Contribution of the Chemistry Department
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Coordination Compounds of Hydrazine Derivatives with Transition Metals. V.* Square Planar Nickel(II) Complexes with Hydrazine-S-methyl Dithiocarboxylate Schiff Bases

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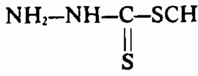
Schiff bases derived from the condensation of hydrazine-S-methyl dithiocarboxylate with substituted benzaldehyde and heterocyclic aldehydes were prepared. Their reactions with Ni^{II} chloride and acetate were investigated. Magnetic and spectral data have shown that square planar Ni^{II} complexes resulted from all the Schiff bases. Bis neutral complexes were obtained with the Schiff bases acting as monobasic bidentate ligands. In addition, 1:1 complexes were isolated with salicylaldehyde and pyridine-2-carbaldehyde derivatives where the Schiff bases functioned as dibasic tridentate and monobasic tridentate ligands respectively. The interaction of the square planar Ni^{II} complexes with pyridine was also investigated.

Introduction

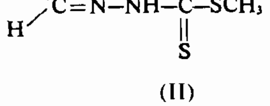
In a previous work (part IV) hydrazine-S-methyl dithiocarboxylate(I) functioned as a neutral bidentate ligand toward nickel(II) chloride with the formation of bis and tris cationic complexes. With nickel(II) acetate the ester was shown to act as a monobasic bidentate molecule, forming a bis neutral complex, through the deprotonation of the α-hydrogen of the hydrazine residue. On the other hand, the isopropylidene derivative of hydrazine-S-methyl dithiocarboxylate gave only the bis neutral complex with both nickel(II) chloride and acetate.



$NH_2{-}NH{-}\underset{\underset{S}{\|}}{C}{-}SCH_3$

(I)

This work has now been extended to investigate the chelating properties of the Schiff bases (II) derived from the condensation of hydrazine-S-methyl dithiocarboxylate with some aromatic and heterocyclic aldehydes.



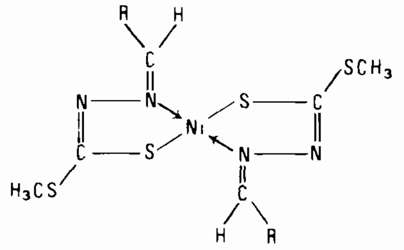
$\begin{matrix}R\\H\end{matrix}\!\!>C{=}N{-}NH{-}\underset{\underset{S}{\|}}{C}{-}SCH_3$

(II)

The nickel(II) chelates of these ligands were prepared and characterized using magnetic and spectral data.

Results and Discussion

N-arylidene Schiff bases (HAr) of the type (II), (R, C_6H_5, p-$CH_3O.C_6H_4$, p-$NO_2C_6H_4$ and o-$NO_2.C_6H_4$), react with nickel(II) acetate or chloride giving complexes of the general $[Ni(Ar)_2]$ (III). These chelates except that of the p-nitrobenzylidene derivative, are soluble in benzene and chloroform, less soluble in ethanol and insoluble in water.



(III)

The infrared spectra of the parent Schiff bases possess a well defined band at 3120 cm^{-1} due to ν(N-H) stretching and a doublet at 2995 and 2850 cm^{-1} due to asymmetric and symmetric stretchings of the CH_3S-grouping[1a]. The nickel chelates $[Ni(Ar)_2]$, as compared to the corresponding ligands do not show any ν(N-H) stretching band and the two bands due to the CH_3S- are reduced to a very weak doublet. These results indicate the deprotonation of the imino hydrogen of the Schiff base upon chelation. Room temperature magnetic measurements reveal that these chelates are diamagnetic, in accordance with square planar environment around Ni^{II} ion.

Attempts to prepare the corresponding protonated chelates $[Ni(HAr)_2Cl_2]$ by passing dry hydrogen chloride into chloroform solutions of the deprotonated chelates $[Ni(Ar)_2]$ were not successful; instead hydrolysis of the azomethine >C=N-group took place and only the anhydrous bis (hydrazine-S-methyl dithio-

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(*) Part IV: M. F. Iskander and L. El-Sayed, *J. Inorg. Nucl. Chem.* 33, 4253 (1971).

