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Stepwise Adduct Formation of Bis(O,O'-Diethyldithiophosphato) Nickel(II) with Primary and Secondary Amines

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Bis(O,O'–diethyldithiophosphato)nickel(II) behaves in a qualitatively similar way with both primary and secondary amines in that 1:1 and 1:2 adducts are found. Data obtained for n–butylamine and diethylamine indicate that the difference in behaviour towards primary and secondary amines is only quantitative, formation constants being much smaller with the latter. Very high concentration of primary amines leads also to the formation of complexes containing the chromophore [NiS_2N_4], presumably with monodentate dithiophosphate ligands.

Introduction

Literature reports on adduct formation between bis(O,O'-diethyldithiophosphato)nickel(II) (hereafter Ni-dtp$_2$) or other low spin [NiS_4] chromophores, and nitrogen bases show varying behaviour with different bases.[1-6] While stepwise 1:1 and 1:2 adduct formation is well established with heterocyclic bases such as pyridine and substituted pyridine[4,6] (provided not sterically hindered, in which case only 1:1 addition occurs[7]), secondary amines have been reported to give exclusively 1:1 adducts,[2,6] and primary amines almost exclusively 1:2 adducts, and only recently has evidence been gained for intermediate 1:1 formation with some primary amines.[8] The problem is interesting in view of the strong influence of the nature of substituents bonded to the donor groups, which resembles the great sensitivity of biological systems or models to substituents.[9] We report the results of a comparative investigation on adduct formation of Nidtp$_2$ with one primary and one secondary aliphatic amine, which we undertook in order to ascertain whether the complexing behaviour of primary and secondary amines was actually qualitatively different or not, and to obtain a picture as detailed as possible of all processes of adduct formation. Although under the experimental conditions employed by us some uncertainty remains in the quantitative evaluation of equilibria, sufficient evidence can be presented to demonstrated that the behaviour of primary and secondary amines is qualitatively the same, since both 1:1 and 1:2, adducts are formed stepwise in both cases. The differences between primary and secondary amines are only quantitative, formation constants being much lower for the latter. The lack of observation until now of 1:2 adduct formation with secondary amines was probably due to the unusually drastic conditions required (high excess of amine, and low temperature). Very high excess of primary amines may lead to 1:4 adducts containing pseudooctahedral [NiS_2N_4] chromophores, hence presumably monodentate dithiophosphate.

Experimental Section

Spectrophotometric Measurements. 1:1, 1:2, and eventually 1:4 adduct formation was followed spectrophotometrically (Beckmann DK-1A) in solutions containing Nidtp$_2$ at constant concentration (1.0×10^{-2} *M*) in an inert solvent (toluene being found most convenient) in the presence of varying amounts of either n–butylamine or diethylamine, at different controlled temperatures in a limited range around room temperature. Magnetic measurements were carried out on concentrated toluene solutions with a Gouy balance.

Reagents and Solvents. Nidtp$_2$ was prepared as in the literature;[10] the amines were Fluka «puriss» grade products and the toluene (Erba RP) was purified by repeated distillation over molten metallic sodium.

Solid 1:2 and 1:4 products with n–butylamine could be isolated, although these were unstable, rapidly losing the amine molecules to finally give Nidtp$_2$.

Analysis: Nidtp$_2$. 2BuNH$_2$ theory C, 33.4; H, 7.4; N, 4.9. Found C, 33.2; H, 7.0; N, 5.0. Nidtp$_2$. 4-BuNH$_2$ theory C, 39.8; H, 10.9; N, 7.7. Found C, 39.3; H, 10.0; N, 7.4.

For all the other cases solid products could not be isolated.

