Inorganica Chimica Acta, 19 (1976) 105–108

Transition Metal Complexes of Organothiophosphorus Ligands.
IV[a]. Six-coordinate Adducts of Nickel(II) Bis(Dialkylphosphorodithioates) with Symmetrically Substituted Ethylenediamines

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Received October 14, 1975

Symmetrically substituted (N,N′-tetramethyl-, N,N′-dimethyl- and N,N′-diphenyl)ethylenediamines form 1:1 or 2:1 adducts with nickel(II) bis(dialkylphosphorodithioates). The adducts are mixed ligand complexes, with both phosphorodithioato and diamine groups coordinated to nickel(II) in a distorted octahedral geometry. The compounds prepared were characterized by electronic and vibration spectra and magnetic moments.

Introduction

In Part III of this series[1] we have prepared some six-coordinate adducts of nickel(II) bis(diphenylphosphorodithioate) with aromatic and heterocyclic amines. In this work we have used diamines with a flexible skeleton and with a various degree of steric crowding at the coordination site (nitrogen). A diamine can possibly act either as bridging group to form six-coordinate polymeric adducts (Figure 1 A) or as chelating ligand, to form *cis*-adducts (Figure 1 B). The nickel(II) bis(phosphorodithioates) reported so far in the literature[2] are mostly *trans*-monoamine adducts (Figure 1 C), or *cis*-orthodiamine adducts (Figure 1 B), but five-coordinate complexes have also been reported[3]. Thus, a variety of structures can be expected when preparing new Ni(II) bis(phosphorodithioate) amine adducts.

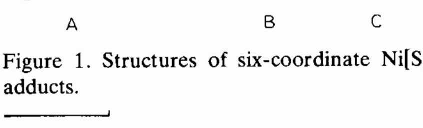

Figure 1. Structures of six-coordinate $Ni[S_2P(OR)_2]_2$ amine adducts.

Experimental

Analytical grade reagents were used throughout this work. The dialkylphosphorodithioic acids, $(RO)_2P(S)SH$ (R = Me, Et, Pr) were prepared from the appropriate alcohol and tetraphosphorus decasulfide according to known procedures[4] and were purified by vacuum distillation. They were converted to nickel(II) chelates by treatment with nickel(II) acetate, followed by extraction with chloroform, concentration and recrystallization from the same solvent.

Infrared spectra were recorded in KBr pellets on a UR-20 C. Zeiss, Jena instrument and electronic spectra on a VSU-2G C. Zeiss, Jena (diffuse reflectance spectra) or a Beckman D-2A (solution spectra) instrument. Magnetic moments were run on a Faraday balance, in solid state at room temperature.

Carbon and hydrogen microanalyses were made in the Microanalytical Laboratory of the Institute (under the supervision of Mrs. L. Nuna). The metal was determined as nickel(II) bis(dimethylglyoximate) and phosphorus as ammonium molybdophosphate (gravimetrically).

After preliminary experiments, in which the combination ratios were established, the adducts were prepared according to the same general procedure, as follows: an acetone solution of nickel(II) bis(dialkylphosphorodithioate) was treated with an acetone solution of the amine, in the proportion required by the stoichiometry. Color changes were immediately observed, from purple to green or blue. Slow evaporation of these solutions deposited the crystalline adducts. The adducts prepared, their properties and analytical data are given in Table I. No compounds other than the 1:1 adducts were obtained with N,N′-diphenylethylenediamine (DPEDA) or N,N′-tetramethylethylenediamine (TMEDA) by using 1:2 or 1:3 complex-to-amine ratio. Also, with N,N′-dimethylethylenediamine (DMEDA) only the 1:2 adduct was formed even with an excess of amine larger than required by the 1:3 ratio.

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TABLE I. Substituted Ethylenediamine Adducts of Nickel(II) Bis(dialkylphosphorodithioates).

