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Reactions of Nickel Chelates Derived from 2-Aminobenzenethiol

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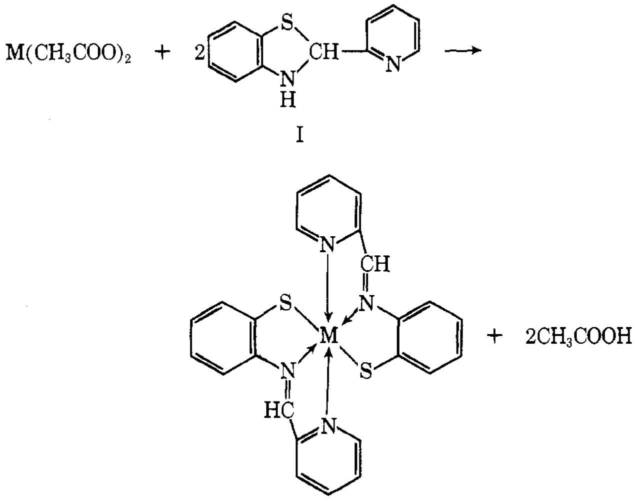
The reactions of bis(2-aminobenzenethiolo)nickel(II) and its derivatives have been investigated and many interconversions have been effected. The resulting system of reactions and interconversions provides a novel method of studying the coordination chemistry of a range of related nickel chelates which, in all cases, were isolated and characterized by elemental analyses and various physical measurements. Nickel chelates of 2-methylthioaniline, 2,2′-pyridylmethylthioaniline, N-2-mercaptophenyl-2′-pyridylmethylenimine, and N-2-methylthiophenyl-2′-pyridylmethylenimine are reported.

Introduction

As part of a general study of the reactions of metal chelates of sulfur-containing ligands, we have previously described the S dealkylation of coordinated thioethers and the S alkylation of coordinated thiolo ligands.[1–5] In addition we have investigated the metal ion induced rearrangement of 2-(2-pyridyl)-benzothiazoline (I) to yield metal complexes of the corresponding Schiff base, N-2-mercaptophenyl-2′-pyridylmethylenimine.[6] A typical reaction of the latter type is shown in Scheme I (M = Zn, Cd).

SCHEME I



I

II

We now report that the reactions of the nickel chelates of 2-aminobenzenethiol (N–SH) and its derivatives can be used to produce a number of new chelates. In this manner it has been possible to prepare and study the nickel chelates of a range of closely related ligands.

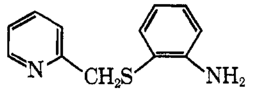
Results and Discussion

The various reactions and interconversions discussed in this paper are summarized in Scheme II. Reaction of methyl iodide with a suspension of bis(2-aminobenzenethiolo)nickel(II) (III; Scheme II) yields the paramagnetic six-coordinate diiodobis(2-methylthioaniline)nickel(II) (IV). We have previously reported the preparation of this compound directly from 2-methylthioaniline (N–SCH_3) and nickel iodide.[3]

Busch, *et al.*,[7,8] have reported the analogous reaction of bis(2-aminoethanethiolo)nickel(II) with methyl iodide and more recently[9] with chloroacetic acid, to yield the pseudo-octahedral neutral complex bis(5-amino-3-thiapentaneato)nickel(II).

Bis(2-aminobenzenethiolo)nickel(II) (III) was first reported by Hieber and Brück,[10,11] who suggested that its insolubility was due to a polymeric structure involving sulfur bridges. Subsequently Livingstone[12] showed that this compound is diamagnetic and assigned to it a square-planar monomeric structure. The present investigation indicates that no sulfur bridges are present in this compound since S alkylation under normal circumstances is known to occur only at sulfur atoms which are terminal and not bridging.[7] This example illustrates the manner in which the reactions of a metal chelate can sometimes be used as an aid to its characterization.

In previous investigations,[5,7,8,13] S alkylation has been effected with a range of alkyl halides, and, in view of this, we have attempted to prepare a complex of 2-(2-pyridylmethylthio)aniline (V; N–S–N) directly from bis(2-aminobenzenethiolo)nickel(II) (III) by alkylation with 2-chloromethylpyridine; however, attempts to



V

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[1] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Australian J. Chem.*, **19**, 1391 (1966).

[2] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature*, **211**, 519 (1966).

[3] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Australian J. Chem.*, **20**, 471 (1967).

[4] S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Chem. Letters*, **3**, 35 (1967).

[5] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).

