

Heterocyclic Amine Adducts of Bis(2-thiopyridine N-oxide)nickel(II)

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Abstract

Heterocyclic amine adducts of bis(2-thiopyridine N-oxide)nickel(II), Ni(OS)_2 , have been isolated with the following stoichiometries: $\text{Ni(OS)}_2 \cdot \text{B}$ (B = pyridine, piperidine, pyrazine and 3,5-lutidine) and $\text{Ni(OS)}_2 \cdot 2\text{B}$ (B = 3-picoline, 4-picoline and 3,4-lutidine). In addition, a stable 1:1 adduct was formed with piperazine as well as a thermally unstable 2:1 adduct. The thermal decomposition enthalpies of these adducts and their infrared and electronic spectra are discussed.

Introduction

Since the preparation [1] of 2-thiopyridine N-oxide there has been only limited study of its metal ion complexes. The first report of the preparation of such complexes was a study of their bacterial and fungicidal properties [2]; little attention was given to their chemical properties. Robinson [3] reported the preparation of some first row transition metal ion complexes of this ligand. Molecular weights, molar conductivities, magnetic susceptibilities, and electronic spectra were reported, and a few infrared bands were assigned. We included infrared assignments for the chromium(III) complex in our study of the lanthanide complexes of this ligand [4]. More recently a structural study of this ligand's complexes of lanthanides and actinides has been reported [5].

An ESR study of the amine adducts to the bis(2-thiopyridine N-oxide)copper(II) complex has been communicated [6]. There have been a substantial number of adduct studies involving copper(II) complexes due both to copper's biological importance [7] and to the ease of obtaining spectral changes upon adduct formation [8]. In contrast, adducts involving nickel(II) complexes have been studied to a lesser extent. The smaller number of planar 4-coordinate Ni(II) complexes compared to

those of Cu(II) may be the principal reason for the fewer reports on Ni(II) adducts.

Adducts can be formed with NiO_4 chromophores; however, substitution may also occur [9] depending on the lability of the oxygen-donor ligand. With NiS_4 chromophores substitution is unlikely, but adduct formation does not always occur [10]. Since there is little information available concerning addition compounds of NiO_2S_2 systems, we have isolated a number of adducts of bis(2-thiopyridine N-oxide)nickel(II) with heterocyclic bases. The resultant compounds have been characterized by spectral and thermal techniques. It should be noted that the analogous copper(II) compounds could not be isolated, and our previous report was limited to solution studies [6].

Experimental

Bis(2-thiopyridine N-oxide)nickel(II) was isolated from aqueous solution as described by Robinson [3]. Adducts were prepared by dissolving 0.4 g of the nickel complex in 10 ml of chloroform and then adding the base dropwise until the color of the solution changed from brown to green. The majority of solvent was removed by vacuum distillation, and the product crystallized upon refrigeration. The crystals were removed by vacuum filtration, washed with a small portion of cold chloroform, and stored in a vacuum desiccator. The thermal measurements were carried out with a Perkin-Elmer DSC 2C Scanning Calorimeter and a TGS-2 Thermogravimetric System. Dissociation enthalpies were calibrated against the heat of fusion of tin. The remaining instrumentation and procedures employed were identical to those of previous reports from this laboratory [4].

Results and Discussion

Molecular addition compounds between bis(2-thiopyridine N-oxide)nickel(II) (Ni(OS)_2 from here on) and eight different heterocyclic amines

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TABLE I. Thermal Data for the Decomposition of Ni(OS)₂·2B and Ni(OS)₂·B Adducts.

Ligand	Mole ratio ligand:Ni	Decomposition temperature ^a (°C)	Experimental weight loss (%)	Theoretical weight loss (%)	Decomposition enthalpy ^b
3-picoline	2:1	100	37.4	37.5	32.8
4-picoline	2:1	103	37.7	37.5	30.9
3,4-lutidine	2:1	148	40.5	40.8	36.9
3,5-lutidine	1:1	140	25.0	25.6	15.6
pyridine	1:1	112	20.5	20.3	14.7
piperidine	1:1	112	21.8	21.5	12.4
pyrazine	1:1	135	20.5	20.5	14.4
piperazine	2:1 ^c	ambient <i>in vacuo</i>	20.0	17.8	15.1
piperazine	1:1	155	23.0	21.7	16.3

^aAt end of mass loss. ^bKcal mol⁻¹. ^cData are for loss of 1 mol of ligand.

