

Thermodynamics of adduct formation of $[\text{Ni}(\text{dtp})_2]$ ($\text{dtp} = (\text{C}_2\text{H}_5\text{O})_2\text{PS}_2$) with some nitrogen-donor bases in benzene

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Abstract

The adduct formation of $[\text{Ni}(\text{dtp})_2]$ ($\text{dtp} = (\text{C}_2\text{H}_5\text{O})_2\text{PS}_2$) with pyridine (py), 4-cyanopyridine (4-cyp), 2-aminopyridine (2-amp), piperidine (pip) and benzylamine (ba) has been studied by spectrophotometry and calorimetry in benzene at 25 °C. With $L = 2\text{-amp}$, the formation of $[\text{Ni}(\text{dtp})_2L]$ only is concluded. For other bases, the formation of $[\text{Ni}(\text{dtp})_2L]$ and $[\text{Ni}(\text{dtp})_2L_2]$ is established, and their formation constants, reaction enthalpies and entropies were determined. All the $[\text{Ni}(\text{dtp})_2L]$ complexes exhibit virtually the same electronic spectra arising from the five-coordinate NiNS_4 chromophore. On the other hand, the $[\text{Ni}(\text{dtp})_2L_2]$ ($L = \text{py}, 4\text{-cyp}, \text{ba}$) complexes are octahedral with a triplet Ni^{II} center. However, the $[\text{Ni}(\text{dtp})_2(\text{pip})_2]$ complex is not, and its spectrum suggests five-coordination with an NiN_2S_3 chromophore. Unusual thermodynamic behavior is also observed for the formation of the latter complex.

Introduction

Macrocyclic ligands with nitrogen as donor atoms and chelating ligands with sulfur donor atoms form diamagnetic square-planar complexes with nickel(II) [1], which, as Lewis acid, react with various Lewis bases to give adducts with coordination number five or six. The adduct formation is often associated with a change in the ground state of nickel(II) (singlet to triplet) to bring about significant change in the electronic absorption spectrum [2–4]. Indeed, spectrophotometric measurements, particularly spectrophotometric titration, has been widely used for elucidating the adduct formation equilibria in a variety of systems. The stability of the adducts depends on various factors including the strength of Lewis acid–base interaction, the steric interaction between basal and apical ligands, and the change in spin state. Hence the equilibrium data should be complemented by thermodynamic parameters for detailed discussion to be substantiated. However, only limited information is available concerning the change in

enthalpy and entropy associated with such adduct formation [5, 6].

Usefulness of thermodynamic titration for revealing various binary and ternary metal–ligand interaction equilibria in solution has been demonstrated by our previous works [7–10]. We have explored a sophisticated automatic titration technique, in which both spectrophotometric and thermal changes are observed side by side, and the data are analyzed by a computer.

This paper deals with the spectrophotometric and thermodynamic studies on the adduct formation between bis(*O,O'*-diethyldithiophosphato)-nickel(II) ($[\text{Ni}(\text{dtp})_2]$) with various nitrogen bases in benzene. The crystal structures of this complex [11], the adduct with coordination number 6, $[\text{Ni}(\text{dtp})_2(\text{py})_2]$ (py, pyridine) [12], $[\text{Ni}(\text{dtp})_2(\text{bpy})]$ (bpy, 2,2'-bipyridine) [13] and $[\text{Ni}(\text{dtp})_2(\text{phen})]$ (phen, 1,10-phenanthroline) [14] and that with coordination number 5 $[\text{Ni}(\text{dtp})_2(2,9\text{-Me}_2\text{phen})]$ (2,9-Me₂phen, 2,9-dimethyl-1,10-phenanthroline) [15] are already known. However, the thermodynamics of adduct formation is not well established. This square-planar complex $[\text{Ni}(\text{dtp})_2]$ is soluble in apolar solvents such as benzene and seems particularly suited for studying the solution equilibrium of adduct formation with coordination numbers 5 and 6.