[6] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, **1**, 365 (1967).

[7] D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 125.

[8] D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

[9] N. J. Rose, C. A. Root, and D. H. Busch, *Inorg. Chem.*, **6**, 1431 (1967).

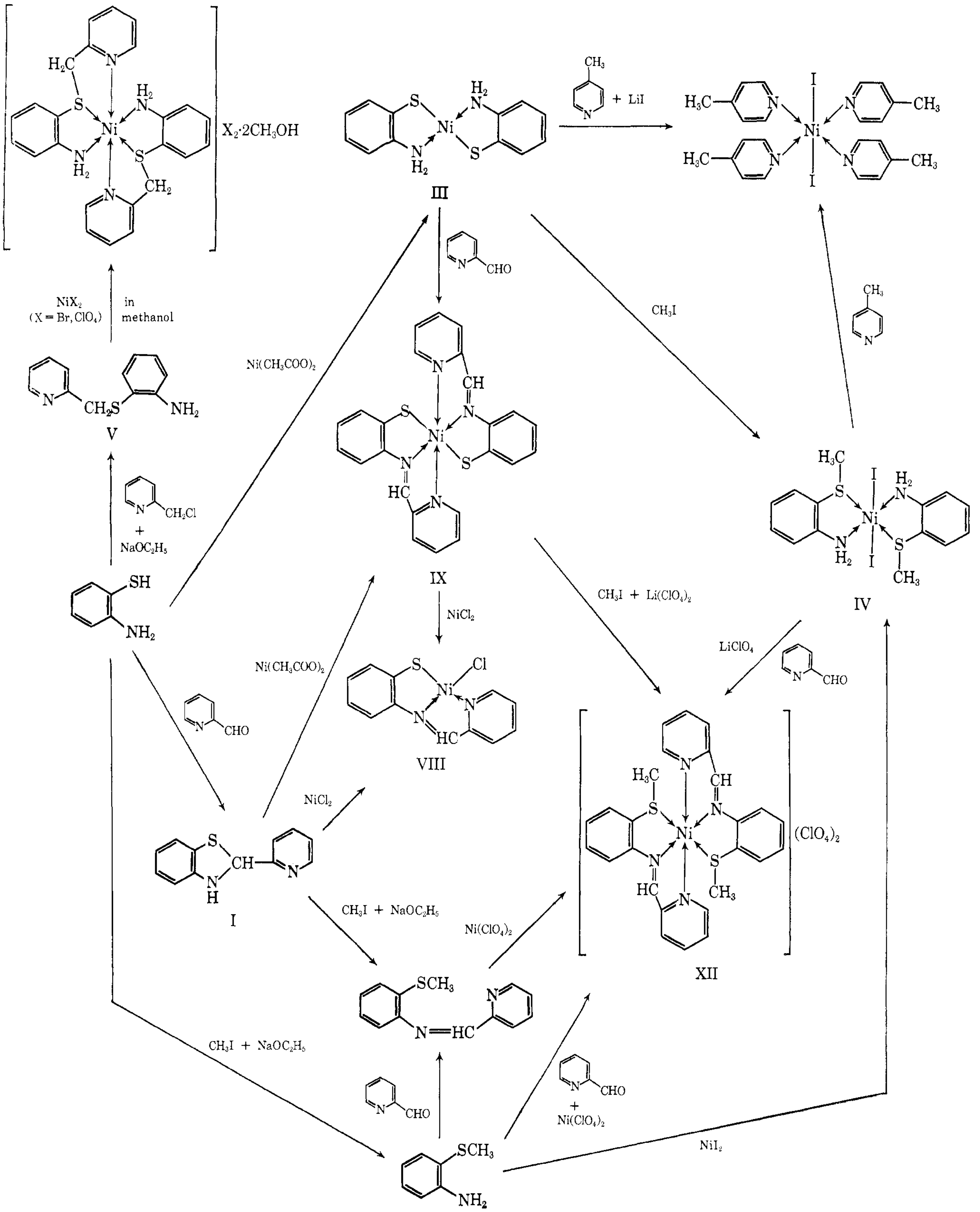
[10] W. Hieber and R. Brück, *Naturwissenschaften*, **36**, 312 (1949).

[11] W. Hieber and R. Brück, *Z. Anorg. Allgem. Chem.*, **269**, 13 (1952).

[12] S. E. Livingstone, *J. Chem. Soc.*, 1042 (1956).

