NICKEL((II) COMPLEXES OF PHOSPHINETRIACETIC ACID*

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The interaction of phosphinetriacetic acid (H_3X) with nickel(II) was examined under various conditions using potentiometric study of solution equilibria, preparation of solid complexes, spectra (electronic and IR) and other methods. In aqueous solution, the ligand acts as tridentate through the phosphorus atom and two carboxylic groups to form hexacoordinate complexes, NiX^-, $NiHX$ and NiX_2^{4-}. At $0.8 < X/Ni < 1.7$ and pH 6—8, these complexes are slowly transformed to Ni_3X_2, an insoluble polymeric compound. In non-aqueous solvents, *trans*-square planar complexes $Ni(hal)_2(H_3X)_2$ (hal = Cl, Br, I) are formed, which contain the ligand coordinated through the phosphorus atom alone. While the solid iodocomplex is also planar, the solid chlorocomplex is hexacoordinated with carbonyl oxygens in axial sites. Both isomeric forms of the bromocomplex were isolated in the solid state.

In a previous paper in this series[1], the synthesis of a new ligand structurally related and analogous to nitrilotriacetic acid — trisodium phosphinetriacetate $P(CH_2.COONa)_3$ was described. This work was carried out to study the coordination behaviour of this compound. Similarly as with the previously studied phosphineacetic acids[2-4], nickel(II) was selected as a typical representative of the transition metals for study of the coordination behaviour because of its comparable affinity for both kinds of ligand donor atom.

EXPERIMENTAL

The synthesis of the ligand has been described previously[1]. Other chemicals, methods and data treatment have also been described[2-4]. Molecular weights were determined by vapor-pressure osmometry on a Knauer instrument. The magnetic susceptibility in solution was measured by the Evans NMR-method[5] with 5% t-BuOH as a standard.

RESULTS

Complexes in Aqueous Solution

Equilibria in the $Ni(ClO_4)_2$–H_3X system were studied by pH-titration at 25° and $I = 0.1$ (Na)ClO_4. In addition to water, 50% v/v aqueous dioxane was also used as

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a solvent to enable comparison with the previously studied water-insoluble phosphine-acetic acids. The existence of three complexes NiX^-, $NiHX$ and NiX_2^{4-} followed from the statistical treatment of data sets lying within the total reagent concentrations, $c_{Ni} = 0.002 - 0.005M$, $c_X = 0 - 0.02M$ and $-\log H^+ = 2 - 9$. The cummulative stability constants, defined as $\beta_{110} = [NiX]/([Ni][X])$, $\beta_{111} = [NiHX]/([Ni][X][H])$, $\beta_{210} = [NiX_2]/([Ni][X]^2)$ (charges omitted), are given in Table I. The criteria for model selection were essentially identical with those recommended by the authors of the computer program used[6-7].

In order to measure the electronic spectra of the individual complexes, the solution compositions were such as to ensure the highest possible percentage of the complex under study. The "pure" spectra calculated from these data by the SQUAD program[8] were finally treated by Gaussian deconvolution[9]. The spectra in water and 50% dioxan were found to be practically identical. The parameters and assignment are given in Table II.

All the complexes in aqueous solution are paramagnetic with $3.1 \pm 0.2\mu_B$ per nickel atom.

Synthesis of the Complexes

$Ni_3X_2.24 H_2O$: 0.77 g $Na_3X.2 H_2O$ (2.5 mmol) and 0.93 g $Ni(ClO_4)_2.6 H_2O$ (2.5 mmol) were dissolved in 5 ml water and 25 ml ethanol was added. The precipitate which separated overnight was washed thoroughly with ethanol and ether and air-dried at room temperature. A product of identical composition is formed with the stoichiometric ratios $X/Ni = 0.8$ to 1.7.