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Experimental

Materials

Bis(*O,O'*-diethyldithiophosphato)nickel(II) was prepared according to the literature [16], and was recrystallized from acetone and chloroform. The product was identified by elemental analysis and infrared spectra. Benzene was dried over KOH and distilled before use. 4-Cyanopyridine was recrystallized from a CH₂Cl₂/ethyl ester mixture and 2-amp from a benzene/petroleum ether according to the literature [17], while py, pip and ba of reagent grade were used without further purification.

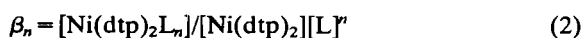
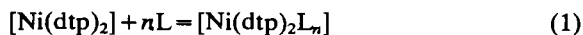
Measurements

Spectrophotometric measurements were carried out by using a fully automatic titration system, which involves a spectrophotometer (Hitachi 340). A flow cell with a pathlength of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. A test solution thermostatted at 25 °C was circulated by using a Teflon pump to pass through the flow cell. Initially, an [Ni(dtp)₂] solution (25 cm³, 7–10 mmol dm⁻³) was placed in a vessel under a dry argon atmosphere, and then titrated with a 0.2 mol dm⁻³ base solution from an autoburet (APB-118, Kyoto Electronics). No ionic medium was used. Observed electronic spectra were recorded in 1 nm intervals over the wavelength range 400–850 nm. The spectrophotometric data at selected 50 wavelengths were employed for the least-squares calculation of the formation constants.

Calorimetric measurements were carried out also by using a fully automatic titration system [10] in a room thermostatted at 25 ± 0.2 °C. A solution (20 cm³, 4–15 mmol dm⁻³) containing [Ni(dtp)₂] was placed in a stainless steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry argon and isolated from moisture by a P₂O₅ drying tube, was inserted in an aluminium block thermostatted at 25.0 ± 0.0001 °C in an air-bath. Portions of a base solution (0.2 mol dm⁻³) were added to this solution from an autoburet. Heats of complexation at each titration point were measured with a certainty of ± 0.02 J, and corrected for the heat of dilution of the titrant. The heat of dilution had been determined in advance by separate experiments and was found to be very small.

Data analysis

We assumed the overall formation equilibria of [Ni(dtp)₂L] and [Ni(dtp)₂L₂] as



The absorbance A_{ij} of a given solution i at the wavelength λ_j is represented by the formation constants β_n and molar extinction coefficients $\epsilon_n(\lambda_j)$ of the [Ni(dtp)₂L_n] complex as in eqn. (3).

$$A_{ij} = \sum \epsilon_n(\lambda_j) \beta_n [\text{Ni}(\text{dtp})_2]_i [\text{L}]_i^n + \epsilon_{\text{Ni}}(\lambda_j) [\text{Ni}(\text{dtp})_2]_i + \epsilon_{\text{L}}(\lambda_j) [\text{L}]_i \quad (3)$$

Similarly, the heat q_i measured at the i th titration point is expressed by the formation constants β_n and overall enthalpies $\Delta H_{\beta_n}^\circ$, eqn. (4)

$$q_i = - (V_i \sum \beta_n \Delta H_{\beta_n}^\circ [\text{Ni}(\text{dtp})_2]_i [\text{L}]_i^n - V_{i-1} \sum \beta_n \Delta H_{\beta_n}^\circ [\text{Ni}(\text{dtp})_2]_{i-1} [\text{L}]_{i-1}^n) \quad (4)$$

where V_i denotes the volume of the test solution.

The concentrations of free [Ni(dtp)₂] and L are related to their total concentrations, $C_{\text{Ni},i}$ and $C_{\text{X},i}$, respectively, according to the mass-balance eqns. (5) and (6).

$$C_{\text{Ni},i} = [\text{Ni}(\text{dtp})_2]_i + \sum \beta_n [\text{Ni}(\text{dtp})_2]_i [\text{L}]_i^n \quad (5)$$

$$C_{\text{X},i} = [\text{L}]_i + \sum n \beta_n [\text{Ni}(\text{dtp})_2]_i [\text{L}]_i^n \quad (6)$$

The formation constants and molar absorption coefficients were thus obtained by minimizing $U = \sum (A_{i,\text{obs}} - A_{i,\text{calc}})^2$, and the reaction enthalpies by minimizing $U = \sum (q_{i,\text{obs}} - q_{i,\text{calc}})^2$ on the basis of the measured formation constants.

