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Four, Five and Six Coordinate Complexes of Nickel(II) with the 1,3-Monothio Ligand O,O'-Diethylmonothiomalonate

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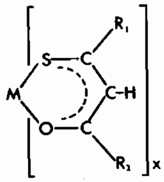
Complexes of O,O'-diethylmonothiomalonate have been prepared and characterized. With divalent nickel, this ligand promotes the formation of both 5- and 6-coordinate adducts with aromatic, heterocyclic bases; being the first time this feature has been noted for a 1,3-monothio ligand. Several series of 4-, 5- and 6-coordinate species of Ni(II) have been characterized with particular emphasis on their electronic spectra.

Introduction

Although many complexes with 1,3-monothio ligands (I) have recently been prepared and characterized, most support *alkyl* or *aryl* substituents.[1,2]



(I)

(a) $R_1 = R_2 = OEt \equiv Ni(OEt\text{-}SacOEt\text{-}ac)_2$
(b) $R_1 = CH_3$; $R_2 = OEt \equiv Ni(OEt\text{-}acSac)_2$
(c) $R_1 = R_2 = CH_3 \equiv Ni(Sacac)_2$

The replacement of methyl by the ethoxy substituent in dithioacetylacetone modifies the properties of the complexes significantly.[3–5] During these studies we have prepared and characterized analogous complexes of O,O'-diethylmonothiomalonate (Ia) where both the substituent groups are $-OCH_2CH_3$. The nickel complex, $Ni(OEt\text{-}SacOEt\text{-}ac)_2$, is square planar and low-spin, and a spectral study of its interaction with various nitrogenous aromatic bases has afforded evidence for five-coordinate complexes. In contrast, the 1,3-*dithio* chelate of dithioacetylacetone, $Ni(SacSac)_2$ cannot be induced to increase its coordination number by the addition of a base[6] although $Co(SacSac)_2$ forms five-coordinate complexes which have been characterized in solution and in the solid state.[7,8]

Careful calorimetric and spectrophotometric examinations of the addition of nitrogen bases to 1,3-monothio complexes of nickel(II) failed to reveal evidence of five-coordinate species.[9] The following data appear to be the first presented for five-coordinate complexes of 1,3-monothio chelates, although penta-coordinate adducts of other *bis*-chelates have received much attention.[10]

Experimental

1,3-diethoxy-3-thione-1-propanone, [OEt-acOEt-SacH]

The protonated ligand was prepared by the method of Barnikow and Strickmann.[11]

Na[OEt-SacOEt-ac] Solutions

OEt-SacOEt-acH (3.5 g) was added dropwise to an ice-cold suspension of NaH (0.96 g of 50% dispersion in oil) in anhydrous diethyl ether (30 ml). When the evolution of hydrogen has ceased, cold water (30 ml at 5° C) was carefully added. The aqueous phase was extracted with diethyl ether (2×20 ml) and the resulting aqueous solution of Na[OEt-SacOEt-ac] was used to form the complexes described below.

Bis(1,3-diethoxy-3-thioloprop-2-ene-1-one)nickel (II), $[Ni(OEt\text{-}SacOEt\text{-}ac)_2]$

The solution of $[OEt\text{-}SacOEt\text{-}ac]^-$ was added with stirring to $NiCl_2 \cdot 6H_2O$ (2.4 g) in H_2O (200 ml) at room temperature. The resulting red-brown complex was filtered off and washed with water. The complex is readily recrystallized from petroleum ether (40°–60° C) as red platelets. The complex is diamagnetic.

Anal. Calcd. for $C_{14}H_{22}NiO_6S_2$: C, 41.2; H, 5.4; Ni, 14.3; S, 15.7. Found: C, 41.3; H, 5.5; Ni, 14.3; S, 15.4.

bis(1,3-diethoxy-3-thioloprop-2-ene-2-one)zinc(II), $[Zn(OEt\text{-}SacOEt\text{-}ac)_2]$

The $[OEt\text{-}SacOEt\text{-}ac]^-$ solution was added to $ZnCl_2 \cdot 6H_2O$ (2.4 g) in H_2O (200 ml) and the white flocculant precipitate was collected, washed and recrystallized from diethyl ether and finally from petroleum ether (40°–60° C) to give the pure complex as large white needles.