[13] M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

Scheme II



carry out this reaction, under a variety of conditions, were unsuccessful. It is significant that reaction of benzyl chloride with III also failed to result in S alkylation, and it seems likely that the failure of both this reagent and also 2-chloromethylpyridine to effect S alkylation is largely due to their lower reactivity compared with methyl iodide. It is possible, however, to synthesize ligand V directly by allowing 2-chloromethylpyridine to react with 2-aminobenzenethiol (N–SH) in sodium ethoxide. Reaction of V with nickel bromide or perchlorate in methanol yields the high-spin six-coordinate complexes $[Ni(N\text{–}S\text{–}N)_2]X_2 \cdot 2CH_3OH$

($X = Br, ClO_4$); see Table I. Although the bromide complex is insoluble in nitromethane, the conductivity of the perchlorate compound in this solvent (Λ_{5000} = 167 ohm^{-1} cm^2 mol^{-1} at 25°) confirms that it is a bi-univalent electrolyte.

TABLE I

MAGNETIC DATA FOR NICKEL COMPLEXES

Complex	Color	$\chi_M'^a$	μ, BM	Temp, °K
Ni(N–S)$_2$^{b}	Buff	200	Diam	292
Ni(N–SCH$_3$)$_2$I$_2$^{c}	Olive green	4250	3.20	299
[Ni(N–S–N)$_2$]Br$_2$·2CH$_3$OH	Lilac	4650	3.30	292
[Ni(N–S–N)$_2$](ClO$_4$)$_2$· 2CH$_3$OH	Lilac	4320	3.20	292
NiCl(N–N–S)	Deep red	160	Diam	293
Ni(N–N–S)$_2$	Bluish black	5000	3.42	290
[Ni(N–N–SCH$_3$)$_2$](ClO$_4$)$_2$^{d}	Brown	3990	3.09	299

[a] Molar susceptibility corrected for diamagnetism. [b] See ref 12. [c] See ref 3. [d] See ref 15.

The visible reflectance spectra of these two compounds are virtually identical and display maxima at 510, 620, and 850 mμ and a broad shoulder at *ca.* 950 mμ and thus are similar to the reflectance spectrum of the six-coordinated complex [Ni(H$_2$NCH$_2$CH$_2$SCH$_2$CH$_2$NH$_2$)$_2$](ClO$_4$)$_2$ which exhibits bands at 560, 665 sh, 860, and 950 mμ.[14]

The infrared spectra of these compounds (Table II) are consistent with the presence of methanol and the position of ν(N–H) in each spectrum is typical of that reported for coordinated amine groups.[3] A thermogravimetric study of the bromide complex showed that the methanol is not lost before decomposition of the complex begins at *ca.* 190°. A molecular model of ligand V indicates that it can readily act as a tridentate, and it would seem most likely that the methanol molecules are not coordinated but instead are strongly held in the crystal lattice in a similar manner to the solvent molecules in other clathrate complexes previously described.[15]

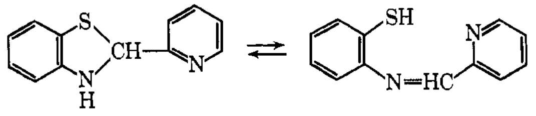
TABLE II

INFRARED ASSIGNMENTS OF AMINE COMPLEXES (CM^{-1})

	ν(O–H)	ν(N–H)	δ(N–H)
[Ni(N–S–N)$_2$]Br$_2$·2CH$_3$OH	3360 br	3045 br 3010 br	1555
[Ni(N–S–N)$_2$](ClO$_4$)$_2$·2CH$_3$OH	3450 br	3200 br 3140 br	1560
Ni(N–S)$_2$		3135	1540
		3110 sh	1526
		3075	
Ni(N–SCH$_3$)$_2$I$_2$		3175	1540
		3145	
		3110	
		3075	

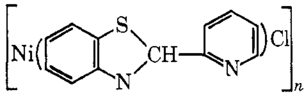
The isolation of these nickel complexes directly from V is in keeping with our contention that the failure to synthesize similar compounds by the S alkylation reaction is largely due to the lower reactivity of 2-chloromethylpyridine as an alkylating agent.