TABLE II. Infrared Band Assignments (cm⁻¹) for Ni(OS)₂ and its Heterocyclic Amine Adducts.

Compound ^a	$\nu(\text{NO})$	$\delta(\text{NO})$	$\nu(\text{CS})$	$\rho(\text{op})$	$\rho(\text{ip})$	$\nu(\text{NiO})$	$\nu(\text{NiN})$	$\nu(\text{NiS})$
Ni(OS) ₂	1191s	822m	692m	—	—	398m	—	270m,b
Ni(OS) ₂ ·Py	1199s	833s	708m	(641s) 618s	453s 439s	—	362s	268s
Ni(OS) ₂ ·2(3Pic)	1195s	835m	699w	620s	435s	393s	325s	248s
Ni(OS) ₂ ·2(4Pic)	1200s	831s	707s	619s	452s	—	343s	276m 258m
Ni(OS) ₂ ·(3,4Lut)	1209s	932s	709s	612m	430s	—	342s	266m
Ni(OS) ₂ ·(3,5Lut)	1205s	830s	705m	612m	469s	—	357s	250s,b
Ni(OS) ₂ ·(Pyraz)	1201s	830s	708m	620s	456m	—	349m	259s 250s
Ni(OS) ₂ ·(pip)	1209s	832s	709m	—	—	—	350m	268s
Ni(OS) ₂ ·(pipz)	1201s	828s	709m	—	—	387m	340m	235m

^aNi(OS)₂ = bis(2-thiopyridine N-oxide)nickel(II), py = pyridine, 3 Pic = 3-picoline, 4-Pic = 4-picoline, 3,4Lut = 3,4-lutidine, 3,5Lut = 3,5-lutidine, pyraz = pyrazine, pip = piperidine and pipz = piperazine.

were prepared. The adducts were either of 1:1 or 2:1 stoichiometry as evidenced by mass loss in thermogravimetric analysis. The compounds and their thermal data are shown in Table I. Although four of the amines were found to interact in a 2:1 mole ratio with the nickel(II) complex, only the bis(piperazine) adduct showed a discrete mass loss for each of the two ligand molecules. All other adducts gave a single mass loss that corresponded either to one or two amine ligands per Ni(OS)₂ molecule.

NMR investigation of the adducts showed broad unresolved absorptions characteristic of paramagnetic species as expected for 5- and 6-coordinate Ni(II) complexes. Infrared spectral data are shown in Table II. Consistent with the assignments for numerous other 2-substituted pyridine N-oxide complexes [11], we assign the band at 1191 cm⁻¹ to $\nu(\text{NO})$ in the 4-coordinate nickel(II) solid. The bands at 822, 398 and 270 cm⁻¹ are assigned to $\nu(\text{NO})$, $\nu(\text{NiO})$ and $\nu(\text{NiS})$, respectively. The assignment of $\nu(\text{NiO})$ is

within the range of 376–421 cm⁻¹ expected for coordinated pyridine N-oxides [12], and our assignment of $\nu(\text{NiS})$ is in agreement with the assignment in the complexes of imidazoline-2-thione [13]. In addition, the assignment of $\nu(\text{NiS})$ is reasonable when compared to the 300–320 cm⁻¹ range found for the series of trivalent lanthanide complexes of this ligand [4].

Upon formation of a 5- or 6-coordinate adduct, the bonding by the 2-thiopyridine N-oxide ligands would be expected to be weakened and a number of bands to be shifted. Specifically, $\nu(\text{NO})$, $\nu(\text{CS})$ and $\delta(\text{NO})$ should be shifted to higher energy and $\nu(\text{NiO})$ and $\nu(\text{NiS})$ to lower energy. All of the adducts have $\nu(\text{NO})$ shifted to higher energy by 4–18 cm⁻¹. Also both $\delta(\text{NO})$ and $\nu(\text{CS})$ are increased to a similar extent. In the case of the $\nu(\text{NiO})$ and $\nu(\text{NiS})$ bands, both are apparently shifted to lower energy although the shifts of $\nu(\text{NiS})$ are of lower magnitude and less regular than the intraligand bands considered above.