Anal. Calcd. for $C_{14}H_{22}O_6S_2Zn$: C, 40.4; H, 5.3; S, 15.4; Zn, 15.7. Found: C, 39.7; H, 5.3; S, 15.4; Zn, 15.4.

Bis(1,3-diethoxy-3-thioloprop-2-ene-1-one)bis (pyridine)nickel(II), [Ni(OEt-SacOEt-ac)$_2$*(py)*$_2$]

Ni(OEt-SacOEt-ac)$_2$ was dissolved in a minimum volume of acetone at room temperature and a five-fold excess of pyridine was added dropwise with stirring. The pale green crystals were collected, washed with acetone and dried at room temperature. The complex has a magnetic moment of 3.11 BM and a molar conductance of 0.6 ohm^{-1} cm$^2 M^{-1}$ in nitromethane solution.

Anal. Calcd. for $C_{24}H_{32}N_2NiO_6S_2$: C, 50.8; H, 5.7; N, 4.9; Ni, 10.4; S, 11.3. Found: C, 50.9; H, 5,7; N, 4.8; Ni, 10.4; S, 10.9.

Bis(1,3-diethoxy-3-thioloprop-2-ene-1-one)-2,2'-dipyridylnickel(II), [Ni(OEt-SacOEt-ac)$_2$*dipy*]

Dipyridyl (0.16 g) in a minimum volume of acetone was added with stirring to Ni(OEt-SacOEt-ac)$_2$ (0.41 g) in acetone (5 ml). The complex separated as an oil which was solidified by stirring with diethyl ether. The resulting pale green solid was washed with diethyl ether and dried at room temperature. The complex has a magnetic moment of 3.12 BM and a molar conductance of 3.0 ohm^{-1} cm$^2 M^{-1}$.

Anal. Calcd. for $C_{24}H_{30}N_2NiO_6S_2$: C, 51.0; H, 5.3; N, 5.0; Ni, 10.4; S, 11.3. Found: C, 50.8; H, 5.3; N, 5.1; Ni, 10.4; S, 11.6.

Bis(1,3-diethoxy-3-thioloprop-2-ene-1-one)bis(3-methylpyridine)nickel(II), [Ni(OEt-SacOEt-ac)$_2$ (β-pic)$_2$]

An excess of β-picoline was added to a saturated solution of Ni(OEt-SacOEt-ac)$_2$ in acetone. Although no complex separated, the solution turned green. Three-quarters of the acetone was boiled off and the solution filtered. On cooling, the complex separated as blue-green crystals which were washed (MeOH) and dried at the pump. The complex has a magnetic moment of 3.18 BM and a molar conductance of 1.1 ohm^{-1} cm$^2 M^{-1}$.

Anal. Calcd. for $C_{26}H_{36}N_2NiO_6S_2$: C, 52.4; H, 6.1; N, 4.7; Ni, 9.9; S, 10.8. Found: C, 52.2; H, 6.1; N, 4.9; Ni, 10.4; S, 10.7.

Bis(1,3-diethoxy-3-thioloprop-2-ene-1-one)bis (4-methylpyridine)nickel(II), [Ni(OEt-SacOEt-ac)$_2$ (γ-pic)$_2$]

This complex was prepared as for the β-picoline adduct. On reducing the volume to one-half and cooling, the pure complex separated as blue-green crystals with μ_{eff} = 3.01 BM and λ_M = 0.9 ohm^{-1} cm$^2 M^{-1}$.

Anal. Calcd. for $C_{26}H_{36}N_2NiO_6S_2$: C, 52.4; H, 6.1; N, 4.7; Ni, 9.9; S, 10.8. Found: C, 52.4; H, 6.1; N, 4.6; Ni, 9.9; S, 10.7.

Instrumentation and Methods

Magnetic moments were obtained by the Gouy method at room temperature with diamagnetic corrections estimated from tabulated Pascal constants. Conductance measurements were obtained at 20° C on $\sim 10^{-3} M$ solutions in nitromethane. Diffuse reflectance spectra were obtained with a Beckman DK-2A spectrophotometer on undiluted samples using $BaSO_4$ as reference whilst transmission spectra were measured with Cary 14 and Hitachi EPS-3T spectrophotometers. Base lines corrections have been applied to the data in Figure 2.

