

Lutidine Adducts of Co(II) & Ni(II) Dithiophosphinates

R. N. MUKHERJEE, M. S. VENKATESHAN & M. D. ZINGDE

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076

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The adducts of Co(II) and Ni(II) dithiophosphinates with 2,6- and 3,5-lutidines have been characterized on the basis of their electronic and IR spectral and magnetic moment data. The studies reveal that whereas Ni(II) is able to form both pentacoordinated 1:1 and hexacoordinated 1:2 adducts depending on the nature of lutidine, Co(II) forms only pentacoordinated 1:1 adduct with both the lutidines. The studies further reveal a change in adduct-forming ability of the metallic dithiophosphate as the organic moiety on phosphorus atom changes from phenyl to *p*-tolyl. Steric effect is thus a major factor controlling the reaction of the metallic dithiophosphinates, $M(X)_2$, where $M=Co(II)$ or $Ni(II)$ and X =diphenyldithiophosphate (dtpi) or its *p*-tolyl analogue (Medtpi), with nitrogen heterocycles.

STABLE complexes of picolines with chlorides of Co(II) and Ni(II) and Ni(II) derivatives of β -diketones have been reported^{1,2}. However, 2,6-lutidine does not form such addition compounds. This prompted us to see if 2,6- and 3,5-lutidines will form adducts with the dithiophosphinates of Ni(II) and Co(II). The results of such a study are reported in this paper. In our earlier studies^{3,4}, it was found that steric factors play an important role in the formation of pentacoordinated addition compounds of picolines with dithiophosphinates of Co(II) and Ni(II).

Materials and Methods

The metallic dithiophosphinates, $M(X)_2$, were prepared as reported elsewhere^{5,6}. Pure grade lutidines (Fluka) were used without further purification.

$Co(X)_2L$ ($L = 2,6$ -lutidine or $3,5$ -lutidine) — To $Co(X)_2$ dissolved in slightly warm chloroform, was added the nitrogen base in slight excess. The resulting blue solution was quickly filtered, diluted with an equal amount of methanol and slowly evaporated when the required complex precipitated. This was washed with methanol, dried and stored *in vacuo*.

$Ni(X)_2L$ ($L = 3,5$ -lutidine) — To a solution of $Ni(X)_2$ in chloroform the nitrogen base was added dropwise till a deep brown solution was obtained. The solution was allowed to evaporate slowly when brown crystals of $Ni(X)_2L$ separated. The crystals were quickly washed with methanol, dried and stored *in vacuo*.

The magnetic measurements were carried out on a Guoy's balance using $Hg[Co(SCN)_4]$ as the calibrant. For low temperature measurements the sample was cooled to 80°K with liquid nitrogen and the temperature gradually raised using controlled heating.

The visible spectra were recorded on SF-10 (Russian), Unicam SP-700A and a Perkin-Elmer 402 spectrophotometers. The infrared spectra were recorded on a Carl-Zeiss spectrophotometer. The colour and analytical data of the complexes are given in Table 1.

Results and Discussion

All the complexes are soluble in non-polar solvents. Change of organic moiety on phosphorus from phenyl to tolyl reveals that $M(dtpi)_2$ is not as versatile in adduct formation as $M(Medtpi)_2$ [$M =$

TABLE 1 — COLOUR MAGNETIC MOMENT AND ANALYTICAL DATA OF Co(II) AND Ni(II) COMPLEXES

Compound	Mol. formulae	Found (%)			Calc. (%)			μ_{eff} (BM)
		S	N	M	S	N	M	
$Co(dtpi)_2(3,5-lut)^*$	$C_{31}H_{29}CoNP_2S_4$	18.35	2.04	8.94	19.30	2.11	8.87	4.58
$Co(Medtpi)_2(3,5-lut)^*$	$C_{35}H_{37}CoNP_2S_4$	17.59	1.83	8.31	17.80	1.94	8.16	4.51
$Co(dtpi)_2(2,6-lut)^*$	$C_{31}H_{29}CoNP_2S_4$	19.19	2.09	8.61	19.30	2.11	8.87	4.63
$Co(Medtpi)_2(2,6-lut)^*$	$C_{35}H_{37}CoNP_2S_4$	17.45	1.81	7.98	17.80	1.94	8.16	4.69
$Ni(dtpi)_2(3,5-lut)^\dagger$	$C_{31}H_{29}NiNP_2S_4$	19.06	1.92	8.79	19.31	2.11	8.84	2.90
$Ni(Medtpi)_2(3,5-lut)^\dagger$	$C_{35}H_{37}NiNP_2S_4$	17.03	2.24	7.93	17.80	1.93	8.10	2.85
$Ni(Medtpi)_2(3,5-lut)^\ddagger$	$C_{42}H_{46}N_2NiP_2S_4$	14.86	3.60	7.02	15.50	3.39	7.09	2.91

dtpi = diphenyldithiophosphate and Medtpi is its di(*p*-tolyl) analogue.

