

Chelated and Free Phosphine Adducts of Nickel(II)Dithiocarbamates: Synthesis, Spectroscopy and Valence Bond Parameter Calculations

Arumugam Manohar*, Kottamalai Karpagavel and
Arumugam Murugan

Department of Chemistry, Kalasalingam University, Krishnankoil-626 190, India

*Corres.author: navmanohar@yahoo.co.in

Abstract: Mononuclear Ni(II)dithiocarbamates with chelated, free phosphine ligands of composition, $[\text{Ni}(\text{dtc})(\text{P-P})]\text{ClO}_4^-$ and $[\text{Ni}(\text{dtc})(\text{PPh}_3)(\text{NCS})]$ (where $\text{dtc}^- = \text{dedtc}^-$, diethyldithiocarbamate; $\text{padtc}^- = \text{N,N}'$ - imino diethylenebis(phthalimide)dithiocarbamate; $\text{P-P} = \text{dppm}$, bis(diphenylphosphino)methane; dppe , (1,2-bis(diphenylphosphino)ethane; 1,3-dppp, (1,3-bis(diphenylphosphino)propane; 1,4-dppp, (1,4-bis(diphenylphosphino)butane) and $\text{PPh}_3 = \text{triphenylphosphine}$ were prepared. The complexes were characterized by using elemental analysis, IR, UV-Visible spectroscopy, magnetic and conductivity measurements. The spectral studies confirm the planarity of the chromophore in all the complexes, the contribution of the thioureide form to the molecular structure and the decrease of electron density on nickel atoms in the phosphine complexes compared to parent nickel(II)dithiocarbamates. Magnetic and conductivity measurements show that all the complexes are diamagnetic and 1:1 electrolytes. Also valence bond sum (VBS) investigations have been made on some NiS_2P_2 chromophores and results are reported.

Keywords: Nickel(II)dithiocarbamate, chromophore, chelated phosphines, valence bond sums.

Introduction

Dithiocarbamates are versatile compounds owing to their interesting chemistry and wide applications [1-4]. One of the most interesting aspects of dithiocarbamates is their applications in coordination chemistry. Dithiocarbamate complexes of transition metal ions and main group elements continue to attract the attention of researchers. In particular nickel(II) dithiocarbamates with a planar NiS_4 chromophore are found to show interesting variations in reactivity towards soft Lewis bases such as phosphines and hard bases such as nitrogenous ligands [5,6]. Nickel dithiocarbamates in their reaction with substituted phosphines form planar NiS_2P_2 chromophores, which are diamagnetic in nature [7]. Steric, electronic and structural studies on mixed ligand complexes of the general types such as $[\text{NiX}(\text{dtc})(\text{PPh}_3)]$, $[\text{Ni}(\text{dtc})(\text{PPh}_3)_2]\text{Y}$ and $[\text{Ni}(\text{dtc})(\text{P-P})]\text{Y}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NCO}, \text{CN}$; $\text{Y} = \text{ClO}_4, \text{PF}_6, \text{BPh}_4, \text{Cl}, \text{Br}, \text{NCS}$) have been reported extensively[8-30].

The structural studies show that the central nickel atom is in a planar environment in all the complexes. The planarity of the molecules is supported by the observed diamagnetism of the complexes. In [NiX(dtc)(PPh₃)] type complexes the Ni–S distances are significantly different due to steric and electronic effects of the donors. And is asymmetric with respect to the Ni–S distances, attributed to the trans influence exerted by PPh₃ and NCS. IR spectra of the complexes show the contribution of the thioureide form to the structures. ¹H, ¹³C and ³¹P NMR spectra of the complexes showed chemical shifts of all the complexes indicating the influence of PPh₃, NCS, CN respectively on the mesomeric drift of electron density towards nickel and strong interaction on complexation. Cyclic voltammetry studies showed a higher reduction potential for the parent complex indicating the reluctance to add more electron density to the already electron rich metal centre. The X-ray photoelectron(XPS) spectral studies on NiS₄, NiS₂PCl and NiS₂P₂ chromophores in different nickel complexes have been reported. XPS studies showed reduced electron density on NiS₂P₂ chromophores. The BVS data support the highly covalent nature of the Ni–S interaction. [30]