Results and discussion

Electronic spectral changes of an [Ni(dtp)₂] benzene solution upon the addition of pip and ba are depicted in Figs. 1(a) and 2(a), respectively. These can be well reproduced by taking into account the

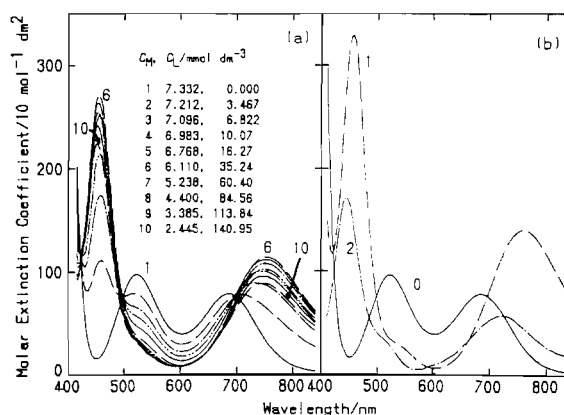


Fig. 1. (a) Measured electronic spectra of [Ni(dtp)₂] obtained upon the addition of piperidine in benzene. Intensities are normalized with the concentration of [Ni(dtp)₂]. (b) Electronic spectra of [Ni(dtp)₂] (0), [Ni(dtp)₂L] (1) and [Ni(dtp)₂L₂] (2) (L = pip).

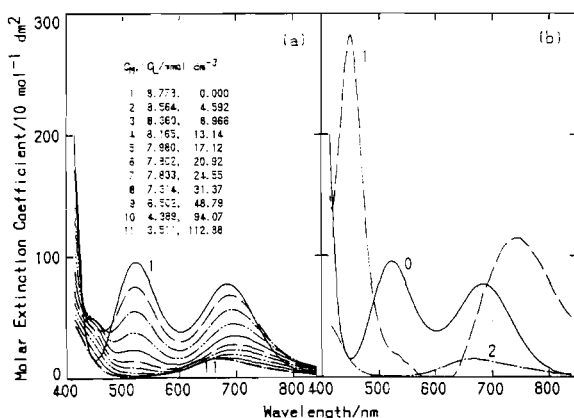


Fig. 2. (a) Measured electronic spectra of $[\text{Ni}(\text{dtp})_2]$ obtained upon the addition of benzylamine in benzene. Intensities are normalized with the concentration of $[\text{Ni}(\text{dtp})_2]$. (b) Electronic spectra of individual $[\text{Ni}(\text{dtp})_2\text{L}]$ (1) and $[\text{Ni}(\text{dtp})_2\text{L}_2]$ (2) ($\text{L} = \text{ba}$).

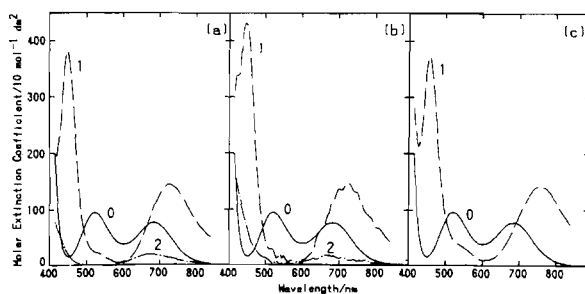


Fig. 3. Electronic spectra of individual $[\text{Ni}(\text{dtp})_2\text{L}]$ (1) and $[\text{Ni}(\text{dtp})_2\text{L}_2]$ (2), $\text{L} = \text{py}$ (a), 4-cyp (b) and 2-amp (c).