Results and Discussion

Bis-chelated Complexes

Although most six-membered ring 1,3-monothio complexes can be formed readily from the metal acetate and the protonated form of the monothio ligand[1,2], formation of the present complexes required deprotonation of the ligand with a strong base (NaH) prior to reaction with the metal ion. The neutral chelates are exceedingly soluble in the usual organic solvents and quite soluble in ethers. The NMR spectra of the dia-

TABLE I. N.m.r. Spectra in $CDCl_3$.

Compound	Chemical Shift Relative to TMS at δ = 0 ppm						
	Adjacent to C–O			Adjacent to C–S			
	CH_2	CH_3	J_{Et}	CH_2	CH_3	J_{Et}	H
Ni(OEt-SacOEt-ac)$_2$	3.99	1.19	7	4.12	1.26	7	5.06
Zn(OEt-SacOEt-ac)$_2$	4.21	1.25	7.1	4.30	1.34	7.1	5.43
Ni(SacOEt-ac)$_2$	4.08	1.25	7.4	–	–	–	5.76
Zn(SacOEt-ac)$_2$	4.22	1,26	7	–	–	–	5.99
Ni(Sacac)$_2$[a]	–	–	–	–	–	–	6.41

[a] C. G. Barraclough, R. L. Martin and I. M. Stewart, *Aust. J. Chem., 22,* 891, (1969).

magnetic *bis* chelates of zinc(II) and nickel(II) complexes (Table I) distinguish the two types of OEt groups in the ligands. The trend noted previously, that the substituent at the thiocarbonyl group is deshielded with respect to the same substituent at the carbonyl unit,[5] has been invoked to assign the two types of ethoxy groups. The downfield chemical shift of the methine resonance of the zinc(II) compared with the nickel(II) compound[8] observed for 1,3-dithio chelates is also present with these monothio complexes. The progressive upfield shift of the methine absorption in the monothio complexes of nickel(II) with $[\text{Sacac}]^-$ (6.41 ppm), $[\text{SacOEt-ac}]^-$ (5.76 ppm) and $[\text{OEt-SacOEt-ac}]^-$ (5.06 ppm) in steps of approximately 0.7 ppm illustrates the 'shielding' effect of the $-\text{OEt}$ group relative to $-\text{CH}_3$ group.

If it is assumed that the lowest energy band in the optical spectrum corresponds to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, the monothio-chelates may be located in the spectrochemical series as follows on the basis of their Δ_1 values ($F_2 = 10F_4 = 800\ \text{cm}^{-1}$):

$\text{Ni(OEt-SacOEt-ac)}_2$
16,700 cm^{-1}, cyclohexane
$< \text{Ni(SacOEt-ac)}_2$[13]
17,700 cm^{-1}, CHCl_3
$< \text{Ni(Sacac)}_2$[13]
18,500 cm^{-1}, CHCl_3
$< \text{Ni(Et}_2\text{dtp)}_2$[12]
17,300 cm^{-1}, EtOH
$< \text{Ni(Etxan)}_2$[12]
18,300 cm^{-1}, CHCl_3
$< \text{Ni(Et}_2\text{dtc)}_2$[12]
18,600 cm^{-1}, CHCl_3

Substitution of $-\text{CH}_3$ by $-\text{OEt}$ produces a substantial hyposochromic shift. This dramatic shift is in contrast to the small range (~500 cm^{-1}) which encompasses the corresponding transition in most *alkyl* and *aryl* substituted nickel(II) monothio complexes.[1,2]

Six-Coordinate Complexes

Six-coordinate, aromatic nitrogen base adducts of $\text{Ni(OEt-SacOEt-ac)}_2$ are readily prepared by addition of excess base to an acetone solution of $\text{Ni(OEt-SacOEt-ac)}_2$. The di-adducts do not appear to lose base at room temperature and are quite soluble in the usual organic solvents. The magnetic moments of these compounds are almost identical (~3.1 BM; see Experimental) and are consistent with a six-coordinate nickel (II) ion in a $t_2{}^6e^2$ configuration. The very low molar conductivities of the compounds in nitromethane (0.0 to 3.0 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$; see Experimental) substantiate the formulation of the compounds and their dissociation products as non-ionic, molecular adducts.

As the di-adducts undergo an equilibrium dissociation to five-coordinate species in solution (see later), approximate extinction coefficients for the six-coordinate complexes have been obtained from solutions containing a large excess of the appropriate base (Table II) where the concentrations of the four- and five-coordinate complexes were considered negligible. The octahedral complexes are generally characterized by three *d–d* bands at approximately 24,000, 16,000 and

TABLE II. Electronic Spectra (Diffuse Reflectance and Transmission) of $\text{Ni(OEt-SacOEt-ac)}_2$[a] and its Six-coordinate Adducts[b] [$\nu(\text{cm}^{-1})$; $\varepsilon(1\ \text{cm}^{-1}\ \text{mol}^{-1})$].