Compound[a]	Color	M.p. °C	Analysis: % found (calcd.)			
			C	H	Ni	P
1 : 1 Adducts						
$Ni[S_2P(OMe)_2]_2 \cdot DPEDA$	Intense Green	102–3° (dec.)	36.7 (36.9)	4.3 (4.7)	10.0 (9.6)	10.9[b] (10.4)
$Ni[S_2P(OEt)_2]_2 \cdot DPEDA$[c]	Intense Green	91–6° (dec.)	41.4 (41.1)	5.2 (5.0)	9.1 (9.0)	10.3[d] (9.6)
$Ni[S_2P(OMe)_2]_2 \cdot DMEDA$	Yellow–Green	121–4°	21.3 (20.8)	4.5 (5.2)	12.1 (12.7)	9.9 (10.6)
$Ni[S_2P(OEt)_2]_2 \cdot DMEDA$	Green	103°	28.2 (27.9)	6.2 (6.2)	11.5 (11.3)	11.8 (12.0)
$Ni[S_2P(OPr^i)_2]_2 \cdot DMEDA$	Green	89°	34.0 (33.5)	7.1 (6.9)	9.8 (10.2)	–
$Ni[S_2P(OMe)_2]_2 \cdot TMEDA$	Yellow–Green	111–2°	24.7 (24.5)	5.6 (5.7)	12.1 (12.0)	12.1 (12.4)
$Ni[S_2P(OEt)_2]_2 \cdot TMEDA$	Yellow–Green	103°	30.4 (30.8)	6.3 (6.6)	10.1 (10.8)	11.1 (11.4)
$Ni[S_2P(OPr^n)_2]_2 \cdot TMEDA$	Yellow–Green	60–1°	35.9 (35.9)	7.1 (7.2)	–	–
$Ni[S_2P(OPr^i)_2]_2 \cdot TMEDA$	Yellow–Green	121°	36.4 (35.9)	6.9 (7.3)	–	–
1 : 2 Adducts[e]						
$Ni[S_2P(OEt)_2]_2 \cdot 2DMEDA$	Blue	120°	32.2 (31.8)	6.8 (7.3)	9.3 (9.7)	9.8 (10.0)
$Ni[S_2P(OPr^i)_2]_2 \cdot 2DMEDA$	Blue	143°[f]	36.4 (36.3)	7.7 (7.9)	9.2 (8.9)	–

[a] Abbreviations used: DPEDA = $PhHNCH_2CH_2NHPh$; TMEDA = $Me_2NCH_2CH_2NMe_2$; DMEDA = $MeHNCH_2CH_2NHMe$. [b] Also found N 4.8% (calcd. N 4.8%). [c] Adducts of DPEDA with n-propyl and iso-propyl analogues could not be obtained. [d] Also found N 4.6% (calcd. N 4.3%). [e] The methyl and n-propyl analogues could not be isolated. A blue solution was formed on mixing $Ni[S_2P(OMe)_2]_2$ with DMEDA in 1 : 2 ratio, which on evaporation leaves a green gummy product. [f] At 138°C becomes green and then melts at 143°C.

Results and Discussion

Symmetrically substituted ethylenediamines, R'RN CH_2CH_2NRR', with a variable degree of steric crowding at nitrogen (R = H, R' = Me or Ph; R = R' = Me) were found to form adducts with nickel(II) bis(dialkylphosphorodithioates). The composition of the compounds obtained (listed in Table I) shows that the steric properties of the ligands exert some influence upon the nature of the adducts formed. Thus, the sterically crowded DPEDA and TMEDA form only 1 : 1 adducts. For these compounds there are several structural possibilities, shown in Figure 1A, B and Figure 2D. Spectral data support a six-coordinate structure, but they are not entirely diagnostic because of possible additional splittings in the electronic spectra, caused by the distorsion of the coordination octahedra. An X-ray diffraction investigation of two of our compounds, namely $Ni[S_2P(OEt)_2]_2 \cdot TMEDA$[5] and $Ni[S_2P(OEt)_2]_2 \cdot DPEDA$[6] confirmed that Ni(II) is six-coordinate and the ligands are bidentate, forming a rather distorted *cis*-octahedral complex, of the type shown in Figure 1B, thus ruling out other possibilities. Very probably all other 1 : 1 adducts have a similar structure.

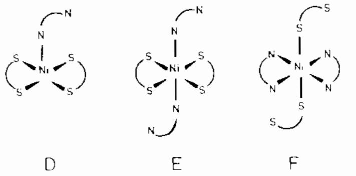

Figure 2. Some other possible structures of $Ni[S_2P(OR)_2]_2$ amine adducts.