As a continuation of our interest in exploring the synthetic and structural chemistry of transition metal dithiocarbamates and to understand the influence of phosphines on the NiS₂P₂ chromophore, we investigated some mixed ligand complexes of the general types [Ni(dtc)(NCS)(PPh₃)] and [Ni(dtc)(P-P)]ClO₄⁻ (where dtc⁻ = dedtc⁻, ⁻S₂CN(C₂H₅)₂; padtc⁻, ⁻S₂CN(CH₂CH₂N(CO)₂C₆H₄)₂, P-P = dppm, bis(diphenylphosphino)methane; dppe, (1,2-bis(diphenylphosphino)ethane; 1,3-dppp, (1,3-bis(diphenylphosphino)propane; 1,4-dppp, (1,4-bis(diphenylphosphino)butane).

Experimental

IR spectra were recorded on a JASCO IR-700 spectrophotometer (range 4000 – 400cm⁻¹) as KBr pellets. The UV-Visible spectra in CH₂Cl₂ were recorded in a JASCO UVIDEK- 340 double beam spectrophotometer. Elemental analyses(C,H,N) were carried out with an Heraeus Erba 1108 instrument. All the reagents and solvents employed were commercially available, high-grade purity materials (E-merck) used as supplied without further purification.

Preparation of the complexes

Preparation of [Ni(dtc)(P-P)]ClO₄ (dtc⁻ = dedtc, padtc, P-P = dppm,dppe, dppp, dppb): A mixture of Ni(dtc)₂ (1 mmol), dppm (or) dppe (or) dppp (or) dppb (1mmol), NiCl₂.6H₂O (0.5 mmol) and NaClO₄(1 mmol) in CH₃CN – MeOH (2:1, 75 cm³) was refluxed for about 3 hours. Resulting purple red solution was filtered and left for evaporation. After two days purple red crystals were obtained.

Preparation of [Ni(dtc)(PPh₃)(NCS)] (dtc⁻ = dedtc, padtc): A mixture of Ni(dtc)₂ (0.5 mmol), PPh₃ (1 mmol), NiCl₂ 6H₂O (0.5mmol), and NH₄SCN(1 mmol) was refluxed for 3 h in CH₂Cl₂–CH₃CN (1:1). The purple red solution obtained was filtered and left for evaporation. After 3 days, fine crystals were obtained.

The padtc ligand and parent dithiocarbamate complexes were prepared by already reported methods [31,32].

Table 1. Important IR bands and analytical data for the complexes

Compound	νC - N	νC - S	C%		H%		N%	
			Calcd	Found	Calcd	Found	Calcd	Found
[Ni(dedtc) ₂]	1518	998	33.8	33.6	5.6	5.5	7.9	7.8
[Ni(dedtc)(dppm)] ⁺	1530	997	52.0	51.9	4.6	4.4	2.0	1.9
[Ni(dedtc)(dppe)] ⁺	1533	997	52.7	52.5	4.8	4.6	2.0	1.8
[Ni(dedtc)(dppp)] ⁺	1535	998	53.3	53.0	5.0	4.7	1.9	1.8
[Ni(dedtc)(dppb)] ⁺	1538	999	54.0	53.7	5.2	5.1	1.9	1.7
[Ni(padtc) ₂]	1497	998	53.9	53.8	3.4	3.2	9.0	8.8
[Ni(padtc)(dppm)] ⁺	1510	1001	56.2	56.0	3.8	3.7	4.2	4.1
[Ni(padtc)(dppp)] ⁺	1515	997	57.8	57.6	4.2	4.1	4.2	4.1
[Ni(padtc)(dppb)] ⁺	1517	999	58.4	58.2	4.4	4.3	4.2	4.1
[Ni(padtc)(PPh ₃)(SCN)]	1507	998	58.9	58.7	3.8	3.7	6.9	6.7