$\text{Ni(OEt-SacOEt-ac)}_2$			$\text{Ni(OEt-SacOEt-ac)}_2\text{(py)}_2$			$\text{Ni(OEt-SacOEt-ac)}_2\text{(dipy)}$			$\text{Ni(OEt-SacOEt-ac)}_2(\beta\text{-pic})_2$			$\text{Ni(OEt-SacOEt-ac)}_2(\gamma\text{-pic})_2$		
D.R.[c]	Soln.	ε	D.R.	Soln.	ε	D.R.	Soln.	ε	D.R.	Soln.	ε	D.R.	Soln.	ε
(24000)	(24000)	259	(26000)	(24300)	(219)	(24300)	(24000)	(592)	n.m.[d]	(23900)	(226)	n.m.	(24300)	(202)
20400	19200	165				(21300)	(20500)	(140)						
14500	13900	40	16100	15800	28	16500	(16600)	(45)	16200	15500	38	16200	15800	29
				(12000)		(11900)	(11600)		(12200)	(11700)		(12000)	(11700)	
			9800	9800	15	9900	9700	32	10100	9800	18	10200	9700	16

[a] Solution spectra in cyclohexane. [b] Solution spectra (25000–4600 cm^{-1}) obtained in benzene containing a five to six-fold excess of base to force the equilibria to the six-coordinate species. [c] D.R.: diffuse reflectance spectra over range (28000–5300 cm^{-1}), all diffuse reflectance spectra show relatively sharp peaks at 7400, 6100, 5800 and 5600 cm^{-1}. [d] n.m.: not measured.

9,800 cm^{-1} and a very weak shoulder at ~12,000 cm^{-1}. Sharp peaks at lower energies than 8,000 cm^{-1} in the diffuse reflectance spectra of the parent compound and its adducts are attributed to infrared overtone bands. Although the adducts with their $NiS_2O_2N_2$-cores will have a symmetry lower than O_h, the nickel ion is six-coordinate and presumably "octahedrally" coordinated. The electronic spectra, magnetism and conductivity confirm this assumption.

The absorptions at ~10,000 cm^{-1} are believed to correspond to $^3A_{2g} \rightarrow {}^3T_{2g}$ in O_h symmetry, whilst the other two absorptions are assigned as ~16,000 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}$) and ~24,000 cm^{-1} as $^3A_{2g} \rightarrow {}^3T_{1g}$ (P). As the last band is present as a shoulder on the steeply rising charge transfer spectrum, the underlying band is believed to have an extinction coefficient in accord with a *d–d* transition. The corresponding band in the base adducts of xanthates is actually obscured by intense UV absorptions.

The present six-coordinate compounds may involve either *cis* or *trans* arrangements of the nitrogen bases although single crystal X-ray studies of the structures of pyridine adducts of related compounds [Ni(acac)$_2$(py)$_2$[14] and Ni(Et$_2$dtp)$_2$(py)$_2$[15]] reveal the presence of *trans* nitrogens, a configuration which is probably adopted by the present complexes.

Consistently higher values of the extinction coefficients for the absorptions of the 2,2′-dipyridyl adducts compared with the other adducts are in accord with this molecule having a *cis* configuration.

Five-Coordinate Complexes

For the present examples, spectral evidence indicates that the di-adducts of Ni(OEt-SacOEt-ac)$_2$ partially dissociate in solution to five-coordinate complexes.

$$\text{Ni(OEt-SacOEt-ac)}_2\text{B}_2 \rightleftharpoons \text{Ni(OEt-SacOEt-ac)}_2\text{B} + \text{B} \quad (1)$$

The spectral characteristics of the five-coordinate complexes (Table III) have been obtained by analysis of the composite spectra of five- and six-coordinate species with the prior knowledge of the spectrum of the six-coordinate species. Although the lowest energy absorptions (~6,000 cm^{-1}) fall into the energy range of IR overtone bands, the band widths at half-height are commensurate with these bands being *d–d* transitions.