$[Ni(hal)_2(H_3X)_2]$ (hal = Cl, Br, I): 0.93 g $Na_3X.2 H_2O$ (3 mmol) was vacuum-evaporated to dryness with 10 ml 2M-HCl. The residue was extracted in an inert atmosphere with 10 ml anhydrous acetic acid, NaCl was filtered off and the filtrate was treated with 1.5 mmol of hydrated nickel halide dissolved in 2 – 4 ml ethanol. The solution was concentrated to a small volume under vacuum, diluted with acetic acid to 15 ml (Cl, Br) or 7 ml (I) and allowed to crystallize. The product was washed with a little acetic acid and dried to 80°C at 2 kPa. Yields were 45 – 51%.

$NiBr_2(H_3X)_2.nCHCl_3$: to a solution of 0.5 g $NiBr_2(H_3X)_2$ in 10 ml warm acetone was added 10 ml chloroform dropwise. The bluish-green crystals which separated on standing at 0° were washed with chloroform and dried briskly at room temperature until the odour of chloroform just disappeared. The yield was c. 50%. The stoichiometric amount of chloroform fluctuated for the individual preparations between $n = 0.5 - 1.5$ although their weight remained constant for several hours.

Properties of the Preparations

The analytical data and further properties are summarized in Tables III – V. None of the compounds are isostructural and $Ni_3X_2.24 H_2O$ yields no X-ray diffraction

pattern. All the preparations are air-stable except the chloroform adduct, which is desolvated over several days to give a substance identical with $NiBr_2(H_3X)_2$. This adduct is stable in atmosphere saturated with chloroform vapours. The complexes $[NiBr_2(H_3X)_2]$ and $[NiI_2(H_3X)_2]$ are soluble without decomposition in poorly

TABLE I

Stability Constants and Statistical Parameters[7] for the Data Sets

Complex	Constant	log β (3σ)	
		water	50% dioxan
NiX^-	β_{110}	3·77 (1)	6·13 (1)
NiHX	β_{111}	7·18 (6)	10·44 (3)
NiX_2^{4-}	β_{210}	6·41 (9)	10·61 (7)
Number of curves (points)		9 (266)	9 (241)
R		0·010	0·012
χ^{2a}		14·1	16·3

[a] Theoretical value for 95% confidence level is 12·6.

TABLE II

The Electronic Spectra of the Complex in Aqueous Solution
$\lambda_{max} \times 10^3$ cm^{-1} (ε_M).

$[NiX(H_2O)_3]^-$	$[NiHX(H_2O)_3]$	$[NiX_2]^{4-}$	Assignment
10·15 (16)	10·05 (17)	11·75 (32)	$^3A_{2g} \rightarrow {}^3T_{2g}$
18·6 sh (11)	18·5 sh (9)	20·8 sh (19)	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
24·0 (195)	24·1 (220)	24·1 (300)	CT(Ni $\rightarrow$ P)
25·9 sh (22)	26·0 sh (25)	29·7 sh (25)	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
35·8 (3 700)	36·0 (4 100)	36·8 (8 300)	CT(P $\rightarrow$ Ni,
40·4 (12 200)	39·9 (10 300)	41·3 (15 300)	COO $\rightarrow$ Ni)

TABLE III

Analytical Data and Properties for the Complexes Prepared

Compound	% Ni cal. (found)	% P cal. (found)	% Hal. cal. (found)	% H_2O(CHCl$_3$) cal. (found)	M.w. cal. (found)	Appearance	M.p., °C[a]	$\mu_{\text{eff}}(\mu_B)$ 77—298 K
$Ni_3X_2.24\,H_2O$	17·29 (16·98)	6·08 (6·16)		42·44 (42·2)[b]	1 018·7 [c]	orange powder	>260 (dec.)	2·99 ± 0·04
$NiCl_2(H_3X)_2$	10·76 (10·95)	11·35 (10·96)	12·99 (13·04)		545·8 [c]	blue crystal	189—191	3·14 ± 0·05
$NiBr_2(H_3X)_2$.1,2-CHCl$_3$	7·55 (7·47)	7·96 (8·01)	20·54 (20·38)	18·41 (18·05[e], 18·5[f])	778·0 [c]	blue-green crystal	191—192[d]	3·15 ± 0·07
$NiBr_2(H_3X)_2$	9·25 (9·32)	9·76 (9·75)	25·18 (25·40)		634·8 (650)	violet crystal	192	diamagn.
$NiI_2(H_3X)_2$	8·06 (8·06)	8·50 (8·44)	34·83 (34·76)		728·7 (715)	brown-green crystal	189—192 (dec.)	diamagn.