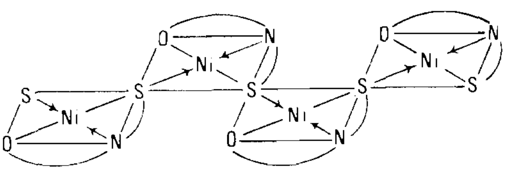
(**) Abstracted from the *M. Sc. Thesis* of A. El-Toukhy.

(1) N. B. Colthup, L. H. Daly and Stephen E. Wiberley, « Introduction to Infrared and Raman Spectroscopy » a) Pp. 307, b) Pp. 305. Academic Press (1964).

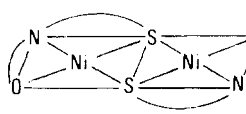
carboxylate) Ni^{II} dichloride was isolated. The failure to prepare the protonated chelates may be due to the stabilization of the deprotonated form by strong conjugation of the $C=N-N=C$ grouping.[2] Deprotonation may proceed through tautomerism. In the solid state, hydrazine-S-methyl dithiocarboxylate and its Schiff base exist mainly in the thio-keto form, as their infrared spectra do not show any band corresponding to the S-H stretching 2590-2540 cm^{-1})[1b]. However, in solution enolization seems to be enhanced by the presence of nickel(II) ions in alkaline or weakly acidic media.

N-salicylidene hydrazine-S-methyl dithiocarboxylate (H_2Sal.Hdth) (II, R = *o*-OH.C_6H_4) reacted in boiling ethanol with an equimolecular amount of nickel acetate yielding a pale brown, amorphous complex of composition [Ni(SalHdth)]. However, reaction with nickel(II) acetate in a 2:1 molar ratio gave a brown precipitate, most of which can be extracted with chloroform, leaving a minor amount of the insoluble [Ni(Sal.Hdth)] complex. From the chloroform extracts, a brown crystalline complex of the formula [Ni(HSal.Hdth)$_2$] was isolated. This chelate was diamagnetic and was found to be soluble in chloroform, carbon tetrachloride and insoluble in water. The [Ni(Sal.Hdth)] complex was also diamagnetic, but insoluble in the above solvents. However, in strong coordinating solvents such as alcoholic ammonium hydroxyde, pyridine, piperidine and quinoline, the compound readily dissolved with the formation of diamagnetic complexes of the type [Ni(Sal.Hdth)B], where B refers to the base used. The same complexes are also obtained when nickel(II) acetate reacts with (H_2Sal.Hdth) in a (1:1) molar ratio in the presence of the corresponding base. The infrared spectra of the parent N-salicylidene hydrazine-S-methyl dithiocarboxylate ligand show the expected band at 3100 cm^{-1}, due to the ν(N-H) stretching. With regard to the OH-stretching, the band could not be detected probably due to strong hydrogen bonding with the azomethine group.[3] The infrared spectra of the [Ni(Sal.Hdth)], [Ni(HSal.Hdth)$_2$] and [Ni(Sal.Hdth)B] chelates as compared to the free ligand suggested deprotonation of the imino hydrogen.

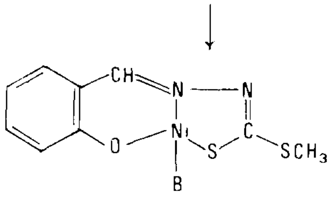
From stereochemical point of view, N-salicylidene hydrazine-S-methyl dithiocarboxylate is able to function as a potent planar tridentate molecule with no steric problems, analogous to the reported N-salicylidene derivatives of benzoyl hydrazine,[4] semicarbazide[5,6] and thiosemicarbazide.[5,7] Accordingly, in both [Ni(Sal.Hdth)] and [Ni(Sal.Hdth)B], the ligand H_2Sal.Hdth acts as a dibasic tridentate ligand. In the latter complex, [Ni(Sal.Hdth)B] the base molecule occupies the fourth coordination site (V). However in [Ni(Sal.Hdth)] complex, square planar configuration is attained through the formation of dimeric (IVb) or most probably polymeric structure (IVa) with sulphur bridges. This is suggest by the insolubility and the amorphous nature of the complex. Polymeric structures were frequently proposed for chelates derived from ligands containing sulphur as one of the donor atoms.[8]