The mono-adduct of the bidentate base 2,2′-dipyridyl does not dissociate to five-coordinate species in solution. However, the di-adducts of the monodentate bases do dissociate with identical absorption data for the five-coordinate species being obtained from solutions of the dissociated di-adduct or by addition of

TABLE III. Electronic Spectral Details of Five-coordinate Complexes in CH$_2$Cl$_2$.

Complex		Absorption (cm^{-1})^a		
A	Ni(OEt-SacOEt-ac)$_2$(py)	5500	14300	22900
B	Ni(OEt-SacOEt-ac)$_2$ (β-pic)	5400	14200	22900
C	Ni(OEt-SacOEt-ac)$_2$ (γ-pic)	5500	14700	23000
D	Ni(OEt-SacOEt-ac)$_2$ (α-pic)	6700	13900	22900

[a] Approximate extinction coefficients (l cm^{-1} mol^{-1}) for compounds A, B and C: 5500 cm^{-1}, 20; 14300 cm^{-1}, 60; band width at half-height, ~2500 cm^{-1} for peaks in region 5400–6700 cm^{-1}; all species appear to have a weak shoulder at ~11300 cm^{-1}.

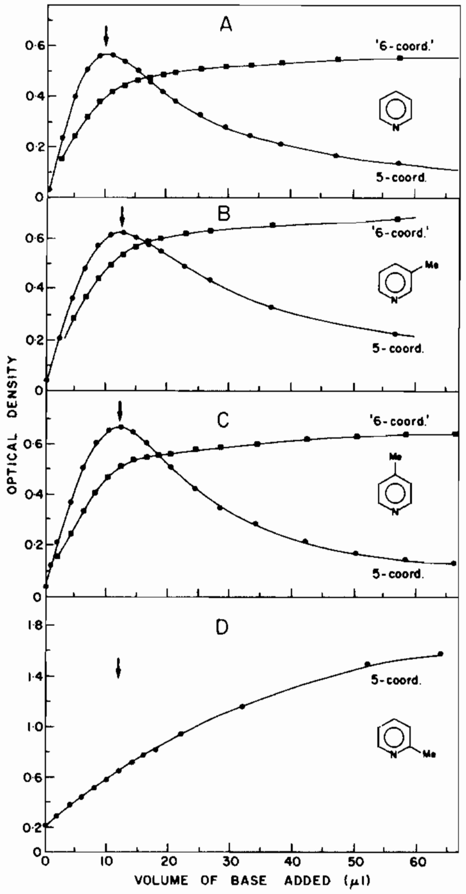


Figure 1. Absorptions of five- and six-coordinate species of Ni(OEt-SacOEt-ac)$_2$ in CH$_2$Cl$_2$ with four bases. 5-coord refers to absorption at ~5,500–6,700 cm^{-1} whilst 6-coord refers to the absorption at ~9,800 cm^{-1}. At low base concentrations, the latter peak has marked contribution from close, intense absorptions and is not a reliable measure of the concentration of this species. Expected 1:1 end-points are arrowed. Concentrations of Ni(OEt-SacOEt-ac)$_2$ solutions (3.00 ml): A, 0.0369*M*; B. 0.0404*M*; C, 0.0404*M*; D, 0.1665*M*.

base to a solution of the four-coordinate compound, *i.e.*, (1) or (2).

$$\mathrm{Ni(OEt\text{-}SacOEt\text{-}ac)_2 + B \rightleftharpoons Ni(OEt\text{-}SacOEt\text{-}ac)_2B} \quad (2)$$

The five-coordinate species fall into two classes with adducts of pyridine, and 3- and 4-methylpyridine having distinctly different spectral properties to those of the 2-methylpyridine adduct. Considering firstly the adducts of pyridine and 3- and 4-methylpyridine, two spectral experiments using various ratios of Ni(OEt-SacOEt-ac)$_2$ and base show that the absorptions at ~5,500 cm^{-1} arise from the 1 : 1 adduct (Figures 1 and 2). As the ratio of base increases, the formation of the six-coordinate species is apparent as monitored by the increasing optical density of the absorption at 9,800 cm^{-1}. Results illustrated were obtained for CH$_2$Cl$_2$ solutions although similar results were obtained in benzene.