Previously[6] we have shown that condensation of 2-pyridinecarboxaldehyde and 2-aminobenzenethiol in alcohol leads to isolation of 2-(2-pyridyl)benzothiazoline (I). In solution this compound almost certainly exists in equilibrium with small amounts of the tautomeric Schiff base, N-2-mercaptophenyl-2′-pyridylmethylenimine (VI; N–N–SH) and it has been shown that conversion to the Schiff base is favored by alkaline conditions and also by the presence of certain metal ions. Other similar metal ion induced rearrangements have been reported by several investigators.[16–20]



I VI

In the present investigation we have treated a solution of 2-(2-pyridyl)benzothiazoline (I) with nickel chloride in equimolar proportions and have obtained a diamagnetic complex which has only a small conductivity in nitromethane (Λ_{1500} = 10.0 ohm^{-1} cm^2 mol^{-1} at 25°). This compound is not sufficiently soluble in organic solvents for a molecular weight determination. Although it is possible that this compound has the polymeric structure VII, its diamagnetism and deep brownish red color suggest that the metal ion induced rearrangement illustrated in Scheme II has occurred to produce a compound with structure VIII (Ni(N–N–S)-Cl). The mass spectrum of this compound displays no peaks above the band of isotopic peaks centered around the principal peaks at *m/e* 306 and 308. These peaks correspond to the monomeric molecular ion. The visible reflectance spectrum of this compound has intense absorptions in the region 400–600 mμ. These broad bands are very similar to those occurring in the spectra of the Schiff base–zinc and –cadmium complexes [II; Scheme I (M = Zn, Cd)]. We have previously ascribed these bands to absorption by the coordinated Schiff base VI.[6]



VII

The reaction of an excess of an alcohol solution of I with nickel acetate also induces the rearrangement of I to yield the crystalline bluish black paramagnetic complex IX (Ni(N–N–S)$_2$) which is virtually a nonelectrolyte in nitrobenzene (Λ_{2000} = 1.8 ohm^{-1} cm^2 mol^{-1} at 25°). This reaction is analogous to that used for the preparation of the corresponding reddish black zinc and cadmium complexes (Scheme I).

The strong ligand field of thiolo ligands normally

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(14) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

(15) L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, and N. C. Stephenson, *Australian J. Chem.*, **19**, 1165 (1966).

(16) H. Jadamus, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **3**, 928 (1964).

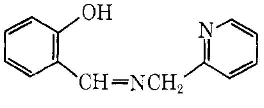
(17) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964); E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, **87**, 3016 (1965).

(18) E. Bayer, *Angew. Chem.*, **73**, 659 (1961).

(19) E. Bayer, *Angew. Chem., Intern. Ed. Engl.*, **3**, 325 (1964).

(20) E. Bayer and G. Schenk, *Ber.*, **93**, 1184 (1960).

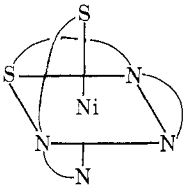
results in the formation of square-planar diamagnetic complexes with nickel; nevertheless, we assign an octahedral stereochemistry to the complex Ni(N–N–S)$_2$ and believe this to be the first reported example of a thiolo tridentate ligand yielding a high-spin, bis-ligand nickel complex. The moment of Ni(N–N–S)$_2$ (3.42 BM) is above the range 2.9–3.3 BM generally accepted as typical of octahedral nickel(II); however, it is within the range (3.3–3.5 BM) found for many tetragonal nickel(II) complexes.[21] The moment of the reddish brown bis-ligand nickel complex of X has been reported to be 3.41 BM.[22]



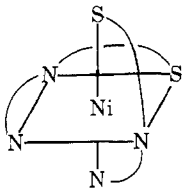
X

Compound IX (Ni(N–N–S)$_2$) was also prepared by reaction of an excess of 2-pyridinecarboxaldehyde with a suspension of bis(2-aminobenzethiolo)nickel(II) (III) in alcohol (Scheme II). The infrared spectrum of this product is identical with that obtained from the previous preparation and confirms that the Schiff base condensation has occurred, since the spectrum contains no bands in the region 3075–3135 cm^{-1}. The spectrum of Ni(N–S)$_2$ (III) displays bands in this region (Table II); these have been assigned to ν(N–H) of the coordinated amine.