(IVa)



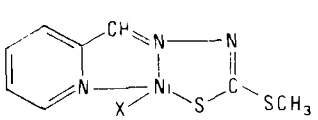
(IVb)



(V)

In the bis chelates [Ni(HSal.Hdth)$_2$], the ligand functions as a monobasic bidentate ligand analogous to the N-arylidene derivatives (III). The phenolic OH is not involved in chelation, and this explains the solubility of the chelate in aqueous KOH solution and its reprecipitation upon acidification with acetic acid.

Schiff bases derived from furan, thiophene and pyridine-2-carbaldehydes (II, R = C_4H_4O, C_4H_4S and C_5H_5N), referred to as HFu.Hdth, HTh.Hdth and HPy.Hdth, where the hetero atom is a possible site of coordination were also investigated. The reaction with nickel acetate in ethanol yielded diamagnetic brown chelates of the general formula [Ni(Fu.Hdth)$_2$], [Ni(Th.Hdth)$_2$] and [Ni(Py.Hdth)$_2$]. With nickel chloride, both HFu.Hdth and HTh.Hdth gave the same product as with the acetate, while the reaction with HPy.Hdth afforded the chloro-(2-pyridyl methylene) hydrazine-S-methyl dithiocarboxylate) Ni^{II} (VI). The corresponding bromo, iodo and thiocyanato complexes were prepared metathetically (see the experimental section).



(VI)

In the bis chelates [Ni(Fu.Hdth)$_2$], [Ni(Th.Hdth)$_2$] and [Ni(Py.Hdth)$_2$] the Schiff base behaves toward Ni^{II} as a monobasic bidentate ligand similar to the N-arylidene derivatives. The hetero atom (O,S and N) in these ligands is not involved in chelation. However, [Ni(Py.Hdth)X] (X=Cl, Br, I and SCN) chelates

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[2] B. A. Gingras and A. F. Sirianni, *Can J. Chem. 42(1)*, 17-19 (1964).
[3] P. Teyssie and J. J. Charette, *Spectrochim. Acta, 19*, 1407 (1963).
[4] L. Sacconi, *J. Am. Chem. Soc., 74*, 4503 (1952); *Idem, Gazz. Chim. Ital. 83*, 884 (1953); *Idem, J. Am. Chem. Soc., 76*, 3400-2 (1954.
[5] Y. Muto, *Bull. Chem. Soc. Japan, 31*, 1017 (1958).
[6] H. El Khadem, M. F. Iskander, and S. E. Zayan, *Z. Anorg. Allg. Chem., 325*, 72-76 (1963).
[7] A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem. (English trans) 9*, 1260 (1964); *10*, 624 (1965).
[8] H. Kerbs, E. F. Weber and H. Fassbender, *Z. Anorg. Allg. Chem., 276*, 128 (1954); S.E. Livingstone, *Quart. Rev., 19*, 386 (1965).

HPy.Hdth acts as a planar tridentate monobasic ligand, with X occupying the fourth coordination site. Diamagnetism, infrared and electronic spectra are in agreement with square planar structure (VI). A similar structure was reported for chloro-1-(2-pyridyl methylene) thiosemicarbazide nickel(II).[9]

Table I. Analytical data of Nickel(II) chelates with Schiff bases of the type (R.CH=N—NH—CSSCH$_3$).

