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Interaction of Dithiophosphinates of Cobalt and Nickel with Pyridine-Type Donors

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The relative isotropic ^{1}H NMR shifts of several pyridine-type base adducts of M(2,4-Me$_2$dtpi)$_2$ [where M=Co, Ni and 2,4-Me$_2$dtpi=bis(2,4-dimethylphenyl)dithiophosphinate] were measured. The opposite signs of ring and methyl proton resonance shifts in α- and γ-picoline complexes of nickel indicate that both σ- and π-mechanisms are operative. In the cobalt cases all proton resonances are shifted down-field suggesting a negative dipolar contribution in addition to contact interaction. The magnetic and electronic spectral studies on these compounds are consistent with either MS$_4$N or MS$_4$N$_2$ chromophores.

The proton isotropic shifts of pyridine-type donors in cobalt and nickel acetylacetonates[1] and β-keto esterates[2,3] have been reported. ^{1}H NMR studies on similar adducts of chelates of these metals with sulfur ligands have received much less attention.[4,5] Dithiophosphinates of transition metals were reported from our laboratory.[6,7] In the present article, complexes of bis(2,4-dimethylphenyl)dithiophosphinates of cobalt and nickel, M(2,4-Me$_2$dtpi)$_2$, with a series of pyridine-type donors have been subjected to magnetic, electronic, IR, and ^{1}H NMR investigations.

Experimental

All the chemicals used were either of analytical or chemically pure grade. Bis(2,4-dimethylphenyl)dithiophosphinic acid was synthesized by the procedure reported in literature.[8)

Preparation of Complexes. Co(2,4-Me$_2$dtpi)$_2$(L) (L= pyridine, α-picoline, β-picoline, γ-picoline, 2,6-lutidine, and 3,5-lutidine): The base (3 ml) was added to a methanolic solution (40 ml) of CoCl$_2$·6H$_2$O (1.1 g). Addition of methanolic solution (25 ml) of Na(2,4-Me$_2$dtpi) (3.1 g) afforded blue/greenish blue solid which was washed with methanol and dried.

Co(2,4-Me$_2$dtpi)$_2$(4-phenylpyridine): To a chloroform (25 ml) solution of Co(2,4-Me$_2$dtpi)$_2$ (1.5 g) methanolic solution (25 ml) of 4-phenylpyridine (0.4 g) was added. On slow addition of methanol (40 ml) bright green product precipitated out. This was washed with methanol and recrystallized from chloroform–methanol.

Co(2,4-Me$_2$dtpi)$_2$(L)$_2$ (L=pyridine and γ-picoline): A mixture of cobalt(II) chloride hexahydrate (1.3 g) and the base (10 ml) in methanol (40 ml) was treated with methanolic solution (30 ml) of sodium salt (3.7 g) of the ligand. The resulting pink crystalline solid was collected, washed with methanol containing a small amount of the base.

Ni(2,4-Me$_2$dtpi)$_2$(α-picoline): A chloroform solution (30 ml) of Ni(2,4-Me$_2$dtpi)$_2$ (1.5 g) was mixed with 3 ml of α-picoline. The resulting solution, on slow evaporation gave the brown adduct, which was washed with methanol and dried.

Ni(2,4-Me$_2$dtpi)$_2$(L) (L=β-picoline and γ-picoline): Nickel(II) chloride hexahydrate (1.1 g) in methanol (40 ml) was treated with 3 ml of base. Na(2,4-Me$_2$dtpi) (3.1 g) in methanol (25 ml) was added dropwise to this solution with stirring. The brown solid, which precipitated was isolated by filtration, washed with methanol and dried.

Ni(2,4-Me$_2$dtpi)$_2$(3,5-lutidine): A solution of Ni(2,4-Me$_2$dtpi)$_2$ (2.2 g) in chloroform (30 ml) was mixed with 3,5-lutidine (4 ml). The brown solid was forced from the resulting solution with methanol, filtered and then recrystallized from chloroform–methanol mixture in presence of small quantity of the base.

Ni(2,4-Me$_2$dtpi)$_2$(L)$_2$ (L=pyridine, β-picoline, and γ-picoline): The light green adduct was obtained by the interaction of a solution of Ni(2,4-Me$_2$dtpi)$_2$ (2.0 g) in chloroform (30 ml) with the base (6 ml) and on slow evaporation of the solvent. It was then recrystallized from chloroform–methanol in presence of base.