In the Schiff base VI (N–N–SH) all of the atoms are in conjugation, and hence this ligand is planar. As a consequence of this planarity, the only two possible arrangements of the donor atoms in IX (Ni(N–N–S)$_2$) are represented by the enantiomorphic configurations XIa and XIb.[23] In both XIa and XIb the benzene rings in each pair of ligands are not coplanar as they are in their precursor III (Ni(N–S)$_2$), and this implies that at least partial ligand displacement must occur when III reacts with 2-pyridinecarboxaldehyde. Although we have arbitrarily assigned *trans*-planar structure III for bis(2-aminobenzenethiolo)nickel(II), it may have a *cis* configuration, since bis(2-aminoethanethiolo)nickel(II) has been assigned a *cis* configuration on the basis of chemical and spectral studies.[13,24]



XIa

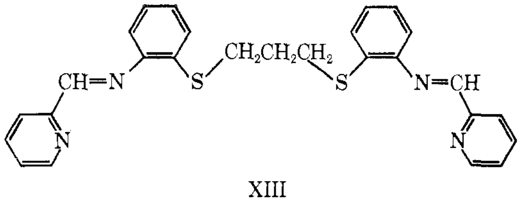


XIb

The behavior of the heterocyclic base γ-picoline (γ-pic) with the nickel complex III has been investigated. A suspension of the nickel complex in refluxing alcohol containing lithium iodide undergoes ligand exchange to yield the complex Ni(γ-pic)$_4$I$_2$. As an aid to its characterization, it was found that pyrolysis of this compound results in the loss of two γ-picoline molecules to yield Ni(γ-pic)$_2$I$_2$. The compounds Ni(γ-pic)$_4$X$_2$ (X = Cl, Br, I) have been reported to yield Ni(γ-pic)$_2$X$_2$ on being heated.[25] The occurrence of ligand displacement when γ-picoline reacts with III suggests that, during the Schiff base formation just discussed, the 2-pyridinecarboxaldehyde may effect the prior displacement of the ligand (or amine group) before condensation occurs.

Reaction of equimolar proportions of IX (Ni(N–N–S)$_2$) and nickel chloride in alcohol (Scheme II) yields the monoligand complex VIII (Ni(N–N–S)Cl) which was also obtained directly from the reaction of an alcohol solution of 2-(2-pyridyl)benzothiazoline (I) with nickel chloride in equimolar proportions. The ease of this reaction may reflect the tendency of the thiol VI (N–N–SH) to form low-spin, square-planar nickel complexes. The treatment of the low-spin mono complex VIII (Ni(N–N–S)Cl) with excess ligand in alcohol did not lead to the isolation of the bis-ligand complex IX (Ni(N–N–S)$_2$).

The presence of nonbridging thiolo groups in IX was confirmed by its behavior with methyl iodide (Scheme II). Reaction of a suspension of IX with methyl iodide in the presence of perchlorate ion led to S methylation, and the brown, high-spin complex [Ni(N–N–SCH$_3$)$_2$](ClO$_4$)$_2$ (XII) was isolated from the reaction mixture. We have described previously the preparation of N-2-methylthiophenyl-2′-pyridylmethylenimine (N–N–SCH$_3$) by the reaction of 2-(2-pyridyl)-benzothiazoline (I) with sodium ethoxide and methyl iodide and have found that the crude product, which was obtained as a brown oil, reacted with nickel perchlorate to yield XII.[15] This compound was originally prepared for comparison with the analogous high-spin nickel complex of the sexadentate ligand XIII.



XIII

The ligand N–N–SCH$_3$ has now been prepared by the alternative method of a Schiff base condensation between 2-methylthioaniline and 2-pyridinecarboxaldehyde and the product was obtained as yellow crystals. Reaction of the product from this preparation with nickel perchlorate also yielded the brown complex XII.

It is noteworthy that this compound (XII) is very resistant to hydrolysis and can be recrystallized from hot water without decomposition. Other examples of the stabilization, on coordination, of Schiff bases containing the α-diimine linkage –N=CC=N– have been

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(21) A. B. P. Lever, *Inorg. Chem.*, **4**, 763 (1965).

(22) R. W. Oehmke and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **27**, 2209 (1965).

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reported.[26] Compound XII is also obtained when 2-methylthioaniline and 2-pyridinecarboxaldehyde are allowed to condense *in situ* in the presence of nickel perchlorate. An identical product can also be obtained by reaction of 2-pyridinecarboxaldehyde with a suspension of diiodobis(2-methylthioaniline)-nickel(II) (IV) in acetone containing lithium perchlorate (Scheme II); the reaction proceeds smoothly at room temperature. The infrared spectrum of this product, which was identical with the spectra of the products from the other preparations, showed the absence of the strong bands at *ca.* 3130 and 1540 cm^{-1} which were found in the spectrum of IV and which we have previously assigned as ν(N–H) and δ(N–H) of the coordinated amine group. Stereochemical considerations again dictate that at least partial ligand displacement must occur during this reaction. It is significant that this reaction occurs much more readily than the related reaction between bis(2-aminobenzenethiolo)-nickel(II) (III) and 2-pyridinecarboxaldehyde, and this undoubtedly reflects the greater lability of the thioether ligand in IV compared to its thiolo counterpart in III. It is well known that thioethers normally form weaker bonds to nickel than do thiolo groups.[27] As might be expected, reaction of γ-picoline with IV readily results in ligand displacement to yield Ni(γ-pic)$_4$I$_2$.