R	m.p°C (decomp.)	Found Ni%	Found S%	Formula	Required Ni%	Required S%
C_6H_5	205-7	12.30	26.87	$Ni(C_9H_9N_2S_2)_2$	12.29	26.86
p-CH_3O . C_6H_4	246-7	10.75	23.47	$Ni(C_{10}H_{11}N_2OS_2)_2$	10.92	23.86
p-$NO_2C_6H_4$	282-4	10.30	22.65	$Ni(C_9H_8N_3O_2S_2)_2$	10.35	22.60
o-$NO_2C_6H_4$	220-2	10.40	22.60	$Ni(C_9H_8N_3O_2S_2)_2$	10.35	22.60
o-HO . C_6H_4	300	20.35	22.30	$Ni(C_9H_8N_2OS_2)$	20.67	22.28
o-HO . C_6H_4	215-16	11.40	25.00	$Ni(C_9H_9N_2OS_2)_2$	11.53	25.18
o-HO . C_6H_4	275	19.32	21.40	$Ni(C_9H_8N_2OS_2)NH_3$	19.50	21.30
o-HO . C_6H_4	156-8	16.20	17.60	$Ni(C_9H_8N_2OS_2)C_5H_5N$	16.17	17.66
o-HO . C_6H_4	169-170	15.95	17.60	$Ni(C_9H_8N_2OS_2)C_5H_{10}N$	15.95	17.42
o-HO . C_6H_4	168-170	14.10	15.10	$Ni(C_9M_8N_2OS_2)C_9H_{11}N$	14.07	15.37
C_4H_3O	219-221	12.75	28.00	$Ni(C_7H_7N_2OS_2)_2$	12.84	28.04
C_4H_3S	247-249	12.10	38.97	$Ni(C_7H_7N_2S_3)_2$	11.99	39.31
C_5H_4N	260-262	12.30	26.50	$Ni(C_8H_8N_3S_2)_2$	12.25	26.75
C_5H_4N	255-257	19.30	21.30	$Ni(C_8H_8N_3S_2)Cl$	19.28	21.06
C_5H_4N	238-240	16.53	18.21	$Ni(C_8H_8N_3S_2)Br$	16.82	18.38
C_5H_4N	232-234	14.83	16.01	$Ni(C_8H_8N_3S_2)I$	14.83	16.19
C_5H_4N	236-238	17.90	24.21	$Ni(C_8H_8N_3S_2)SCN$	17.95	29.408

Table II. The Electronic Spectra of Square planar nickel(II) chelates with Schiff bases of the general formula R . CH=N—NH . CSSCH$_3$

R	Medium	Band maxima in cm^{-1} ($\varepsilon mole^{-1}$ $liter^{-1}$ cm^{-1})					
i. Bis(Arylidene Schiff base) Ni^{II}:					ν_3	ν_2	ν_1
C_6H_5	N		25,640	22,220	17,540	15,870(sh)[b]	
	B		25,640	22,220	17,540	15,870(sh)	14,080(sh)
			(11,450)	(6,180)	(222)	(135)	(50)
p-CH_3O . C_6H_4	N			22,220	17,540	15,900	
	B *		25,640	22,220	17,540	15,870	
p-NO_2 . C_6H_4	B		25,650	22,220	16,670	15,630	
o-NO_2 . C_6H_4	N		24,000	21,280	16,700		
	B	29,412	24,000	21,280(sh)	17,100	16,390(sh)	14,280(sh)
		(15,240)	(6,800)	(3,350)	(200)	(155)	
o-HO . C_6H_4	N		24,100		19,620(sh)	16,450(sh)	14,700(sh)
	B	27,400	24,100		19,610(sh)	16,400(sh)	14,500(sh)
		(31,780)	(13,260)		(684)	(134)	(22)
ii. Bis(Heterocyclic Aldehyde Schiff base) Ni^{II}:							
C_4H_3O	N			21,280	15,870	14,390(sh)	
	B		25,000	21,280	15,873	~14,390(sh)	13,330(sh)
			(22,670)	(11,500)	(206)	(110)	(35)
C_4H_3S	N		25,000	20,000	15,630	14,290(sh)	
	B		24,700	21,280	15,630	15,000(sh)	14,390
			(20,000)	(11.250)	(200)	(180)	(140)
C_5H_4N	N					14,290(sh)	
	B *		27,780	21,740	18,180(sh)	14,290(sh)	
iii. Ni(Py . Hdth)X Complexes: (X = NCS, Cl, Br, I.)							
X=NCS	N		24,400	22,200	19,500	16,400	
	B *	29,850	25,000		20,200	17,700(sh)	16,260
Cl	N		24,400	22,200	20,400	16,500	
	B *	29,410	24,690	21,980(sh)	19,610	17,700(sh)	15,500
Br	N		25,000	21,000	19,000	17,000	
	B	28,990	24,690	20,830(sh)	19,610	17,390(sh)	15,380
	N	(12,240)	(12,490)	(2,970)	(2,260)		
I			25,640	21,980	19,000	16,200	
	B	28,570	24,690	20,830(sh)	18,520	16,670	14,930
		(12,140)	(11,300)	(2,020)	(229)		