TABLE III. Electronic Spectral Bands (kK) for Ni(OS)₂ and its Heterocyclic Amine Adducts.

Compound	d-d transitions			Charge transfer	
				S → Ni	O → Ni
Ni(OS) ₂	7.87	13.76	18.45sh	21.88sh	25.00sh
Ni(OS) ₂ ·Py	5.10	10.87	15.02	21.83sh	25.38sh
Ni(OS) ₂ ·2(3Pic)		10.10	17.48	21.28sh	25.13sh
Ni(OS) ₂ ·2(4Pic)		10.31	17.73	22.22sh	25.25sh
Ni(OS) ₂ ·2(3,4Lut)		9.80	17.30	22.22sh	27.02sh
Ni(OS) ₂ ·(3,5Lut)	5.87sh	10.65	14.18	20.53sh	24.45sh
	4.51				
Ni(OS) ₂ ·(Pyrz)		9.43	16.50	21.65sh	26.32sh
Ni(OS) ₂ ·(pip)	5.21	10.64sh	14.51	21.65sh	25.64sh
Ni(OS) ₂ ·(pipz)		9.52	16.13	(22.47sh)	27.25sh
			14.77sh		

For $\nu(\text{NiO})$ we are able to assign bands in only two of the adducts' spectra and assume that this band is in combination with $\nu(\text{NiN})$ in the spectra of the majority of these solids. The assignment of $\nu(\text{NiN})$ to the bands found primarily in the 340–350 cm^{-1} range in the spectra of the adducts is consistent with the assignment of others [14]. There are no significant differences in the shifts of the intraligand bands or the metal–ligand bands when the spectra of the 5- and 6-coordinate adducts are compared.

Other bands which are often used to establish coordination of heterocyclic aromatic amines are the out-of-plane and in-plane ring deformations. The former is found at *ca.* 600 cm^{-1} and the latter at *ca.* 400 cm^{-1} in the free aromatic amines [15], and positive shifts of 20–30 cm^{-1} for each of these bands occur on coordination. For the piperidine adduct $\nu(\text{NH})$ occurs at 3268 cm^{-1} , which is within the range of 3285–3160 cm^{-1} suggested as typical for secondary amines [16]. In the spectrum of the 2:1 piperazine adduct a very broad band precludes assignment of $\nu(\text{NH})$ bands. This may be due to the presence of both coordinated and non-coordinated amine groups. The 1:1 adduct of piperazine, however, gave only a sharp $\nu(\text{NH})$ absorption at 3285 cm^{-1} , which is at the upper range of energies for coordinated secondary amines [16] and is indicative of rather weak coordination of the amine. This suggests octahedrally coordinated nickel, with the piperazine molecule bridging nickel centers to give a polymeric product.

The band energies (Table III) for the solid state electronic spectrum of Ni(OS)₂ are in reasonable agreement with those of the DMF solution spectrum reported earlier [4]. The lower energy band (*i.e.*, 7.87 kK) in the DMF spectrum was split and shifted to higher energy, and was assigned to a singlet–triplet transition because of its weakness. Lever [17] indicates that spectra of square planar Ni(II) complexes are not well understood and definite assignment

of the bands is to be avoided. However, a band between 15.0 and 25.0 kK is often assigned as ν_2 (18.45 kK) and in the case of ligands with sulfur donor atoms a ν_1 (13.76 kK) is often observed. The corresponding bands in DMF solution were found at 19.61 and 13.93 kK, respectively. A third band (ν_3), which may be found between 23.0 and 30.0 kK for some square planar complexes, would be expected to be obscured by charge transfer bands in the spectrum of Ni(OS)₂. For example, 2-substituted pyridine N-oxide complexes of divalent metal ions have a L(O) → M charge transfer band at 25.0–27.0 kK [18]. Therefore, the shoulder at 25.0 kK can be assigned to O → Ni(II) and the shoulder at 21.88 kK to S → Ni(II) transfer band in the spectrum of Ni(OS)₂.