We have recently observed many similar reactions with related copper(II) complexes. These will be reported in due course.

Experimental Section

Microanalyses for carbon, hydrogen, and nitrogen were determined by Dr. E. Challen of the Microanalytical Laboratory of the University of New South Wales. Sulfur was determined by the Australian Microanalytical Service, Melbourne. Nickel was determined gravimetrically as its dimethylglyoximate.

Molar Conductivities.—These were measured on a Philips Philoscope in conjunction with a Philips immersion cell with platinized electrodes.

Magnetic Moments.—The magnetic moments were determined by the Gouy method. Diamagnetic corrections were calculated from Pascal's constants.

Thermogravimetric Measurements.—The thermogravimetric measurements were made on a Stanton thermobalance, Model TR-01.

Infrared Spectra.—These were obtained on Halocarbon mulls of the samples using a Perkin-Elmer 337 spectrometer.

Visible Reflectance Spectra.—These were obtained on a Zeiss PMQII spectrophotometer.

Mass Spectrum.—The mass spectrum was recorded on an MS9 mass spectrometer.

After isolation, all compounds were washed with alcohol and dried *in vacuo* over P$_4$O$_{10}$.

Bis(2-aminobenzenethiolo)nickel)(II).—This compound was prepared as previously described.[28] *Anal.* Calcd for Ni(C$_6$H$_6$NS)$_2$: Ni, 19.1. Found: Ni, 18.9.

Diiodobis(2-methylthioaniline)nickel(II).—Finely ground bis(2-aminobenzenethiolo)nickel(II) (0.2 g) was suspended in a mixture of acetone (20 ml) and methyl iodide (6 ml), and this suspension was shaken for 4 days in a sealed flask. After this time the original compound had been converted to the sparingly soluble olive green iodo complex; yield 0.16 g. *Anal.* Calcd for Ni(C$_7$H$_9$NS)$_2$I$_2$: Ni, 9.9; C, 28.45; H, 3.1; N, 4.7. Found: Ni, 10.0; C, 28.1; H, 3.1; N, 5.1.

2-(2-Pyridylmethylthio)aniline.—2-Chloromethylpyridine (3.4 g) in alcohol (10 ml) was added to a solution of sodium (0.62 g) and 2-aminobenzenethiol (3.4 g) in alcohol (25 ml). The solution was warmed at 60° for 8 hr, and during this time sodium chloride was deposited. After concentration of the solution to 15 ml, water (250 ml) was added. The brown oil that separated was extracted with ether and the ethereal extract was dried over anhydrous sodium sulfate, treated with charcoal, and evaporated to yield the crude product as a yellow oil which was purified by vacuum distillation; yield 3 g. *Anal.* Calcd for C$_{12}$H$_{12}$N$_2$S: C, 66.6; H, 5.6; N, 12.95. Found: C, 66.2; H, 5.7; N, 12.4.

Bis[2-(2-pyridylmethylthio)aniline]nickel(II) Bromide.—Nickel bromide trihydrate (0.2 g) in hot methanol (20 ml) was treated with 2-(2-pyridylmethylthio)aniline (0.3 g) in methanol (10 ml). The complex, which contained two molecules of methanol, was deposited as mauve crystals; yield 0.4 g. *Anal.* Calcd for Ni(C$_{12}$H$_{12}$N$_2$S)$_2$Br$_2\cdot$2CH$_3$OH: Ni, 8.2; C, 43.7; H, 4.5; N, 7.8; S, 9.0. Found: Ni, 7.8; C, 43.8; H, 4.3; N, 7.9; S, 9.1.

Bis[2-(2-pyridylmethylthio)aniline]nickel[II] Perchlorate.—By a similar procedure nickel perchlorate hexahydrate (0.2 g) gave mauve crystals of the complex, which also contained two molecules of methanol; yield 0.4 g. *Anal.* Calcd for Ni(C$_{12}$H$_{12}$N$_2$S)$_2$(ClO$_4$)$_2\cdot$2CH$_3$OH: Ni, 7.8; C, 41.4; H, 4.3; N, 7.4; S, 8.5. Found: Ni, 7.5; C, 41.6; H, 4.4; N, 7.6; S, 8.6.