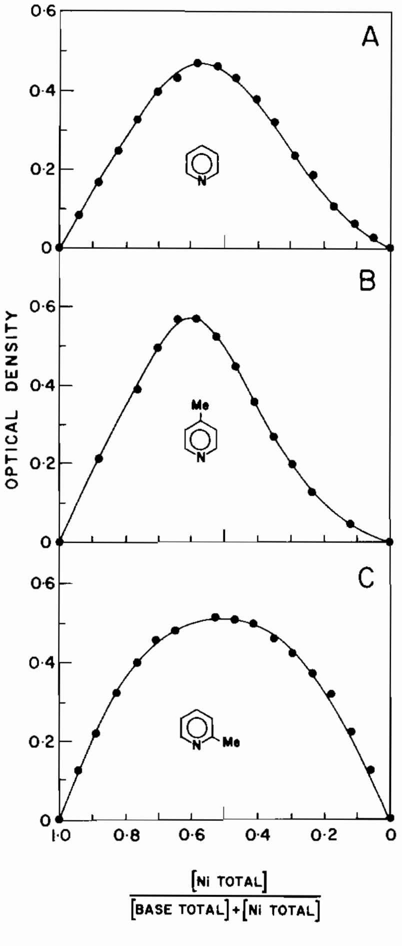


Figure 2. Spectral plots of the absorptions at ~6,000 cm^{-1}. Series prepared from equimolar solutions of Ni(OEt-SacOEt-ac)$_2$ and base in CH$_2$Cl$_2$ with the following concentrations: A, 0.0597*M*; B, 0.0669*M*; C, 0.1690*M*.

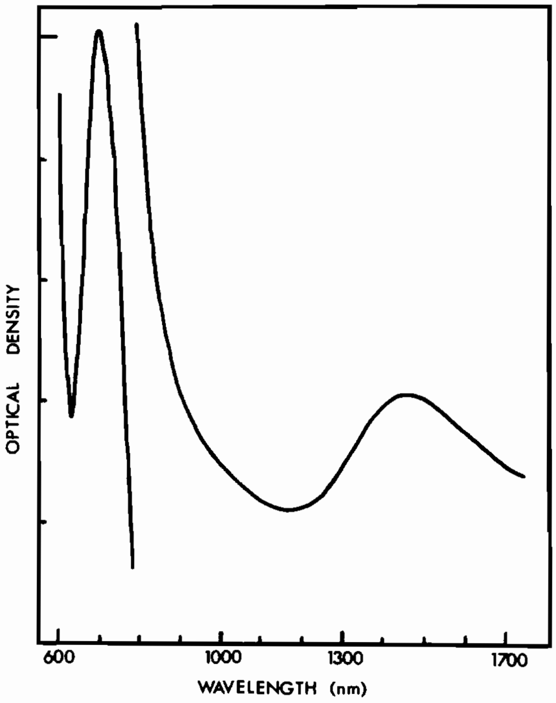
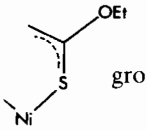
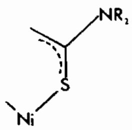


Figure 3. Electronic spectrum of the five-coordinate species, Ni(OEt-SacOEt-ac)$_2$(α-pic) in CH$_2$Cl$_2$ solution.

With 2-methylpyridine, solutions of Ni(OEt-SacOEt-ac)$_2$ change from red to green-brown although no adduct could be isolated. Apparently the steric hindrance proffered by the methyl group on this base renders this adduct rather unstable. Similar spectrophotometric experiments to those described above indicate that the five-coordinate species is characterized by the absorption at 6,700 cm^{-1} being approximately 2000 cm^{-1} higher in energy than those obtained for the non-hindered bases (Figure 3). The solution concentration of this species increases slowly in excess base (30 molar excess) although there is no spectral evidence of six-coordinate species.

Assignment of structures to the two types of five-coordinate compounds is not practicable from the spectral data in view of the marked spectral changes which accompany relatively small distortions from strictly square pyramidal geometry.[10] However, on consideration of the steric requirements of the 2-methylpyridine base, it would appear that this complex would be more likely to be trigonal bipyramidal whilst the other adducts may approach more closely a square pyramidal structure.

Adduct formation with primary and secondary amines has not been examined for the present system in view of the proven ability of some secondary amines at least to eliminate EtOH[16] from the  group to yield 

Similar complicating substitution reactions with primary and/or secondary amines have been noted for dithiophosphates[17] and xanthates[18] and even dithiocarbamates,[19] although some workers have been able to characterize adducts of these amines in solution with dithiophosphate complexes.[20]

Acknowledgement

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