N,N'-Dimethylethylenediamine (DMEDA) forms two series of adducts, with 1 : 1 and 1 : 2 combination ratio. Spectral data show that the yellow–green 1 : 1 adducts have probably monomeric *cis*-octahedral structures (Figure 1B), similar to those of 1 : 1 adducts of TMEDA. For the blue 1 : 2 adducts either structure E (Figure 2) with a free amine end (not coordinated) or structure F (Figure 2) with monodentate phosphorodithioate groups (containing the NiS_2N_4 chromophore) can be considered. It should be noted that another Ni(II) bis(phosphorodithioate)–amine adduct containing the NiS_2N_4 chromophore, the blue $Ni[S_2P(OEt)_2]_2 \cdot 4BuNH_2$, has been previously reported in the literature[7]. Infrared spectral data of our DMEDA 1:2 adducts show that both NH groups of the diamine are coordinated, therefore structure F (Figure 2) is more probable.

Electronic Spectra and Magnetic Moments

The electronic spectra of the adducts prepared were recorded in solid state (reflectance spectra) and for some compounds in acetone solution. The diffuse reflectance spectra are better resolved and exhibit several sharp peaks. The positions of the observed bands are listed in Table II, together with the magnetic moments. The solution spectra (recorded in the range from 12 kK to 40 kK) showed two broader bands (ν_2 and ν_3); the ν_1 band was outside the range explored. The positions of the absorption bands are shown in Table III.

The six-coordinate nickel(II) complexes (O_h symmetry) have ground state $^3A_{2g}$ and the electronic spectrum should exhibit three transitions: ν_1 ($^3A_{2g}$–$^3T_{2g}$) between 7–13 kK, ν_2 ($^3A_{2g}$–$^3T_{1g}(F)$) between 11–20 kK, and ν_3 ($^3A_{2g}$–$^3T_{1g}(P)$) between 20–27 kK. Possible distortions of the coordination octahedron may result in further splitting of the main bands, which is indeed the case with our compounds.

The spectra of the green 1:1 and blue 1:2 adducts are in agreement with a six-coordinate, distorted octahedral coordination in the NiS_4N_2 and NiS_2N_4 chromophore. In fact, the X-ray diffraction investigations quoted above[5,6] showed rather strong distorsions from the regular geometry of the coordination octahedron. Therefore, it is not surprising that a splitting of the ν_3 band is observed in some diffuse reflectance spectra. Thus, the shoulder at *ca.* 20 kK can possibly be due to a forbidden transition such as $^3A_{2g}$–$^1T_{1g}$.

Infrared Spectra

In the infrared spectra of the compounds investigated, of particular interest are the stretchings of PS_2 groups, directly involved in coordination. The data are listed in Table IV. Unfortunately, it is very difficult to distinguish between mono- and bidentate $(RO)_2PS_2$ ligands on the basis of νPS_2 absorption bands, although

TABLE II. Electronic Spectra (Diffuse Reflectance) and Magnetic Moments of Nickel(II) Bis(dialkylphosphorodithioate) Adducts.

Compound	Absorption Bands (Maxima in kK)				Magnetic Moment B.M.
	ν_1	ν_2	ν_3		
1:1 Adducts					
$Ni[S_2P(OMe)_2]_2 \cdot DPEDA$	10.0	14.3	19.2sh	23.0	3.24
$Ni[S_2P(OEt)_2]_2 \cdot DPEDA$	10.0	13.7	18.8sh	23.2	3.14
$Ni[S_2P(OEt)_2]_2 \cdot TMEDA$	9.8	14.0	20.8sh	22.8	3.15
$Ni[S_2P(OEt)_2]_2 \cdot DMEDA$	10.0	15.2	20.2sh	23.9	3.24
1:2 Adducts					
$Ni[S_2P(OEt)_2]_2 \cdot 2DMEDA$	10.0	15.8		18.4	2.95

TABLE III. Electronic Spectra (in Acetone Solution) of Some Nickel(II) Bis(dialkylphosphorodithioate) Adducts

Compound	Absorption Bands (Maxima in kK)		Magnetic Moment B.M.
	ν_2	ν_3	
1:1 Adducts			
$Ni[S_2P(OMe)_2]_2 \cdot TMEDA$	14.0	22.7	3.10
$Ni[S_2P(OMe)_2]_2 \cdot DMEDA$	14.9	20.6	3.08
$Ni[S_2P(OPr^i)_2]_2 \cdot TMEDA$	14.0	22.5	3.18
$Ni[S_2P(OPr^i)_2]_2 \cdot DMEDA$	15.0	23.8	3.12
1:2 Adducts			
$Ni[S_2P(OPr^i)_2]_2 \cdot 2DMEDA$	15.0	24.0	3.34

TABLE IV. Infrared Spectral Data on Nickel(II) Bis(dialkylphosphorodithioate) Chelates and Their Amine Adducts.