Ni(2,4-Me$_2$dtpi)$_2$(4-phenylpyridine)$_2$: A solution of 4-phenylpyridine (1.0 g) in chloroform (30 ml) was added slowly to a chloroform solution (30 ml) of Ni(2,4-Me$_2$dtpi)$_2$ (2.1 g). This solution on slow evaporation gave the green complex and was recrystallized from chloroform–methanol in presence of base.

Physical Measurements: A Pye-Unicam SP-2000 infrared spectrophotometer was used for recording IR spectra of the samples in KBr. The room-temperature magnetic measurements were carried out on a Gouy balance using Hg[Co(SCN)$_4$] as the standard. The electronic spectra were observed on a Varian Super Scan 3 UV-visible spectrophotometer. ^{1}H NMR spectra of the adducts in deuteriochloroform were recorded on a Varian XL-100 high resolution NMR spectrometer using tetramethylsilane as the internal calibrant.

Results and Discussion

The color, magnetic moment, analytical and thermal data of the complexes are given in Table 1.

The monoadducts of the composition Co(2,4-Me$_2$dtpi)$_2$(L) were obtained with pyridine, α-picoline, β-picoline, γ-picoline, 3,5-lutidine, 2,6-lutidine, and 4-phenylpyridine whereas the diadducts of the composition Co(2,4-Me$_2$dtpi)$_2$(L)$_2$ could be isolated only with pyridine and γ-picoline. Ni(2,4-Me$_2$dtpi)$_2$ forms 1:1 adducts with α-picoline and 3,5-lutidine whereas both 1:1 and 1:2 adducts have been obtained with β-picoline and γ-picoline. Electronic spectral studies show that a 1:2 adduct is also formed with 3,5-lutidine in solution. With pyridine and 4-phenylpyridine only 1:2 adducts could be isolated. Similar adducts with piperidine could not be isolated. However, the change in color of M(2,4-Me$_2$dtpi)$_2$ solution upon the addition of piperidine; electronic and

Table 1. Color, Magnetic Moment, Analytical, and Thermal Data of the Complexes

Complex[a)]	Color	Magnetic moment	Found (Calcd)/%			Temp[e)]
		BM	M[b)]	S[c)]	Loss of base[d)]	°C
$\mathrm{Co(X)_2(py)}$	Blue	4.64	7.95 (7.87)	17.27 (17.13)	10.48 (10.56)	140
$\mathrm{Co(X)_2(\alpha\text{-}pic)}$	Blue	4.63	7.61 (7.73)	16.67 (16.81)	12.08 (12.21)	155
$\mathrm{Co(X)_2(\beta\text{-}pic)}$	Blue	4.69	7.59 (7.73)	16.62 (16.81)	12.12 (12.21)	165
$\mathrm{Co(X)_2(\gamma\text{-}pic)}$	Blue	4.69	7.79 (7.73)	16.65 (16.81)	12.23 (12.21)	170
$\mathrm{Co(X)_2(2,6\text{-}lut)}$	Greenish blue	4.66	7.42 (7.59)	16.37 (16.51)	13.56 (13.79)	140
$\mathrm{Co(X)_2(3,5\text{-}lut)}$	Greenish blue	4.65	7.45 (7.59)	16.39 (16.51)	13.63 (13.79)	170
$\mathrm{Co(X)_2(4\text{-}phpy)}$	Bright green	4.70	6.96 (7.14)	15.29 (15.55)	18.62 (18.81)	175
$\mathrm{Co(X)_2(py)_2}$	Pink	5.09	7.06 (7.12)	15.28 (15.49)	19.02 (19.12)	140
$\mathrm{Co(X)_2(\gamma\text{-}pic)_2}$	Pink	4.89	6.78 (6.89)	14.72 (14.98)	21.59 (21.76)	170
$\mathrm{Ni(X)_2(\alpha\text{-}pic)}$	Brown	3.12	7.42 (7.70)	16.57 (16.82)	12.20 (12.21)	125
$\mathrm{Ni(X)_2(\beta\text{-}pic)}$	Brown	3.23	7.59 (7.70)	16.54 (16.82)	12.13 (12.21)	115
$\mathrm{Ni(X)_2(\gamma\text{-}pic)}$	Brown	3.14	7.47 (7.70)	16.69 (16.82)	12.24 (12.21)	135
$\mathrm{Ni(X)_2(3,5\text{-}lut)}$	Brown	3.20	7.45 (7.56)	16.54 (16.51)	13.82 (13.80)	160
$\mathrm{Ni(X)_2(py)_2}$	Light green	3.09	6.98 (7.09)	15.32 (15.49)	18.95 (19.10)	130
$\mathrm{Ni(X)_2(\beta\text{-}pic)_2}$	Light green	3.15	6.72 (6.86)	14.73 (14.99)	21.53 (21.76)	115
$\mathrm{Ni(X)_2(\gamma\text{-}pic)_2}$	Light green	3.22	6.83 (6.86)	14.57 (14.99)	21.49 (21.76)	135
$\mathrm{Ni(X)_2(4\text{-}phpy)_2}$	Light green	3.25	5.83 (5.99)	12.89 (13.09)	31.43 (31.67)	170