N = Nujol mull. B = Benzene solution. * Saturated solution.

Table III. Solution Spectra of Square planar nickel(II) Complexes in Pyridine.

R	Band maxima in cm^{-1} (εmole^{-1} liter^{-1} cm^{-1})							
			ν_3	ν_2			ν_1	
Type I: Coordination number 6 Bis chelates (Ni(RCH=N–N=CSSCH$_3$)$_2$								
C_6H_5	27,780 (25,000)	25,640(sh) (15,300)	21,050(sh) (290)	16,810 (36)	16,130(sh) (30)	12,820(wsh)	10,930 (28)	
p-CH_3O . C_6H_4	27,460 (34,600)		21,510(sh) (510)	16,950 * (45)			10,990 (30)	10,360 (28)
p-NO_2 . C_6H_4		23,800 (25,000)	22,000(sh) (10,000)	16,950 (150)	15,600(sh) (70)		10,810 (28)	
o-NO_2 . C_6H_4		25,640 (15,000)	22,220 (4,400)	16,130 (135)	14,930(sh) (60)		11,110 (27)	10,000 (18)
C_4H_3O	26,670 (34,000)	25,000(sh) (18,000)	21,280(sh) (260)	17,240 (45)	15,150(sh) (20)	12,500(wsh)	11,110 (30)	10,310 (28)
C_4H_3S	27,000 (30,850)		22,220(sh) (600)	16,950			11,110	
Type II: Coordination number 5 a) Bis chelates Ni(RCH=N–N=CSSCH$_3$)$_2$								
o-HO . C_6H_4	28,170 (30,520)	23,810 (13,500)		18,180(sh) (60)			12,350 (31)	11,630 (28)
C_5H_4N	28,570 (27,900)	22,220 (17,240)		18,800(sh)		12,240(wsh)	12,200 (58)	
b) [Ni(Py . Hdth)X] Complexes								
X	Band maxima in cm^{-1} (mole^{-1} litre cm^{-1})							
NCS	28,980 (12,950)	22,730 (9,870)		17,500(sh) (100)			11,360 ** (40)	
Cl	28,570 (15,000)	22,730 (9,650)		~16,500(sh) (60)			11,750 (20)	10,640 (25)
Br	28,980 (13,370)	22,990 (9,520)		~16.810(sh) (70)			11,560 ** (28)	
I	28,570 (12,380)	22,990 (9,450)		17,850(sh) (65)			11,900 ** (35)	

* Asymmetric band. ** Broad, probably consists if two bands.

Electronic Spectra. The nujol as well as the solution spectra in benzene of the bis Ni^{II} chelates prepared in the present work do not show any absorption in the near infrared region (> 13500 cm^{-1}). This suggests that the ground state of nickel(II) ion in these chelates is the singlet $^1A_{1g}$ in accordance with the diamagnetism of these chelates in both solid state as well as in benzene or chloroform solutions. No indication of square planar ⇄ tetrahedral equilibrium (at least at room temperature) is observed in chloroform solutions.