Compound	$\nu_{sym}PS_2$ cm^{-1}	$\nu_{as}PS_2$ cm^{-1}	νNH cm^{-1}
Ni(II) Bis(dialkylphosphorodithioates)			
$\mathrm{Ni[S_2P(OMe)_2]_2}$	523m	648s	–
$\mathrm{Ni[S_2P(OEt)_2]_2}$	543m	641s	–
$\mathrm{Ni[S_2P(OPr^n)_2]_2}$	550m	640s	–
$\mathrm{Ni[S_2P(OPr^i)_2]_2}$	546m	636s	–
1:1 Adducts			
$\mathrm{Ni[S_2P(OMe)_2]_2 \cdot DPEDA}$	535m	675s, 665sh	3240m[a]
$\mathrm{Ni[S_2P(OEt)_2]_2 \cdot DPEDA}$	546m	660s	3258m[a]
$\mathrm{Ni[S_2P(OMe)_2]_2 \cdot TMEDA}$	534m	667s, 655sh	–
$\mathrm{Ni[S_2P(OEt)_2]_2 \cdot TMEDA}$	557m	675s	–
$\mathrm{Ni[S_2P(OPr^n)_2]_2 \cdot TMEDA}$	580m, 560m	670s, 665sh	–
$\mathrm{Ni[S_2P(OPr^i)_2]_2 \cdot TMEDA}$	565m, 558m	668s, 657sh	–
$\mathrm{Ni[S_2P(OMe)_2]_2 \cdot DMEDA}$	535m	675s, 655sh	3252s[b]
$\mathrm{Ni[S_2P(OEt)_2]_2 \cdot DMEDA}$	552m	672s	3260s
$\mathrm{Ni[S_2P(OPr^n)_2]_2 \cdot DMEDA}$	560m	670s	3170s
$\mathrm{Ni[S_2P(OPr^i)_2]_2 \cdot DMEDA}$	556m	654s	3278s
1:2 Adducts			
$\mathrm{Ni[S_2P(OEt)_2]_2 \cdot 2DMEDA}$	575m	664s	3185s
$\mathrm{Ni[S_2P(OPr^i)_2]_2 \cdot 2DMEDA}$	558m	667s	3143s

[a] NH stretching band of the free amine (DPEDA) at 3420 cm^{-1}.
[b] NH stretching band of the free amine (DMEDA) at 3338 cm^{-1}.

some such attempts have been made in certain cases[1]. Some observations are, however, of interest. A comparison of the spectral data for the four-coordinate nickel(II) bis(dialkylphosphorodithioates) and the diamine adducts (Table IV) shows in each case an increase of both ν_{sym} and $\nu_{as}PS_2$ stretching when additional nitrogen atoms are coordinated to the metal. The X-ray structure determination[5] of $\mathrm{Ni[S_2P(OEt)_2]_2 \cdot TMEDA}$, for example, showed an increase of the Ni–S bond from 2.23 Å in $\mathrm{Ni[S_2P(OEt)_2]_2}$[8,9] to 2.52–2.55 Å in the adduct. Thus, the changes in the electron density of Ni–S bonds caused by additional coordination of amines are reflected in the vibrational spectra as changes in the νPS_2 stretching frequencies.

Other absorption bands of interest are those of NH groups in the spectra of DPEDA and DMEDA complexes. Thus, the free diamine exhibits bands at 3338 cm^{-1} due to NH vibrations; these are shifted in the spectra of the DMEDA adducts to 3260–3143 cm^{-1} (see Table IV) and no bands due to free (noncoordinated) NH groups are observable. This proves that the diamines act as bidentate ligands with both NH groups involved in coordination to nickel(II), in agreement with the structure shown in Figure 1B for 1:1 adducts and the structure shown in Figure 2F for the 1:2 adducts.

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