Bis(N-2-thiolophenyl-2′-pyridylmethylenimine)nickel(II).—Nickel acetate (1 g) in alcohol (120 ml) was added over 45 min to a refluxing solution of 2-(2-pyridyl)benzothiazoline (1.8 g) in alcohol (120 ml) under nitrogen. A bluish black crystalline product was deposited; yield 1.7 g. *Anal.* Calcd for Ni(C$_{12}$H$_9$N$_2$S)$_2$: Ni, 12.1; C, 59.4; H, 3.7; N, 11.55; S, 13.2. Found: C, 59.2; H, 4.4; N, 11.0.

This compound was also prepared by heating at the reflux a suspension of finely ground bis(2-aminobenzenethiolo)nickel(II) in alcohol (100 ml) containing 2-pyridinecarboxaldehyde (3 ml). After 3 hr the bluish black product was isolated, finely ground, and again suspended in alcohol (100 ml) containing 2-pyridinecarboxaldehyde (3 ml). This suspension was heated at the reflux for a further 3 hr to yield the complex as bluish black crystals; yield 0.4 g. *Anal.* Found: Ni, 12.0; C, 58.9; H, 3.6; N, 11.2; S, 12.8.

Chloro-(N-2-thiolophenyl-2′-pyridylmethylenimine)nickel(II).—Nickel chloride hexahydrate (0.48 g) in alcohol (100 ml) was added over 30 min to a refluxing solution of 2-(2-pyridyl)benzothiazoline (0.43 g) in alcohol (100 ml.) under nitrogen. The solution was allowed to cool and the reddish brown product deposited; yield 0.5 g. *Anal.* Calcd for Ni(C$_{12}$H$_9$N$_2$S)Cl: Ni, 19.1; C, 46.9; H, 2.95; N, 9.1; S, 10.4; Cl, 11.5. Found: Ni, 19.0; C, 47.3; H, 3.0; N, 8.9; S, 10.2; Cl, 11.3.

This compound was also prepared by treating bis(N-2-thiolophenyl-2′-pyridylmethylenimine)nickel(II) (0.9 g) with nickel chloride hexahydrate in alcohol (150 ml). The resulting suspension was refluxed under nitrogen for 2 hr to give a deposit of the deep reddish brown crystalline product; yield 1.0 g. *Anal.* Found: Ni, 18.7; C, 46.8; H, 2.9; N, 9.1; S, 9.8.

N-2-Methylthiophenyl-2′-pyridylmethylenimine.—2-Pyridinecarboxaldehyde (3.2 g) and 2-methylthioaniline (4.2 g) were mixed. The solution became hot and, on standing, solidified. This crude product was recrystallized from hot alcohol containing charcoal to give yellow crystals of the pure compound; yield 3 g; mp 85°. *Anal.* Calcd for C$_{13}$H$_{12}$N$_2$S: C, 68.4; H, 5.3; N, 12.3. Found: C, 68.3; H, 5.4; N, 11.9.

Bis(N-2-methylthiophenyl-2′-pyridylmethylenimine)nickel(II) Perchlorate. Preparation 1.—Diiodobis(2-methylthioaniline)-nickel(II) (0.5 g) was suspended in acetone (100 ml) containing 2-pyridinecarboxaldehyde (0.2 g) and lithium perchlorate trihydrate (1 g). The mixture was stirred at room temperature until all of the nickel complex had dissolved. The brown solution was allowed to evaporate and the brown product which de-

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posited was recrystallized from hot water; yield 0.3 g. *Anal.* Calcd for $Ni(C_{13}H_{12}N_2S)_2(ClO_4)_2$: Ni, 8.2; C, 43.7; H, 3.4; N, 7.8; S, 9.0. Found: Ni, 8.0; C, 43.1; H, 3.4; N, 7.6; S, 8.8.

Preparation 2.—Bis(N-2-thiolophenyl-2′-pyridylmethylenimine)nickel(II) (0.5 g) was suspended in hot alcohol (45 ml) containing lithium perchlorate trihydrate (1 g). Methyl iodide (5 ml) was added to the hot solution which was then shaken in a sealed flask. The crude brown product (0.6 g) was recrystallized from water and then from an acetone–water mixture; yield 0.2 g. *Anal.* Found: Ni, 8.0; C, 44.1; H, 3.6; N, 7.9.