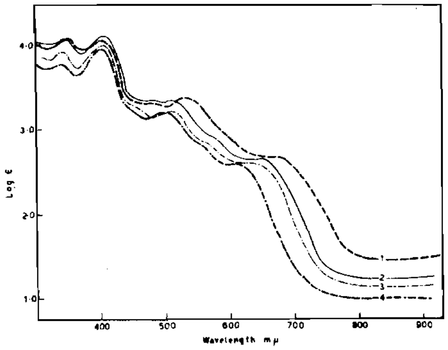

Figure 1. Electronic spectra of [Ni(Py . Hdth)X] in benzene 1) X=I; 2) X=Br; 3) X=Cl; 4) X=SCN.

The spectra of the bis chelates (Table II-i,ii) in the 20,000 - 13,500 cm^{-1} region exhibit two bands ν_3 and ν_2 besides a relatively weak band ν_1. These three bands may be attributed to singlet-singlet transitions. Generally the ν_3 and ν_2 are tentatively assigned to $^1A_{1g} \rightarrow {}^1B_{3g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions in D_{2h} symmetry.[10,11] Above the 20,000 cm^{-1} region, there are two very intense bands. The lowest energy band $\varepsilon \simeq 10,000$) cannot be attributed to d-d transitions but can be assigned to (L → M) charge tranfer transition while the highest energy band is probably due to $\pi \rightarrow \pi^*$ transition of the ligand.

The spectra of the complexes [Ni(Sal.Hdth)B] (B = NH_3, pyridine, piperidine and quinoline) do not show any shift in the position of the bands with changes of the base strength of B. This indicates that in the case of square planar Ni^{II} complexes the ligand field splitting is not much affected by the base strength of the ligand and depends mainly on the chromophores around the Ni(II) ion.

In the case of the complexes of the type [Ni(Py. Hdth)X] (X=NCS, Cl, Br and I) (Table II-iii) the position of the three bands in the 20,000 - 14,500 cm^{-1}

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(9) C. J. Jones and J. A. McCleverty, *J. Chem. Soc.* (A) 38 (1971).
(10) G. Maki, *J. Chem. Phys.*, *28*, 651 (1958).
(11) B. Bosnich, *J. Am Chem Soc.*, *90*, 627 (1968).

region in the mull and solution spectra in benzene are sensitive to the nature of X. A shift to lower frequencies occurs in the order NCS>Cl>Br>I, in agreement with the field strength of these ligands in the spectrochemical series.[12] The position of the thiocyanate group in this series indicates that coordination occurs via the nitrogen atom. The appearance of the CN stretching band at 2110 cm^{-1} [13] is consistent with the above assignment.

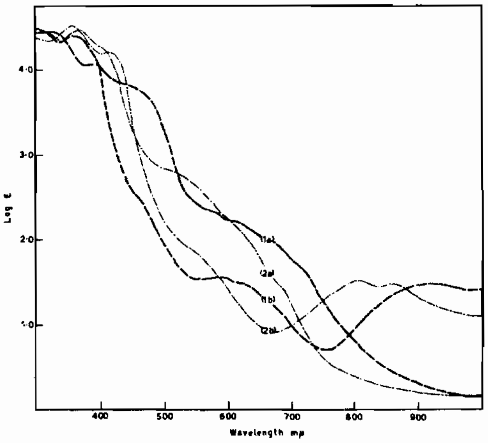

Figure 2. Electronic spectra of bis-(N-benzylidene hydrazinato-S-methyl dithiocarboxylate) Ni^{II} 1a) in benzene; 1b) in pyridine and bis-(N-salicylidene hydrazinato-S-methyl dithiocarboxylate) Ni^{II} 2a) in benzene; 2b) in pyridine.