Results And Discussion

IR Spectra

Important absorptions in the dithiocarbamate complexes are due to $\nu\text{C-N}$ and $\nu\text{C-S}$ stretching modes. The $\nu\text{C-N}$ band has been used as a measure of the contribution of the thioureide form to the structure of the dithiocarbamate compound. In the mixed ligand complexes, the thioureide $\nu\text{C-N}$ values were found to be larger than those of the parent dithiocarbamates. The increase in wavenumber for the mixed ligand complexes is attributed to the mesomeric drift of electron density towards the nickel atom through thioureide bond from the dithiocarbamate. The $\nu\text{C-S}$ stretching vibrations are observed around 1000 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbamate ligand [33]. In addition to $\nu\text{C-N}$ and $\nu\text{C-S}$ bands, the spectra showed strong band around 1100 cm^{-1} due to ClO_4^- ion [34]. The bands observed at $2,100$ and 850 cm^{-1} are connected with $\nu\text{C-N}$ and $\nu\text{C-S}$ vibrations, which confirm the coordination of the NCS group through the nitrogen atom [21]. For the padtc^- complexes, an intense band due to carbonyl stretch at $1715\text{--}1770\text{ cm}^{-1}$ is due to the asymmetrical and symmetrical stretching modes, which remains unaffected on complexation. Apart from $\nu\text{C-N}$ (thioureide), an intense band around 1393 cm^{-1} is assigned to $\nu\text{C-N}$ (tertiary) for padtc^- complexes, whereas in free ‘‘paH’’ amine and padtc^- , $\nu\text{C-N}$ (tertiary) are observed at 1392 and 1394 cm^{-1} , respectively. Other responses in the IR spectra are due to the appearance of $\nu\text{C-H}$ and phenyl C-H vibrations at $2830\text{--}3060$ and $650\text{--}790\text{ cm}^{-1}$, respectively.

IR spectral studies on the complexes confirm the thioureide contribution to the structures. The shift in $\nu(\text{C-N})$ (thioureide) values to higher wave numbers than the parent complexes is the clear indication of increased electron density on nickel centre in the mixed ligand complexes and, hence, these complexes are expected to be more difficult to reduce. But, in reality, the mixed-ligand complexes are the most easily reduced based on the cyclic voltammetry data reported earlier [35,36]. All the mixed ligand complexes have lower reduction potentials than the parent $\text{Ni}(\text{dtc})_2$, which shows a reluctance to add more electron density to the already electron rich nickel center in the parent complexes. This is probably because of the extensive π -back bonding with the phosphorus atom which drains the excess negative charge on the nickel and hence lowers the reduction potential. Based on the above observations, the structures proposed for these complexes are given in Fig. 1 and 2.

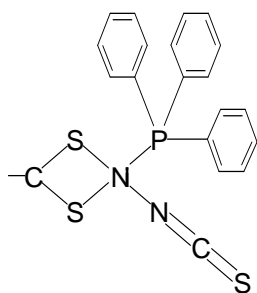


Fig. 1 Structure of NiS_2PN chromophore in $[\text{Ni}(\text{dtc})(\text{PPh}_3)(\text{SCN})]$

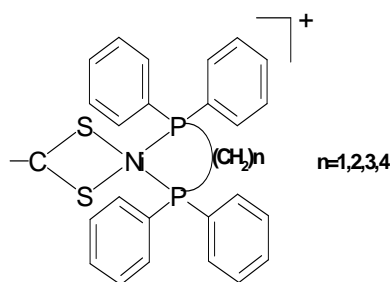


Fig. 2 Structure of NiS_2P_2 chromophore in $[\text{Ni}(\text{dtc})(\text{P-P})]^+$

UV-Visible Spectra

Square planar coordination is supported by electronic spectroscopy in all the nickel(II) complexes. Bands below 350 nm are probably connected with intra-ligand transitions in the S_2CN^- group [37]. UV-Visible absorption spectra of NiS_2P_2 chromophores show bands at ca $400, 440, 450, 480, 550, 570$ and 590 nm . Strong bands which appear at $400, 440$ and 450 nm are attributed to the charge transfer processes. In addition to the charge transfer bands, bands observed in the range $450\text{--}590\text{ nm}$ are due to d-d transitions. Based on the single crystal electronic spectral studies of similar complexes, the bands at 480 nm ($d_{z^2} \rightarrow d_{x^2-y^2}$), 550 nm ($dxz \rightarrow d_{x^2-y^2}$), 570 nm ($d_{xy} \rightarrow d_{x^2-y^2}$) and 590 nm ($d_{xy} \rightarrow d_{x^2-y^2}$) are attributed to the d-d transitions. The bands obtained in the mixed ligand complexes show a red shift due to the replacement of the chelating dithiocarbamate ligand by PPh_3 and NCS^- . Comparison of the information already available for similar compounds of this type leads to the conclusion that the coordination around the metal centers is probably square planar [38].