a) X=2,4-$\mathrm{Me_2dtpi}$. b) M=Metal (Co or Ni). c) S=Sulfur. d) Loss of the pyridine-type donor on heating. e) Temperature at which the complex was heated to estimate the loss of base.

^{1}H NMR spectral studies on the resulting solution confirm the formation of adducts in solution.

The IR spectra of these complexes show ν_{as}P–S and ν_{s}P–S around 650 and 585 cm^{-1} respectively.[9)] The bands around 1470 and 1610 cm^{-1} are assigned to both C=C and C=N stretching vibrations.

The magnetic moments for the monoadducts of cobalt and nickel fall in the range 4.63—4.70 and 3.12—3.23 BM respectively consistent with the penta-coordinate geometry.[10,11)] For the diadducts these values are around 5.0 and 3.2 BM respectively as expected for hexa-coordinate cobalt(II) and nickel(II) complexes.

The reflectance and solution spectra of Co(2,4-$\mathrm{Me_2dtpi)_2}$(L) are similar and the observed d-d bands around 14800, 15600, and 17250 cm^{-1} are in agreement with those reported for other penta-coordinate compounds.[12)] Since the overall pattern of the absorption bands for both trigonal bipyramidal as well as square pyramidal cobalt complexes is the same, the choice between the geometries based upon the spectral data is not categorically possible. The reflectance spectra of the pink diadducts exhibit a multicomponent band in the region 14800—21700 cm^{-1} which is assigned to $^4\mathrm{T_{1g}}\rightarrow{}^4\mathrm{T_{1g}(P)}$ transition in an octahedral stereochemistry.[13)] The very weak two electron $^4\mathrm{T_{1g}}\rightarrow{}^4\mathrm{A_{2g}}$ transition expected in this region is obscured by the stronger $^4\mathrm{T_{1g}}\rightarrow{}^4\mathrm{T_{1g}(P)}$ transition. Thermogravimetric analysis of these compounds show two distinct dissociation steps (115 and 140 °C for pyridine and 125 and 170 °C for γ-picoline adducts respectively) indicating the presence of two base molecules in the adducts. The complexes decompose on prolonged exposure to air and are soluble in nonpolar solvents producing blue-colored solutions, indicating dissociation to penta-coordinate species.

The reflectance spectra of the monoadducts of Ni(2,4-$\mathrm{Me_2dtpi)_2}$ show two ligand field bands around 13000 and 21000 cm^{-1} with a shoulder in the intermediate region (18000 cm^{-1}) and are consistent with a square pyramidal penta-coordinate stereochemistry.[14,15)] The solid-state spectra of the diadducts exhibit ligand field bands around 13900 and 21600 cm^{-1} and are assigned to $^3\mathrm{A_{2g}}\rightarrow{}^3\mathrm{T_{1g}}$ and $^3\mathrm{A_{2g}}\rightarrow{}^3\mathrm{T_{1g}(P)}$ transitions in a trans octahedral symmetry of the $\mathrm{NiS_4N_2}$ chromophore. Dis-

Table 2. Relative Isotropic Shifts for Ligands Coordinated with Metal Complexes

Ligand	Proton	Isotropic shifts in Ni(2,4-Me_2dtpi)$_2$ adducts	Isotropic shifts in Co(2,4-Me_2dtpi)$_2$ adducts
Piperidine	α-CH_2	−10.00	−10.00
	β-CH_2	−4.95	−4.02
	γ-CH_2	−2.81	−0.70
Pyridine	α-CH	−10.00	−10.00
	β-CH	−3.53	−3.92
	γ-CH	−0.93	−0.87
α-Picoline	α-CH	−10.00	−10.00
	β-CH	−3.42	−3.00
	γ-CH	−1.81	−0.93
	α-CH_3	+0.74	−0.18
β-Picoline	α-CH	−10.00	−10.00
	β-CH	−3.45	−3.50
	γ-CH	−0.56	−0.21
	β-CH_3	−0.51	−0.42
γ-Picoline	α-CH	−10.00	−10.00
	β-CH	−3.40	−3.87
	γ-CH_3	+1.10	−0.87
3,5-Lutidine	α-CH	−10.00	−10.00
	γ-CH	−0.62	−0.37
	β-CH_3	−0.56	−0.49
4-Phenylpyridine	α-CH	−10.00	−10.00
	β-CH	−3.17	−3.76
	α′-CH	−0.12	−0.55
	β′-CH	+0.11	−0.12
	γ′-CH	+0.11	−0.12

sociation of these complexes in chloroform solution could be prevented by addition of the base.