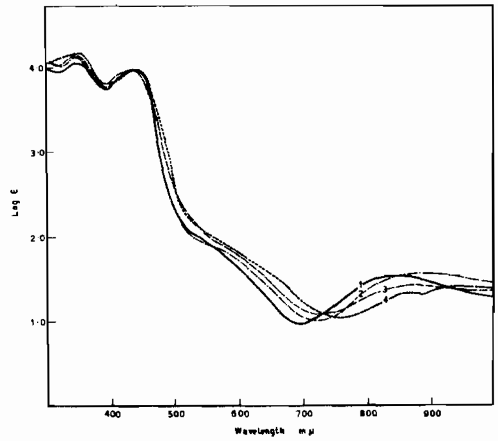

Figure 3. Electronic spectra of [Ni(Py . Hdth)X] in pyridine 1) X=I; 2) X=SCN; 3) X=Br; 4) X=Cl.

In pyridine, the spectra of all the prepared Ni^{II} chelates are completely different from both mull and solution spectra in benzene, suggesting strong interaction of these complexes with pyridine. Inspection of these spectra shows two types of interactions. The spectra of the bis nickel(II) complexes with the exception of [Ni(HSal.Hdth)$_2$] and [Ni(Py.Hdth$_2$] in pyridine (Table III, type II) show the three bands (ν_3, ν_2 and ν_1) characteristic of octahedral Ni^{II} complexes, with the two pyridine molecules most probably occupying the two trans axial positions. Splitting of the ν_1 and ν_2 bands indicates strong tetragonal distortion. Attempts to isolate these 1:2 pyridine adducts failed due to rapid loss of pyridine on filtration. Only in the case of *o*-nitrobenzaldehyde Schiff base yellowish adduct was isolated. Elemental analyses correspond to the 1:2 adduct.

On the other hand, the electronic spectra of [Ni(HSal.Hdth)$_2$], [Ni(Sal.Hdth)B], [Ni(Py.Hdth)$_2$] and [Ni(Py.Hdth)X] in pyridine (Table III, type III) show two intense bands above 20,000 cm^{-1} besides a shoulder in the 17,000 ± 1000 cm^{-1} region and a broad band which is splitted, at 12,000 ± 500 cm^{-1}. The position of the bands as well as their intensities cannot be accounted for octhaedral Ni^{II}, but are similar to those attributed to five coordinate geometry.[14] Such spectral evidence suggests the formation of 1:1 adducts in solution. The pentacoordinate species probably possess a distorted square pyramidal more than trigonal bipyramidal structure. But due to the fluxional nature of the five coordinate structure a wide range of intermediate geometries is possible.[15]

It is of interest to note that the position of both the band and the shoulder in the spectra of [Ni(Py.Hdth)-X] depends on the nature of the ligand X. A shift to higher frequencies is observed in the order I>CNS>-Br>Cl. Since pyridine possesses available π-acceptor orbitals, the observed antispectrochemical series may be explained in terms of back donation. On decreasing the electronegativity of the ligand X in the pentacoordinate complex [Ni(Py.Hdth)X.Py] (Py = pyridine) more negative charge is available on the metal ion, thereby enhancing the overlap between the filled metal d-orbitals and the vacant π-acceptor pyridine orbitals.[16,17] Thermodynamic data[18] in the case of [Co(Py)$_4$X$_2$] and spectral data in the [Ni(Py)$_2$X$_2$] complexes[17] have shown that the effective crystal field splitting energy of pyridine is greater in the bromo than chloro complexes. This is correlated with the expected relative degree of metal → pyridine π bonding.

Experimental

1. *Preparation of the Schiff bases.* A solution of hydrazine-S-methyl dithiocarboxylate (0.01 *M*) is absolute ethanol (20 ml) was refluxed for 10 min. with the corresponding aldehyde (0.015 *M*). On cooling the Schiff base precipitated and was filtered and recrystallised from ethanol.

