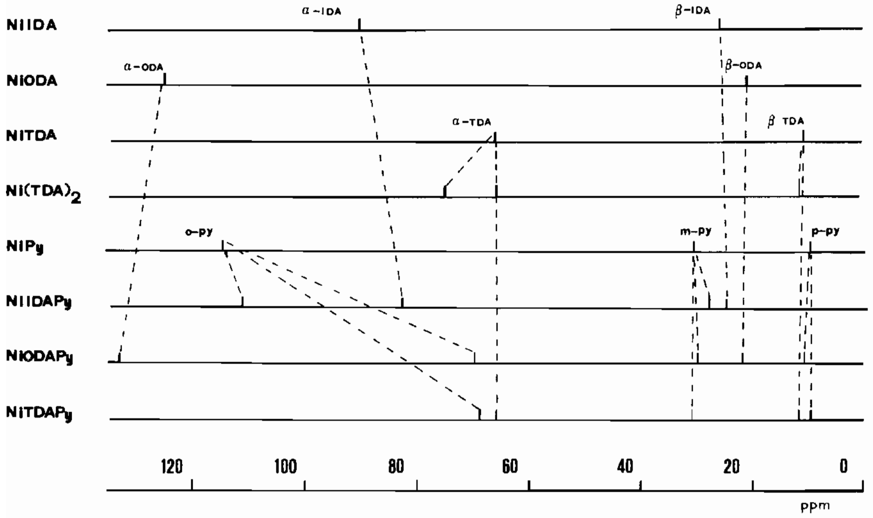

Fig. 2. Schematic PMR spectra of the investigated complexes. The isotropic shifts, referred to the peak of the corresponding free ligand, are all downfield and therefore should be considered as negative.

TABLE IV. Normalized Isotropic Shifts of Pyridine Protons in Different Ni(II) Complexes.

	2-H	3-H	4-H	Ref.
Ni(py)	1	0.26	0.08	[a]
Ni(IDA)(py)	1	0.25	–	[a]
Ni(ODA)(py)	1	0.43	0.16	[a]
Ni(TDA)(py)	1	0.45	0.14	[a]
Ni(AA)$(py)_2$	1	0.29	0.08	25
Ni$(py)_6$	1	0.37	0.12	26

[a] This work.

TABLE V. Comparison between Thermodynamic and PMR Data.

Reaction	Log K	$\Delta(\Delta_p)$[a]
Ni(IDA) + py $\rightleftarrows$ Ni(IDA)py	2.00	–7
Ni(ODA) + py $\rightleftarrows$ Ni(ODA)py	2.73	+8
Ni(TDA) + py $\rightleftarrows$ Ni(TDA)py	2.47	0

[a] $\Delta(\Delta_p)$ is the difference between the isotropic shift of mixed and simple complexes. The positive sign corresponds to a larger downfield shift. $\Delta(\Delta_p)$ values are in p.p.m.

dramatic change in spin delocalization occurs on going from binary to ternary complexes.

On the basis of the number of peaks exhibited by PMR spectra, it appears that in all the investigated complexes the rotation of methylene groups of these tridentate ligands is hindered. In [Ni(TDA)$_2$] only three peaks are observed, probably owing to the overlapping of the peaks due to the β-protons of the two coordinated molecules. In Ni(IDA)py, the peak due to the *p*-proton of pyridine is not observed, probably because it is too close to the peak of free pyridine.

In our PMR spectra we always observe the signal of the free ligand, and the isotropic shifts are not influenced by the amount of free ligand present, as long as the same species exists. On the other hand, a broadening of the peak due to the free ligand (in particular of pyridine, always in excess in our experiments) was observed. This is a typical case of slow chemical exchange, in which the shifts of the paramagnetic species are far greater than the reciprocals of the transverse relaxation times [24]; an additional broadening can be ascribed to the outer sphere relaxation.

Discussion

Simple and mixed complexes of Ni(II) and pyridine have been thoroughly investigated [25–27], with the aim of comparing experimental coupling constants, obtained from NMR spectra, with theoretical calculations. In this regard, INDO methods have proved to be the most effective way to reproduce this kind of experimental data [28, 29].

However, owing to the complete neglect of pseudocontact shifts and the approximations involved in INDO calculations carried out on the parent ligand ions, a quantitative agreement cannot be expected.

On the other hand, the size of the differences observed in Table IV among the normalized isotropic shifts of pyridine protons in the different complexes makes it very hard to explain these differences only on the basis of the above mentioned approximations. This size suggests, rather, that a spin delocalization mechanism, hybrid between σ L → M charge transfer and π M → L charge transfer, is present, and that the differences observed among the different complexes are mainly due to different percentages of 'weight' of the two mechanisms.

In particular, in our complexes the upfield shift calculated by INDO for 2-H and 4-H in pyridine anion are in qualitative agreement with the normalized high shift found experimentally for 3-H. Bearing this in mind, no attempt can be made to correlate the isotropic shifts of pyridine protons with the covalency of M–L bonds.

However, in the chelating ligands there is spin delocalization from filled σ orbitals of the ligand to the half-filled e_g orbitals of the cation. In this case the coupling constants and the isotropic shifts are a direct measurement of the covalency of the ligand–metal bond (disregarding the pseudocontact shifts) [30].

We observe that the α-proton shifts for each tridentate ligand, on going from [NiL$(H_2O)_3$] to [NiLpy$(H_2O)_2$], show three different behaviours, namely a decrease for IDA, no significant variation for TDA, and an increase for ODA. Therefore, on going from simple to ternary pyridine complexes, the covalency of the bonding of the tridentate ligand increases for ODA, while it remains practically constant for TDA and decreases for IDA.

If we calculate the constants of these substitution reactions of a water molecule with pyridine in the three investigated systems, we obtain the values listed in Table V, where we make a comparison between the results of thermodynamic and PMR investigations. As can be seen the results are in excellent agreement, at least from a qualitative point of view, since the increase of M–L bond covalency results, as expected, in an increase in the stability of the complex considered.

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