^{1}H NMR has been used to determine the distribution of unpaired spin density in the ligands of paramagnetic complexes in which the effective electron spin relaxation time is short. The existence of an isotropic hyperfine contact interaction between unpaired electrons and magnetic nuclei leads to large shifts in the nuclear resonance frequencies. Such a shift may be of contact or dipolar origin or a combination of both.[16] The isotropic shifts found for nickel chelates are assumed to arise solely from a contact interaction[17] while for cobalt compounds both contact and dipolar interactions[18] contribute for these shifts.

The observed shifts for dithiophosphinate moiety are very small hence our discussion is confined only to the base proton shifts. As the actual shifts depend upon the solution composition only relative shifts have been discussed. Absorption peaks were assigned to particular ligand protons by observing the approach to the known diamagnetic spectra upon the addition of more and more ligand. The observed shifts have been normalized to give a value of −10.00 for the α-proton shifts. Negative shifts are shifts to lower applied fields and positive shifts to higher applied fields.

The relative isotropic shifts for the protons of different bases complexed with nickel and cobalt dithiophosphinates are included in Table 2. In the nickel adduct with piperidine all the base proton resonances are shifted down-field and attenuate with the increasing number of intervening bonds between the metal ion and relevant proton. This pattern is characteristic of σ-delocalization and is observed in a number of complexes.[19,20] Similar observation was made for pyridine adduct in which all the proton shifts are down-field and the order is $\alpha > \beta > \gamma$. In contrast, the methyl protons of both α- and γ-picoline compounds are shifted up-field indicating the presence of unpaired π-electron density in addition to σ-spin density.

The observed isotropic shifts in cobalt complexes are compared with the corresponding nickel adducts and that of cobalt(II) acetylacetonates to get information about the nature of dipolar shifts. For piperidine adduct of Co(2,4-Me_2dtpi)$_2$ all the observed shifts are down-field in contrast to the up-field shifts reported for corresponding cobalt acetylacetonate derivative. Since piperidine has no π-orbitals, π-delocalization of magnetic t_{2g} electrons is not possible. The observed shift pattern can be explained by considering a negative dipolar contribution in addition to contact interaction while positive dipolar contribution has been reported for Co(acac)$_2$. This is supported by the down-field shift of the methyl protons of α- and γ-picolines in Co(2,4-Me_2dtpi)$_2$. If the spin-transfer mechanisms for nickel and cobalt adducts are assumed to be the same, which of course have been shown to be true,[1,21)] the methyl protons would have shifted up-field in the presence of small positive dipolar shifts. The observation of negative shifts for these protons rules out the possibility of positive dipolar contribution in these cobalt adducts. This is further supported by the down-field shift for β' and γ' protons in 4-phenylpyridine adduct, the corresponding protons in the cobalt acetylacetonate show up-field shifts. In the nickel complex the β' and γ' proton resonances are shifted up-field similar to that in the $Ni(acac)_2$ compound.

Isotropic shifts for all β-picoline protons of nickel adduct were observed down-field and the signs of shifts for β-CH and β-CH_3 protons are identical. The observation is similar to that reported for the corresponding acetylacetonate adduct. This behavior is in contrast to the results obtained for the α- and γ-picoline adducts which were explained on the basis of (σ–π) configuration interaction. Similar observation was made for 3,5-lutidine adduct of $Ni(2,4\text{-}Me_2dtpi)_2$ in which α-CH, γ-CH, and β-CH_3 protons are shifted down-field. However, for the corresponding cobalt complexes the observation is similar to those of α- and γ-picoline adducts.

In $Co(2,4\text{-}Me_2dtpi)_2$(2,6-lutidine) the observed shifts have been normalized to give −10.00 for β-protons and the values obtained for γ-CH and α-CH_3 are −4.12 and −0.11 respectively. The signs of the shifts are identical to those for other bases. The corresponding nickel adduct could not be isolated and ^1H NMR spectrum did not provide evidence for complex formation in solution.

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