[a] Sealed capillary, [b] substance not soluble without decomposition, [c] mass loss at 140°C, [d] desolvation at 50—60°C (turns violet), [e] determination of Cl in the presence of Br by the Schöniger method, [f] gas chromatography.

TABLE IV
The Electronic Spectra of the Complexes Prepared
$\lambda_{max} . 10^3$ cm^{-1} (ε_M).

Ni$_3$X$_2$·24 H$_2$O solid	NiCl$_2$(H$_3$X)$_2$ solid	NiBr$_2$(H$_3$X)$_2$ 1,2 CHCl$_3$ solid	Assignment (O_h)	NiCl$_2$(H$_3$X)$_2$ solution	NiBr$_2$(H$_3$X)$_2$ solution	NiBr$_2$(H$_3$X)$_2$ solid	NiI$_2$(H$_3$X)$_2$ solution	NiI$_2$(H$_3$X)$_2$ solid	Assignment (D_{4h})
8·9	8·85	8·5	$^3A_{2g} \rightarrow {}^3T_{2g}$			15·1 sh		12·5 sh	$^1A_{1g} \rightarrow {}^3B_{1g}$
11·0	11·8 sh	11·6 sh	$^3A_{2g} \rightarrow {}^1E_g(?)$	18·37 (20)	17·30 (32)	18·0	14·3 sh (45)	14·0 sh	$^1A_{1g} \rightarrow {}^1A_{2g}$
18·4 sh	16·3	16·3	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	21·48 (215)	19·39 (180)	20·0	16·12 (210)	15·6	$^1A_{1g} \rightarrow {}^1B_{1g}$
24·4			CT(Ni $\rightarrow$ P)				21·4 sh (860)	21·7	$^1A_{1g} \rightarrow {}^1E_g$
29·6 sh	25·5	24·9	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	28·37 (5 500)	26·01 (3 400)	26·0	25·64 (3 300)	25·0	CT(hal $\rightarrow$ Ni)
	33·9	30·0	CT(hal $\rightarrow$ Ni)	34·83 sh (350)	32·06 sh (820)	33·3	31·68 (4 050)	30·3 sh	
37·0	37·7	39·2	CT(P $\rightarrow$ Ni)	37·1 sh (780)	36·2 sh (2 530)	37·0	35·31 (11 200)	34·9	CT(P $\rightarrow$ Ni + ligand)
				43·1 (6 500)	40·82 (11 200)	41·7	38·94 (7 780)	38·5	

coordinating solvents such as tetrahydrofuran, acetone and acetic acid to give non-conducting, diamagnetic solutions. Further, all the halogeno complexes are soluble in alcohols with partial decomposition and are totally decomposed by water. The effect of tetrahydrofuran, acetone or acetic acid on the chloroform adduct consists firstly of desolvation followed by dissolution to give a solution identical with that of $NiBr_2(H_3X)_2$. The red, non-conducting diamagnetic solution of the chloro complex can be prepared by dissolving anhydrous nickel chloride in tetrahydrofuran containing two equivalents of H_3X.

DISCUSSION

In aqueous solution, the X^{3-} anion is coordinated to Ni(II) similarly as its nitrogen analogue, *i.e.* chelated through the phosphorus atom and dissociated carboxyl groups. The coordination through phosphorus is evident from the electronic spectrum which exhibits bands corresponding to Ni → P and P → Ni charge transfer. The ligand coordination through the carboxyl groups is reflected in a marked decrease in their formal pK_a values on complex formation. A number of experimental observations indicate, however, that — probably for steric reasons — the X^{3-} anion can act as no more than tridentate towards the relatively small Ni(II) ion, with one uncoordinated carboxyl group: *a*), the values of the stability constants are close to those of tridentate phenylphosphine diacetate; *b*), the NiX$^-$ complex is readily protonated without any change in the electronic spectrum, this behaviour being typical for protonation of an uncoordinated carboxyl group; *c*), the relative ratio of the stability constants of the 1 : 1 and 1 : 2 complexes strongly suggests the equal