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Determination of Stability Constants. Visible absorption data were used to obtain an estimate of adduct formation constants by Beer's law and by the observed absorbances at selected wavelengths. Data processing is not difficult with Et_2NH, where the successive complexation stages are sufficiently well separated to enable the absorption spectrum of the 1:1 adduct to be determined directly from measured spectra in intermediate ranges of excess ligand concentration, and the two successive equilibria of 1:1 and 1:2 adduct formation to be evaluated separately and independently. Table I reports formation constants at different temperatures for the system $Nidtp_2/Et_2NH$. A different situation arises with $BuNH_2$, where it was impossible to extract the individual spectrum of the 1:1 adduct directly from experimental spectra, since at each wavelength the contribution to the absorption intensity of other species present at equilibrium cannot be ignored. This is evident *e.g.* from the spectra of Figure 1 showing an only approximate isosbestic point, and only for very low ($\leqslant 1$) ratios x = [amine]/[Ni]. Thus, experimental absorbance values $A_{\lambda x} = \Sigma \varepsilon_{\lambda i} c_{xi}$ at different wavelengths and x ratios were used for the determination of the unknown K_1 K_2 (hence of the c_{xi}'s and $\varepsilon_\lambda(1:1)$) through a least squares fitting, including at least twelve different x ratios within the range 0.4-2.6, for each wavelength. Obviously, such calculations are still subject to considerable uncertainty, particularly because of uncertain determination of c_{xi} of species having low equilibrium concentration and/or low $\varepsilon_{\lambda i}$. Furthermore formation of a higher adduct, probably 1:4, becomes evident in solutions with $x \geqslant 4$, so even the actual values of $\varepsilon_\lambda(1:2)$ had to be extrapolated rather than directly measured from experiments. Values of the successive formation constants K_1 and K_2 as calculated from least squares fitting are reported in Table II. The smallest deviations were found for the wavelength 446 mμ, where the best value for $\varepsilon_{446}(1:1)$ was 187. This value was also confirmed by direct experiment using a compensation method, (see Figure 6) where $[Nidtp_2]$ in the blank solution without ligand was varied until a compensated spectrum was obtained of the sample solution containing x = 0.4 (hence practically only 1:1 adduct besides $Nidtp_2$, the estimated concentration of 1:2 adduct implying only a vanishingly small correction to the experimental absorbance).

Table I. Formation constants for the system $Nidtp_2/Et_2NH$ in toluene.

T(°C)	K_1 (l/mole)	K_2 (l/mole)
—12	$(4.7\pm0.1).10^1$	$(1.15\pm0.02).10^0$
20	$(1.5\pm0.1).10^1$	$(4.2\pm0.2).10^{-1}$
32	$(0.6\pm0.1).10^1$	—

Table II. Formation constants for te system $Nidtp_2/BuNH_2$ in toluene.

T(°C)	K_1 (l/mole)	K_2 (l/mole)
25	$(6.09\pm0.24).10^2$	$(6.17\pm0.14).10^2$
35	$(5.01\pm0.24).10^2$	$(5.31\pm0.14).10^2$
45	$(3.69\pm0.24).10^2$	$(4.09\pm0.14).10^2$

Results

Addition of $BuNH_2$ or Et_2NH to a toluene solution of $Nidtp_2$ causes changes in the spectra clearly indicative of the successive formation of both 1:1 and 1:2 adducts. Figures 1, 2, and 3, 4 show some typical spectra for the systems $Nidtp_2/BuNH_2$ and $Nidtp_2/Et_2NH$,, respectively, while Figure 5 illustrates the changes in absorbance with change in the ratio $[Et_2NH]/[Nidtp_2]$. From the spectra, it is evident that both primary and secondary amines show the same qualitative behaviour. The formation constants for butylamine (Table II) are much higher: at 25°C and relatively small excess of amine ($[BuNH_2]/[Nidtp_2]$ = 3-4), the 1:2 adduct forms almost completely, while Et_2NH forms the 1:2 adduct only partially (71% at 20°C), even at $[Et_2NH]/[Nidtp_2]$ ratio = 500. The formation reactions of the adducts with both kinds of amine are exothermic; indeed the formation of pseudooctahedral species with secondary amines is more evident at low temperature (at −12°C the percentage of adduct formed is 90% for x = 500).