2. *Preparation of the nickel complexes.* i. Bis (N-substituted benzylidene hydrazinato-S-methyl dithiocarboxylate) nickel(II): To a clear solution of nickel acetate (0.01 *M*) in ethanol (20 ml) was added a solution of the corresponding Schiff base (0.02 *M*)

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(12) A. B. P. Lever, « Inorganic Electronic Spectroscopy » Pp. 203, Elsevier (1968).

(13) P. C. H. Mitchell and R. J. P. William, *J. Chem. Soc.*, 1912 (1960).

(14) E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, *20*, 245 (1966).

(15) L. Sacconi, R. Morassi and S. Midollini, *J. Chem. Soc.* (*A*), 1510 (1968).

(16) A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 4761 (1964).

(17) A.B.P. Lever, S.M. Nelson and T.M. Shephere, *Inorg. Chem.*, *4*, 810 (1965).

(18) A.C.A. King, E. Koros, and S.M. Nelson, *J. Chem. Soc.*, 5449 (1963); 4832 (1964).

in ethanol (15 ml), the resulting mixture was refluxed for about 10 min. The complexes separated out on cooling, were filtered and recrystallised from benzene petroleum mixture except the p-nitrobenzylidene complex which was insoluble in most common solvents.

ii. Bis (N-salicylidene hydrazinato-S-methyl dithiocarboxylate) nickel(II): This was prepared by the same method described above for bis arylidene complexes. The solid formed was extracted with chloroform leaving a minor amount of the 1:1 complex. The chloroform solution was evaporated to give the bis(N-salicylidene hydrazinato-S-methyldithiocarboxylate) nickel(II).

iii. Mono(N-salicylidene hydrazinato-S-methyldithiocarboxylate) nickel(II): To a solution of nickel acetate (0.01 *M*) in ethanol (20 ml) was added with vigorous stirring an equimolecular amount of the Schiff base in ethanol (20 ml). The resulting mixture was refluxed for about one hour and the formed precipitate was filtered and washed several times with hot chloroform.

iv. Reaction of mono(N-salicylidene hydrazinato-S-methyl dithiocarboxylate) nickel(II) with bases: A suspension of [Ni(Sal.Hdth)] in ethanol was treated with the base B (B = ammonium hydroxide, pyridine, piperidine or quinoline). The reaction mixture was refluxed for 15 minutes and the formed [Ni(Sal.Hdth)-B] complexes were filtered and recrystallized from carbon tetrachloride.

v. Bis-nickel(II) chelates with heterocyclic Schiff bases: These chelates were prepared by the same method used for the bis-N-arylidene complexes and were recrystallised from chloroform petroleum mixture.

vi. Monochloro, bromo, iodo and thiocynato-1-(2-pyridylmethylene hydrazinato-S-methyldithiocarboxylate) nickel(II): To a solution of $NiCl_2 6.6H_2O$ (0.01 *M*) in ethanol (15 ml) was added a solution of 2-pyridylmethylene hydrazine-S-methyl dithiocarboxylate (0.01 *M*) in ethanol (20 ml). The intense brown solution was refluxed for 15 min. The [Ni(Py.Hdth)-Cl] which separated on cooling was filtered and recrystallised from chloroform-ethanol mixture.

The corresponding bromo, iodo, and thiocyanato complexes were prepared by the reaction of a solution of nickel nitrate (0.01 *M*) in ethanol (25 ml) with the ligand (0.01 *M*) in ethanol (20 ml). To this solution excess of ammonium bromide, iodide and thiocyanate (0.03 *M*) was added and the reaction mixture was refluxed for 15 min. On cooling the complexes separated out, were filtered and recrystallised from chloroform.

Elemental analysis. Nickel was determined volumetrically with EDTA using EBT as indicator. Sulphur content was determined as previously described (part IV). The elemental analyses are shown in Table I.

Physical Measurements. Magnetic measurements, infrared and electronic spectra were obtained using the same procedures previously described.[19]

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(19) L. El-Sayed and M. F. Iskander, *J. Inorg. Nucl. Chem.*, *33*, 435 (1971).