Magnetic and conductivity measurements

Magnetic susceptibilities at room temperature were measured using Faraday method with Co[Hg(NCS)₄] as calibrant. Conductivities were measured with a Spintronix 321 conductivity meter at 25°C. All the complexes are diamagnetic and behaves as 1:1 electrolytes [39,40], in accord with assumption of a square planar arrangement of NiS₄, NiS₂P₂ and NiS₂PN chromophores in the coordination sphere.

Valence bond parameter calculations

Valence bond Sum (VBS) analysis has a number of uses. It can be applied to most salts, minerals and ceramic compounds as well as to many of the environments of metal atoms in coordination complexes and metal ions in organic salts. By checking the bond valence sums against the oxidation states of each atom it is possible to tell if a proposed structure obeys the normal rules of structural chemistry. Valence bond sums should be calculated and checked around both anions and cations. The valence of a bond, *S*, is a quantity whose sum around each atom is equal to the oxidation state of the atom, *V*:

$$V_j = \sum_i S_{ij}$$

It correlates inversely with bond length, which allows it to be calculated if the bond length has been measured. Newly determined crystal structures can therefore be checked by comparing oxidation states (formal ionic charges) with bond valence sums. The agreement is generally good if the structure is correct, but when the agreement is poor the structure or its determination should be carefully examined. Some of the causes of poor agreement and the uses to which bond valences can be put are described here. Reviews of the bond valence model are given by Brown and O'Keeffe [41-43]. Use of valence bond parameter values determined from homoleptic extended solids in the calculations of VBS for divalent zinc, cadmium and mercury metallo-organic compounds resulted in excellent agreement with the formal oxidation state of the metal. The observation is a clear case of a more or less ionic interaction prevailing in metallo-organic compounds involving d¹⁰ metal ions. VBS calculations have been performed on a series of zinc, cadmium dithiocarbamate complexes whose crystal structures have been reported by our research group [44-45].

In this paper VBS values are calculated on some mixed ligand nickel(II) complexes whose crystal structures have been reported from the literature. The investigated results prove that the VBS values are higher than the expected formal ionic charges of +2. Highly pronounced more covalent bonding and back bonding effects associated with the nickel-sulphur and nickel-phosphorous distances are the reasons for the higher value of oxidation states. VBS values for some NiS₂P₂ chromophores are given in Table 2.

Table 2. Valence bond Sums (VBS) for NiS₂P₂ Chromophores

Compound	Vi(OK/B)	Vi(B/OK)	Ref
[Ni(pe ₂ dtc)(PPh ₃) ₂] ⁺	2.81	2.94	14
Ni(pe ₂ dtc)(dppf) ⁺	2.91	3.04	15
[Ni(bzbudtc)(PPh ₃) ₂] ⁺	2.91	3.04	13
[Ni(dchdtc)(PPh ₃) ₂] ⁺	2.87	2.98	11
[Ni(nmedtc)(1,3-dppp)] ⁺	3.15	3.26	28
[Ni(dedtc)(1,4-dppb)] ⁺	3.01	3.15	46

pe₂dtc⁻ = di(pentyl)dithiocarbamate anion, bzbudtc⁻ = benzyl, butyldithiocarbamate anion, dchdtc⁻ = dicyclohexyldithiocarbamate anion, dedtc⁻ = diethyldithiocarbamate anion, nmedtc⁻ = N-methyl,N-ethanoldithiocarbamate, PPh₃=triphenylphosphine, dppf = 1,1'-bis(diphenylphosphino) ferrocene, 1,3-dppp = 1,3-bis(diphenylphosphino) propane. 1,4-dppb = 1,4- bis(diphenyl phosphino) butane.

Conclusions

Free, chelated phosphine adducts of nickel dithiocarbamates have been synthesized and characterized. In all the mixed ligand complexes, the thioureide ν_{C-N} values were shifted to higher wave numbers compared to parent nickel dithiocarbamates, suggesting increased strength of the thioureide bond due to the presence of the π -accepting phosphine. Electronic spectral studies suggest square planar geometries for the complexes. All the complexes are diamagnetic and 1:1 electrolytes. Valence Bond Sum (BVS) calculations have been made on some NiS_2P_2 chromophores and results are reported in this paper. The higher ionic charges on the nickel atom support the fact that the Ni-S, Ni-P bonds are more covalent and the back bonding effects are highly pronounced.

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