Preparation 3.—N-2-Methylthiophenyl-2′-pyridylmethylenimine (0.15 g) in alcohol (10 ml) was added to nickel perchlorate hexahydrate (0.1 g) in alcohol (10 ml). The solution was let stand and brown crystals of the product deposited; yield 0.1 g. *Anal.* Found: C, 43.55; H, 3.5; N, 7.65.

Preparation 4.—Preparation 3 was repeated except that the formation of the ligand (0.15 g) from 2-pyridinecarboxaldehyde and 2-aminobenzenethiol was carried out in the presence of the nickel perchlorate hexahydrate (0.1 g) in hot alcohol; yield 0.1 g. *Anal.* Found: Ni, 8.2; C, 42.9; H, 3.6.

Reaction of γ-Picoline with Diiodobis(2-methylthioaniline)nickel(II).—Diiodobis(2-methylthioaniline)nickel(II) (0.4 g) was dissolved in hot acetone (400 ml) containing γ-picoline (5 ml). On cooling, the solution deposited bright green crystals of diiodotetrakis(γ-picoline)nickel(II); yield 0.2 g. *Anal.* Calcd for $Ni(C_6H_7N)_4I_2$: Ni, 8.6; C, 42.1; H, 4.1; N, 8.2. Found: Ni, 8.7; C, 42.1; H, 4.1; N, 8.1. Loss on heating to 140°: 27.2%. Calcd loss of two γ-picoline molecules: 27.0%.

Reaction of γ-Picoline with Bis(2-aminobenzenethiolo)nickel(II).—Finely ground bis(2-aminobenzenethiolo)nickel(II) (0.4 g) was suspended in alcohol (100 ml) containing γ-picoline (6 ml) and lithium iodide (1 g). This suspension was refluxed for 5 hr and then filtered. The green residue (0.3 g) was discarded and the filtrate was concentrated, treated with charcoal, and let stand. Bright green crystals of diiodotetrakis(γ-picoline)nickel(II), identical with those obtained in the previous preparation, deposited. *Anal.* Found: Ni, 9.0; C, 43.3; H, 4.3; N, 8.1.

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The Spectra of Bis(tertiary arsine) Complexes

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The visible and near-infrared spectra of several complexes of Cr(III), Co(III), and Fe(II) with the ligand *o*-phenylenebis(dimethylarsine) have been obtained both in solution and in the solid state. The electronic transitions which were observed were found to be d–d transitions and were assigned on the basis of a ligand field model. An evaluation of the ligand field parameters, *Dq*, *B*, and *C*, for these compounds indicates that there is a considerable amount of σ bonding between the metal ions and *o*-phenylenebis(dimethylarsine) but that there is no evidence for $d\pi$–$d\pi$ bonding between the metal and the ligand in these complexes.

Introduction

The ligand *o*-phenylenebis(dimethylarsine) (das) is one of the most versatile complexing agents known. After the initial investigations of Chatt and Mann,[2] Nyholm and his coworkers[3] have succeeded in preparing compounds of *o*-phenylenebis(dimethylarsine) with almost every transition metal (excluding the lanthanides and actinides). These compounds include complexes in which the coordination number of the metal is 4, 5, 6, 7, and 8 and in which the oxidation number of the metal ranges from 0 in $Ni(das)_2$ to 5 in $ReX_4(das)_2^+$. However, the factors which are responsible for the extraordinary coordinating power of this ligand and the stability of these complexes remain obscure. The present research was initiated in an attempt to elucidate some of these factors.

Although transition metal complexes of *o*-phenylenebis(dimethylarsine) have been known for over 25 years, there have been only three papers which have dealt with their spectroscopic properties in any detail.[4–6] It is well known that *o*-phenylenebis(dimethylarsine) is a "strong-field" ligand, since most of its complexes are spin paired. The spectrum and magnetism of the complex $Ni(das)_3^{2+}$ have been interpreted on the basis of a molecular orbital model with a trigonal electric field.[5] The spectra of the cobalt(III) compounds $CoX_2(das)_2^+$ have been shown to be consistent with a ligand field model with tetragonal symmetry,[4] but only one d–d transition was observed. The reflectance and solution spectra of the *o*-phenylenebis(dimethylarsine) complexes of Co(III), Fe(II), and Cr(III) are reported and discussed below.

Experimental Section

Materials and Analyses.—The ligand *o*-phenylenebis(dimethylarsine) and its complexes were prepared according to the methods described in the literature.[7–11] In several instances, the compounds were reported to exist, but neither elemental analyses nor details for their preparation were reported. The

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