*Blue.

†Brown.

‡Green.

Co(II) or Ni(II); dtpi = Diphenyldithiophosphate and Medtpi is its di(*p*-tolyl) analogue]. Whereas Ni(Medtpi)₂ is capable of forming 1:1 adduct with 2,6-lutidine and both 1:1 and 1:2 adducts with 3,5-lutidine, the behaviour of Ni(dtpi)₂ is not so versatile. It failed to form stable adduct with 2,6-lutidine and its 1:2 adduct with 3,5-lutidine was markedly unstable. The Co(II) dithiophosphate showed no such changes on varying the substituents on phosphorus atom and unlike the Ni(II) analogue which dissociated in solution to form square planar pentacoordinated complexes, there seems to be no marked change in stereochemistry in case of Co(II) complexes as is evident from the broad similarity of the reflectance and solution spectra.

The solubility and stability of Medtpi complexes is more than the corresponding dtpi complexes. On heating in an oven the complexes quantitatively lose their coordinated base molecule to yield the corresponding dithiophosphinates M(X)₂.

The electronic spectra of Co(X)₂L in the visible region (reflectance and solution) indicate that the complexes can be assigned pentacoordinated stereochemistry with S₄N core around the central metal atom on the basis of similarity of the spectra with other known pentacoordinate complexes⁷⁻⁹. However, the choice between square pyramidal and trigonal bipyramidal structures requires extreme caution⁸. The spectra of mono-adducts of Ni(II) are indicative of a square pyramidal geometry on the basis of good agreement with spectra of similar mono-adducts¹⁰ studied in solution. In a square pyramidal configuration (C_{4v}) the bands observed around 13300 and 21000 cm⁻¹ may be assigned to the transitions ³B₁→³E" and ³B₁→³E'''. Overlapping of these transitions with the transitions ³B₁→³A₂' and ³B₁→³A₂'' respectively is also possible. To obtain green bis-adducts of Ni(X)₂(L)₂, a very large excess of the base was required. Ni(dtpi)₂(3,5-lut)₂ is markedly unstable and all the measurements were carried out on Ni(Medtpi)₂(3,5-lut)₂ which is typical of NiS₄N₂ core complexes. The occurrence of well-defined bands in the reflectance spectra at 15150 and 21750 cm⁻¹ can be assigned to the transitions ³A_{2g}→³T_{1g}(F) and ³A_{2g}→³T_{2g}(P) respectively¹¹. The band disobserved around 18500 cm⁻¹ is probably due to torsion from ideal octahedral symmetry. In solution the bands are observed around 13300, 17800 and 21300 cm⁻¹ indicating that the complexes dissociate in solution forming pentacoordinated species as well as square planar complexes, Ni(X)₂.

To predict the high- or low-spin magnetic moment behaviour of the present complexes, the

electronegativity (χ) scale deduced by Allred and Rochow¹² and the nucleophilic reactivity constant (n°) of the atoms have been used following the procedure of Sacconi¹³. The cross-over value for Co(II) complexes with terdentate ligand is Σχ = 12.65 and Σn° = 29.04 and for Ni(II) complexes Σχ = 12.76 and Σn° = 25.5. Extending this rule to bidentate ligands the Σχ and Σn° values for S₄N core are 12.83 and 22.02 respectively indicating that the complexes should be of high-spin type. This has been confirmed by measurements (Table 1). Measurements between 88° and 303°K for Co(dtpi)₂(3,5-lut) and 88° and 299°K for Ni(Medtpi)₂(3,5-lut) support the proposed structure. Ni(Medtpi)₂(3,5-lut) has θ = +22° and μ_{eff} values of 2.77, 2.78, 2.76, 2.79, 2.81, 2.81, 2.83 and 2.85 BM at 88, 104, 128, 156, 188, 219, 248 and 299°K, respectively. Co(dtpi)₂(3,5-lut) has θ = +8° and μ_{eff} values of 4.50, 4.52, 4.51, 4.49, 4.51, 4.52, 4.54, 4.54, 4.57 and 4.58 BM at 88, 109, 126, 145, 178, 199, 224, 249, 287 and 303°K respectively. The P-S symmetric and asymmetric vibrations are expected in the region 400-700 cm⁻¹ in these complexes¹⁴. An examination of the spectra of the present adducts in conjunction with the corresponding parent metallic dithiophosphate reveals that in 1:1 adducts a band around 650 cm⁻¹ and in 1:2 adducts a doublet around 625 cm⁻¹ may be assigned to one of the P-S vibrations.

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