TABLE V
Selected Bands in the IR Spectra

Compound	ν(Ni—P)	ν(Ni—hal)	ν_{as}(COO)	ν(OH)
$Ni_3X_2.24 H_2O$	285 w, b	—	1 610 vs	~3 300 vs, vb
$NiCl_2(H_3X)_2$	296 m	415 m	1 662 m	~3 150 s, b
			1 680 s	3 510 m
			1 730 s	
$NiBr(H_3X)_2.$	288 m	317 w	1 660 m	~3 180 s, b
$.1,2\ CHCl_3$			1 695 s	3 490 m
			1 725 s	
$NiBr_2(H_3X)_2$	280 s	321 w	1 715 vs	~3 050 s, b
$NiI_2(H_3X)_2$	289 s	220 w	1 710 vs	~3 020 s, vb

denticity of all the ligands involved; d), the position of the $d-d$ bands in both the 1 : 1 and 1 : 2 complexes is consistent with the rule of average environment, provided that the substitution of three water molecules by one ligand is considered; e), lastly, the steric hindrance of the ligand for bonding as tetradentate, caused by the large phosphorus atom, is evident from molecular models.

The electronic spectra and magnetic properties of the complexes in aqueous solution are typical for pseudo-octahedral coordination. The ligand field parameters are $D_q = 1010\,\mathrm{cm}^{-1}$, $B = 805\,\mathrm{cm}^{-1}$ for the 1 : 1 complexes and $D_q = 1170\,\mathrm{cm}^{-1}$ and $B = 786\,\mathrm{cm}^{-1}$ for the 1 : 2 complex. These values are close to those for the complexes of phenylphosphinediacetic acid and correspond to the parameters[10] $f = 1\cdot13$, $h = 2\cdot3$ when applying the rule of average environment.

The compound $Ni_3X_2.24\,H_2O$ exhibits spectral and magnetic features similar to those for the complexes in solution, suggesting an analogous arrangement of the coordination polyhedron. The compound, however, is probably polymeric as indicated by its slow and irreversible separation from the solution. The attempted isolation of solid monomeric complexes was unsuccessful.

The behaviour of the ligand under the conditions of undissociated carboxyl groups is dictated by the donor properties of the phosphorus atom, similarly to the phosphineacetic acids studied previously but quite differently to nitrilotriacetic acid. In non-aqueous solutions, the $[Ni(hal)_2(H_3X)_2]$ complexes are formed, which are trans square-planar with phosphorus and halogen as the donor atoms, as follows from the electronic and IR spectra and magnetic properties[11-13]. The behaviour of solid complexes of this type is critically dependent on the halogen. The solid iodocomplex remains planar as it is diamagnetic and the diffuse reflectance spectrum is identical with that of the solution. In contrast, the solid chlorocomplex is pseudo-octahedral and paramagnetic, its coordination polyhedron probably being completed by an intermolecular interaction with carbonyl oxygen atoms of neighbouring ligand molecules, resulting in the formation of a polymer. This structural model is supported by the insolubility of the complex in common solvents and, especially, by marked splitting of the $\nu(C=O)$ band in the IR spectrum as well as by splitting and shifting of the $\nu(OH)$ band into the region close to that of the free OH-group. The similar behaviour is known for the related hybrid ligand tris(cyanoethyl)phosphine[14] but not for the phosphineacetic acids studied before, which contain bulky phenyl groups instead of carboxyls in the molecule. The remarkable property of the bromo-complex is the possibility of isolation of both its structural forms; the lattice of the hexacoordinate complex is stabilized by chloroform as none of the properties of the chloroform adduct indicate any direct coordination of chloroform to nickel(II). Steric and electronic factors[15] which are usually responsible for structural variations of nickel(II) complexes in the series Cl–Br–I are very subtly balanced in the studied bromocomplex, enabling isolation of both forms by a slight variation in the experimental conditions.

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