formation of $[\text{Ni}(\text{dtp})_2\text{L}]$ and $[\text{Ni}(\text{dtp})_2\text{L}_2]$, and their formation constants were determined. Simultaneously, electronic spectra of individual complexes were isolated as depicted in Figs. 1(b) and 2(b). The spectra of individual py, 4-cyp and 2-amp complexes were also obtained (Fig. 3). The formation constants thus determined by spectrophotometry are listed in Table 1. The calorimetric data are shown in Fig. 4, where the heat of reaction q measured at each titration point is normalized with the volume of the added titrant δv and the concentration of a base in

the titrant solution $C_{\text{base,tit}}$, and the $-q/(\delta v C_{\text{base,tit}})$ values are plotted against $C_{\text{base}}/C_{\text{Ni}}$ in solution. The data were analyzed on the basis of the formation constants in Table 1, and reaction enthalpies thus evaluated are listed in Table 2. As seen in Fig. 4, the solid curves calculated with the constants in Tables 1 and 2 reproduce well the experimental points. The stepwise thermodynamic parameters are then calculated as shown in Table 3.

With respect to the py complexes, their formation constants and reaction enthalpies in benzene have been reported. Carlin and Losee [5] obtained the $\log K_1$ (1.46) and $\log K_2$ (1.89) values by spectrophotometry. They also pointed out that the overall reaction enthalpy of $[\text{Ni}(\text{dtp})_2(\text{py})_2]$ is about -70 kJ mol^{-1} . On the other hand, Dakternieks and Graddon [6] obtained the $\log K_1$ (1.41) and $\log K_2$ (1.34) values by calorimetry, along with the ΔH_1° (-73 kJ mol^{-1}) and ΔH_2° (4 kJ mol^{-1}) values. The $\log K_1$ and $\log K_2$ values obtained in this work are in good agreement with those in ref. 5, while the ΔH_1° and ΔH_2° values are inconsistent with those in ref. 6.

Apparent spectral changes upon the addition of bases are quite different, as seen in the cases for pip and ba in Figs. 1(a) and 2(a). This is mainly due to the difference in the distribution of species (see Fig. 5). In fact, the electronic spectra of individual $[\text{Ni}(\text{dtp})_2\text{L}]$ complexes are very similar to each other for all the bases examined, though the spectrum of $[\text{Ni}(\text{dtp})_2(4\text{-cyp})]$ involve rather large uncertainties because of the weak formation of the complex in benzene. These $[\text{Ni}(\text{dtp})_2\text{L}]$ complexes may have five-coordinate square-pyramidal geometry [18] and the triplet ground state of Ni^{II} , as is established for various pyridine derivatives and amines [5]. However, this may not be the case with 2-amp because, although its donor property ($\text{p}K_a = 6.8$ in water) is stronger than that of pyridine (5.3), the $\log \beta_1$ value is significantly smaller and the formation of $[\text{Ni}(\text{dtp})_2(2\text{-amp})_2]$ is hardly observed, possibly due to the steric hindrance of an amine upon complexation. The same has been observed for the complexes of 2-picoline

TABLE 1. Overall formation constants, $\log \beta_n$ ($\text{mol}^{-n} \text{ dm}^3\text{n}$) of $[\text{Ni}(\text{dtp})_2\text{L}]$ and $[\text{Ni}(\text{dtp})_2\text{L}_2]$ ($\text{L} = \text{py}$, 2-amp, 4-cyp, pip, ba) determined by spectrophotometry in benzene at 25°C ^a

	py	4-cyp	2-amp	pip	ba
$\log \beta_1$	1.47(0.01)	0.14(0.6)	0.80(0.01)	2.52(0.01)	1.99(0.10)
$\log \beta_2$	3.32(0.01)	1.54(0.08)		3.46(0.03)	5.02(0.03)
R^b	0.00318	0.00338	0.00316	0.00619	0.01619

^apy: pyridine, 4-cyp: 4-cyanopyridine, 2-amp: 2-aminopyridine, pip: piperidine, ba: benzylamine. Values in parentheses refer to three standard deviations. The total number of spectrophotometric data are 1250 obtained at selected 50 wavelengths in the range 400–850 nm in each system. ^bHamilton R factor.