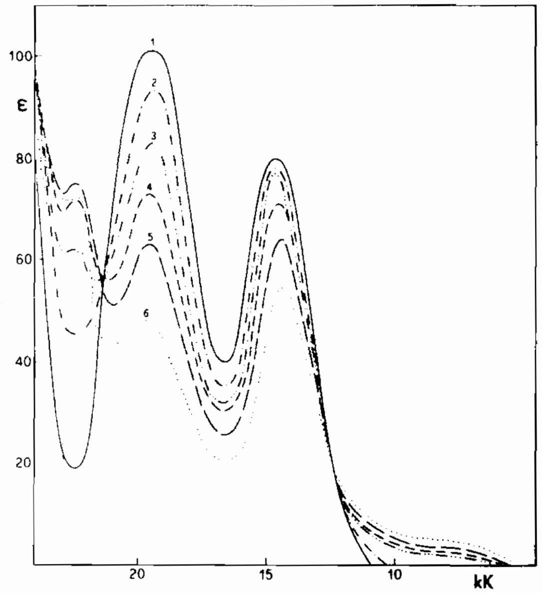

Figure 1. Absorption spectra of the system $Nidtp_2/BuNH_2$ in toluene at 25°C and at different ratios [amine]/[nickel] (ratio in brackets):
1 (0.0); 2 (0.2); 3 (0.4); 4 (0.6); 5 (0.8); 6 (1.0).

Solution magnetic measurements using the values of the constants reported in Table 1 give a value for the magnetic moment of the 1:1 adduct with Et_2NH of 2.9_7 B.M. This confirms the previous measurements and the prediction by the ligand field calculation[8] of a triplet ground state. Recently, it has been suggested[6] that the ground state of the 1:1 adducts depends largely upon the choice of the amine: for instance the 2–picoline and 2,6–lutidine adducts appear to have a singlet ground state in solution.

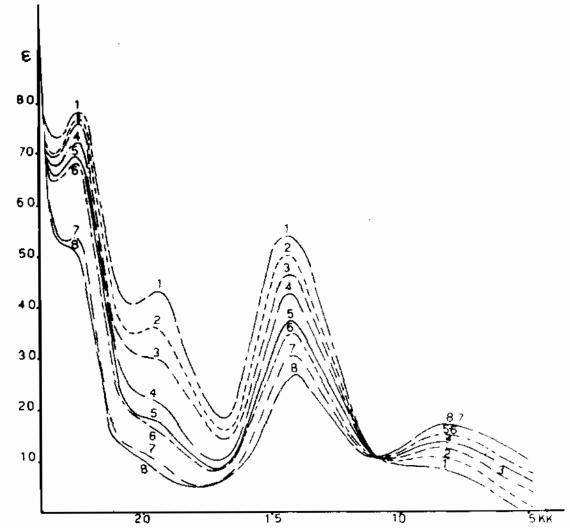

Figure 2 As for figure 1: 1 (1.2); 2 (1.4); 3 (1.6); 4 (1.8); 5 (2.0); 6 (2.2); 7 (2.4); 8 (2.6).

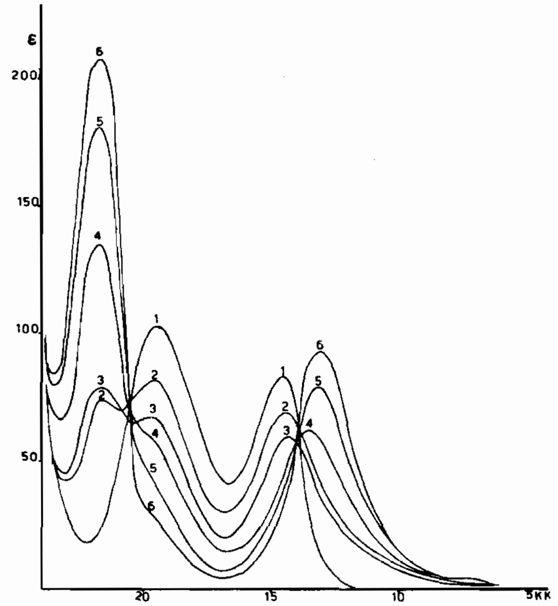

Figure 3 Absorption spectra of the system Nidtp$_2$/Et$_2$NH in toluene at —12°C and at different ratios [amine]/[nickel] (ratio in brackets): 1 (0); 2 (1); 3 (2); 4 (5); 5 (10); 6 (20).