While the infrared spectra did not show significant differences between the 1:1 and 2:1 adducts of this study, the electronic spectra show an important difference. The spectra of the adducts formed with Py, 3,5-lut and pip all have a strong, very broad band located at about 5 kK in the NIR portion of the spectrum, which is absent in the spectra of the remainder of the adducts. As is shown in Table IV this band is assignable to ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$ of a Ni(II) square pyramidal complex [19]. Other assignments are the band at approximately 10.70 kK which is a combination of ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{A}_2(\text{F})$ and ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{B}_2(\text{F})$ and the band at 14.2–15.0 as ${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$. The remaining two bands for a square pyramidal complex which would be found at higher energy are evidently obscured by the S → Ni(II) and O → Ni(II) charge transfer bands.

All of the remaining adducts have electronic spectra consistent with six coordinate, tetragonally distorted octahedral Ni(II). The bifunctional amines pyrazine and piperazine must therefore be bridging nickel centers in their 1:1 adducts, as suggested by the infrared data for the piperazine complex. Distortion from octahedral symmetry is significant since

TABLE IV. Spectral Assignments for the Amine Adducts of Ni(OS)₂.

Compound	ν_1	ν_2	ν_2/ν_1	Dq(approx)
Tetragonally Elongated Octahedral Ni(II) Adducts.				
[Ni(OS) ₂]·2(3Pic)	10100	17480	1.73	1010
[Ni(OS) ₂]·2(4Pic)	10310	17730	1.72	1031
[Ni(OS) ₂]·2(3,4Lut)	9800	17300	1.77	980
[Ni(OS) ₂]·(pyraz)	9430	16500	1.75	943
[Ni(OS) ₂]·(pipz)	9520	16130	1.69	952
Square Pyramidal Ni(II) Adducts				
	${}^3B_1 \rightarrow {}^3E$	${}^3B_1 \rightarrow {}^3A_2$ ${}^3B_1 \rightarrow {}^3B_2$		${}^3B_1 \rightarrow {}^3E$
[Ni(OS) ₂]·py	5100	10870		15020
[Ni(OS) ₂]·3,5lut	4510	10650		14180
	5870sh			
[Ni(OS) ₂]·pip	5210	10640sh		14510

the ν_2/ν_1 ratios range from 1.69 to 1.77. In addition, attempts to calculate ν_3 in idealized O_h symmetry give unlikely values. However, the tetragonal distortion unfortunately is not sufficient to cause a splitting of the very broad ν_1 band, although there is certainly an asymmetric appearance to each of the ν_1 bands suggesting a low energy shoulder. The shape of the peak in this energy range is different from that of the five coordinate species of this study. The latter have a very symmetrical band in this region. Because of the lack of splitting of the ν_1 band, the in-plane and out-of-plane field strengths could not be calculated.

While formation of adducts of 2-substituted ring systems did not occur presumably due to steric factors, there is evidence in this study that other factors affect the nature of the adducts that are formed. The formation of a 1:1 adduct with pyridine but 2:1 adducts with the two picolines and one of the lutidines requires some comment. A possible explanation for this occurrence is that the lattice energy of the five coordinate species with pyridine may be considerably more favorable than the lattice energy of the 1:2 adduct, and the stability gained by adding a second pyridine does not compensate this difference. Because of the methyl substituents on the picolines the favorable lattice energy evidently does not dominate in their case nor that of 3,4-lutidine. For 3,5-lutidine the crowding around the individual Ni(II) centers is presumably the factor which prevents 2:1 adduct formation. The formation of adducts involving bridging ligands with the di-nitrogen rings is as expected. The taking up of

a second molecule of piperazine appears to represent addition of a solvate molecule rather than a 2:1 adduct, based on its low dissociation temperature.

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