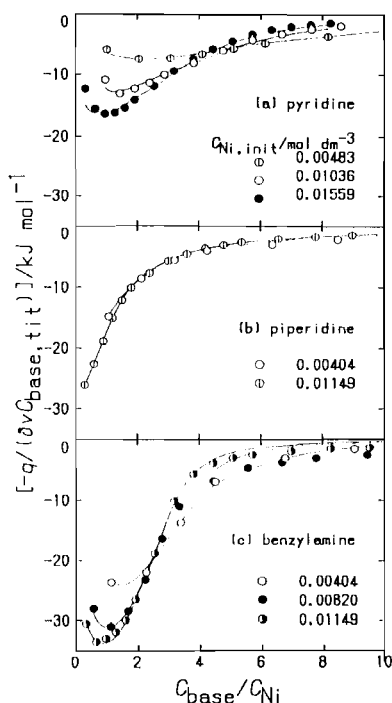


Fig. 4. Calorimetric titration curves obtained by titrating pyridine (a), piperidine (b) and benzylamine (c). The solid lines show the curves calculated by using the constants in Tables 1 and 2.

TABLE 2. Overall reaction enthalpies, $\Delta H_{\beta n}^{\circ}/(\text{kJ mol}^{-1})$ for the formation of $[\text{Ni}(\text{dtp})_2\text{L}]$ and $[\text{Ni}(\text{dtp})_2\text{L}_2]$ ($\text{L} = \text{py}$, 4-cyp, pip, ba) in benzene at 25 °C^a

	py	4-cyp	pip	ba
$\Delta H_{\beta 1}^{\circ}$	-42.0(2)	-4.2(7)	-34.9(2)	-38.5(3)
$\Delta H_{\beta 2}^{\circ}$	-75.0(1)	-24.1(3)	-102.7(6)	-84.1(1)
R^b	0.0268	0.114	0.0558	0.0132
N^c	36	16	24	15

^aReaction enthalpies were evaluated on the basis of the formation constants in Table 1. py: pyridine, 4-cyp: cyanopyridine, pip: piperidine, ba: benzylamine. Values in parentheses refer to three standard deviations. ^bHamilton R factor. ^cThe number of calorimetric data points.

and 2,6-lutidine, and the ground state of Ni^{II} remains singlet upon complexation [5]. In the case of 4-cyp, its complexation is weak, even weaker than that of 2-amp, due to the induced effect of cyano group. However, note that there is no steric hindrance on coordination of 4-cyp. In fact, both $[\text{Ni}(\text{dtp})_2(4\text{-cyp})]$ and $[\text{Ni}(\text{dtp})_2(4\text{-cyp})_2]$ are formed as is evident from their electronic spectra in Fig. 3(b).

With py, pip and ba, the $[\text{Ni}(\text{dtp})_2\text{L}_2]$ complexes are obviously formed. The $[\text{Ni}(\text{dtp})_2(\text{py})_2]$ complex may have *trans*-octahedral geometry in solution as

TABLE 3. Thermodynamic parameters, $\log K_n$ ($\text{mol}^{-1} \text{dm}^3$), ΔH_n° (kJ mol^{-1}) and ΔS_n° ($\text{J K}^{-1} \text{mol}^{-1}$) for the stepwise formation of $[\text{Ni}(\text{dtp})_2\text{L}]$ and $[\text{Ni}(\text{dtp})_2\text{L}_2]$ in benzene at 25 °C^a

	py	4-cyp	pip	ba
$\log K_1$	1.47	0.14	2.52	1.99
$\log K_2$	1.85	1.40	0.94	3.03
$\log(K_1/K_2)$	-0.38	-1.30	1.61	-1.05
ΔH_1°	-42	-4	-35	-39
ΔH_2°	-33	-20	-68	-46
ΔS_1°	-113	-11	-69	-91
ΔS_2°	-75	-40	-210	-96

^apy: pyridine, 4-cyp: 4-cyanopyridine, pip: piperidine, ba: benzylamine.