Solutions of Nidtp$_2$ containing larger execess of BuNH$_2$ ($X \gtrsim 4$) show a gradual change in colour from green to blue with increasing excess of amine. The solution spectra are still those of pseudooctahedral Ni^{II} complexes, but with a shift to higher energy (and a slight change in intensity) with respect to that of the 1:2 adduct. At a ratio BuNH$_2$/Nidtp$_2$>20, no further change on adding amine was observed. The values of the maxima of the first band for several ratios are reported in Table III. Such high-energy shift indicates the formation of compounds with more than two molecules of BuNH$_2$. The blue solution is a non-conductor and give a magnetic moment of 2.9$_5$ B.M. Attempts to isolate this species met with difficulties because of its high solubility in the excess of BuNH$_2$ necessary for its formation. A blue microcrystalline solid was separated, which, however, had a high amine vapor pressure, and successively lost all its molecules of amine to finally give Nidtp$_2$. Such instability accounts for the poor analytical data (experimental part). The reversibility of amine addition rules out the possibility of a chemical reaction between the amine and dithiophosphate. The analysis of the absorption spectrum, which will be discussed later, together with the other experimental evidence shows that this compound is Nidtp$_2$. 4BuNH$_2$, which may possibly contain monodentate dithiophosphate ligands.

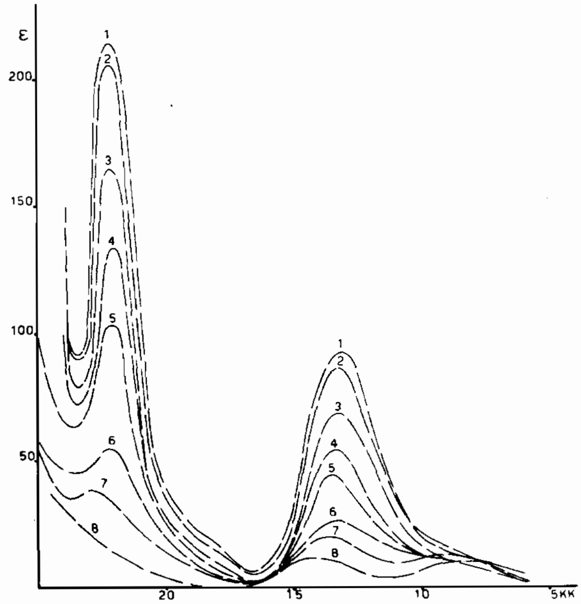

Figure 4. As for figure 3: 1 (20); 2 (40); 3 (60); 4 (80); 5 (150); 6 (200); 7 (300); 8 (500).

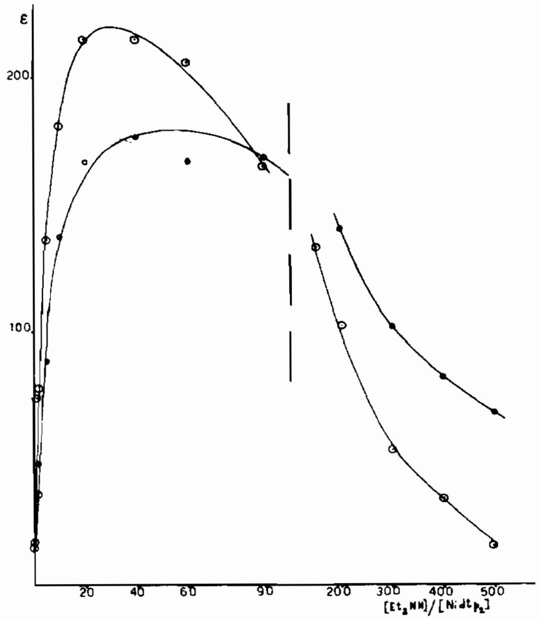

Figure 5. Molar absorbance at 460 mμ of solution of Nidtp$_2$ in toluene against the ratio [Et$_2$NH/Nidtp$_2$]. (⊙ at 20°C; ⊙ at —12°C). Similar diagram for the system Nidtp$_2$/BuNH$_2$ is reported in ref. (8).

Table III. Change in frequency of $\bar{\nu}_1$ band with increase in amine.

$[BuNH_2]/[Ni]$	$^3A_{2g} \rightarrow {}^3T_{2g}$ (O_h) $\bar{\nu}_1$(kK)
4	8.5
5	8.7
7	9.3
10	9.5
20	9.6
30	9.6
40	9.6

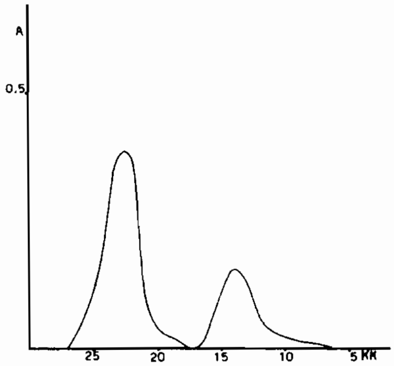

Figure 6. Compensated spectra of $Nidtp_2 . BuNH_2$ from a solution 10^{-2} in $Nidtp_2$ at ratio $[BuNH_2]/[Nidtp_2]$ = 0.4 (see text).

Discussion

The structure of the adducts present are supported by their spectra: while $Nidtp_2$ shows a spectrum characteristic of a quadratic non conjugated $[NiS_4]$ chromophore,[11] the 1:1 adducts presents spectra characteristic of five-coordinated species,[8] the 1:2 and 1:4 adduct of $BuNH_2$ have spectra characteristic of pseudooctahedral species. It is possible to identify tetragonal components only in the spectra of $Nidtp_2 . 2BuNH_2$, although the splitting is not very clear, at 8.3 ($^3B_{2g}$), 8.9 (a^3E_g), 13.4 (b^3E_g), 14.7 (a^3A_{2g}), 23.6 (b^3A_{2g}), and 25.5 (c^3E_g) kK, giving for the spectrochemical parameters $Dq_S=0.83$, $Dq_N=0.95$, $d\sigma=0.48$, and $d\pi=0.14$ kK.[12] As mentioned previously, the spectra of the 1:2 Et_2NH adduct are less clearly defined and consequently it is not possible to determine the relative spectrochemical positions (presumably similar) of the amines.

The spectrum of $Nidtp_2 . 4BuNH_2$ may be analysed in term of «average environment rule»: assuming $Dq=1.08$ for the amine and $Dq=0.73$ kK for dtp^- in a paramagnetic nickel(II) complexes,[8] the first band position for $[NiS_2N_4]$ should be at $\bar{\nu}_1=1/3\times7.3+2/3\times10.8=9.6$ kK, in good agreement with experiment. This suggests a pseudooctahedral structure with four amines coordinated and two monodentate dithiophosphate ligands; that the latter may function as monodentate has been reported[7] for a case complicated by occurrence of steric hindrance, while the similar ligand diethyldithiophosphinate seems to act as monodentate in the compound bis(diethyldithiophosphinato)tetrapyridinecobalt(III).[13] Our data cannot actually exclude a tight ion-pair formation $[Ni(BuNH_2)_4dtp]^+dtp^-$, but this seems unlikely in view of the ascertained ability of dtp^- to act as a unidentate ligand.

Regarding the stability of the adducts, the accuracy of the quantitative evaluation of the formation equilibria from spectrophotometric data is limited by the non-ideality of the solutions investigated (despite the absence of ionic species); by the limited range of temperatures investigated (mainly imposed by the volatility of the amine ligands) and by the unfavourable conditions of spectra overlap and absorbance ratios of the involved species. Nevertheless, stability constants appear sufficiently reliable to show that both primary and secondary amines behave similarly, both giving 1:1 and 1:2 adducts; that both K_1 and K_2 are larger for primary than secondary amines and, as expected for association reactions, all steps of adduct formation are exothermic and accompanied by negative entropy changes. Furthermore, K_2/K_1 is smaller with secondary than with primary amines, which makes 1:1 adducts much more easily observable with the former, and 1:2 adducts more easily obserbable with the latter. Temperature dependence on a weighted average suggests the following range of values for thermodynamic parameters: $\Delta H_1=-6\pm1$ Kcal/mole, $\Delta S_1=-7\pm3$ e.u. and $\Delta H_2=-5\pm1$ Kcal/mole, $\Delta S_2=-4\pm3$ e.u. with $BuNH_2$, respectively, $\Delta H_1=-5.3\pm0.5$ Kcal/mole, $\Delta S_1=-13\pm2$ e.u., $\Delta H_2=-4.8\pm0.3$ Kcal/mole, $\Delta S_2=-18\pm1$ e.u. with Et_2NH. Formation enthalpies appear therefore to be somewhat lower than that of similar adducts (*e.g.* $\Delta H_{1+2}=16.8$ Kcal/mole for $Nidtp_2py_2$[6]), and not greatly different between primary and secondary amines. Rather, the differences between primary and secondary amines can be traced back to entropy differences *i.e.* basicity effects can be regarded as less important than steric effects in determining the observed trend.

Preliminary data with aliphatic tertiary amines (Et_3N) confirms the much smaller capacity of these amines in forming adducts of the above type.

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