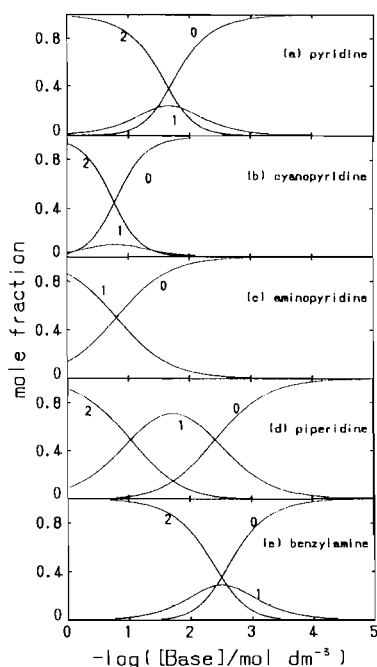


Fig. 5. Species distribution in benzene. The $[\text{Ni}(\text{dtp})_2\text{L}_n]$ complexes are represented by n values.

in the crystal [12]. The $[\text{Ni}(\text{dtp})_2(\text{ba})_2]$ complex may have the same geometry as $[\text{Ni}(\text{dtp})_2(\text{py})_2]$, as their electronic spectra are virtually identical. However, the electronic spectrum of $[\text{Ni}(\text{dtp})_2(\text{pip})_2]$ is significantly different from that of the six-coordinate py and ba complexes. Interestingly, the spectrum is very similar to that of five-coordinate complexes. An unusual feature is also seen in the thermodynamic parameters. As seen in Table 3, the K_1/K_2 value is larger than unity for pip, despite the fact that the reverse is the case for py and ba. Piperidine ($\text{p}K_a = 11.1$ in water) is a stronger base than ba (9.47) or py (5.3). The $\log K_1$ value decreases in the sequence, $\text{pip} > \text{ba} > \text{py}$, and the $\log K_2$ value in the sequence,

ba > py, which is in parallel with the decreasing order of pK_a . However, the $\log K_2$ value of pip is surprisingly small. It is of particular interest that the ΔH_1° value slightly decreases in the decreasing order of pK_a , pip > ba > py, while the reverse is the case for ΔH_2° , and that $\Delta H_1^\circ < \Delta H_2^\circ$ for py, while $\Delta H_1^\circ > \Delta H_2^\circ$ for ba, and especially so for pip. Furthermore, with pip the ΔS_2° value is about three times as negative as the ΔS_1° value.

The electronic spectrum of $[\text{Ni}(\text{dtp})_2(\text{pip})_2]$ might indicate that this complex is five-coordinated with an NiN_2S_3 chromophore, i.e. one dtp is chelating and the other is monodentate like $[\text{Ni}(\text{dtp})_2(2,9\text{-Me}_2\text{phen})]$ [15]. The ΔH° value for the formation of five-coordinate $[\text{Ni}(\text{dtp})_2(2,9\text{-Me}_2\text{phen})]$ is less negative than that of six-coordinate $[\text{Ni}(\text{dtp})_2(\text{bpy})]$ [6]. In contrast, the corresponding $\Delta H_{\beta 2}^\circ$ value for $[\text{Ni}(\text{dtp})_2(\text{pip})_2]$ is appreciably more negative than that for $[\text{Ni}(\text{dtp})_2(\text{py})_2]$ and $[\text{Ni}(\text{dtp})_2(\text{ba})_2]$, though the reason remains still unknown. The $[\text{Ni}(\text{dtp})_2(\text{pip})_2]$ complex might be unstable because, according to Jørgensen [19], the piperidine adduct decomposes gradually in solution at higher base concentration.

Acknowledgements

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