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Mixed ligand complexes involving Bis(dithiocarbamato)Nickel(II) and Phosphorus donors : Synthesis, Spectral, Thermal studies and BVS investigations

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Abstracts: Nickel(II) complexes of the general types [Ni(dtc)(L_2)]ClO_4 and [Ni(dtc)(P-P)]X (where dtc$^-$ = nmedtc$^-$, N-methyl,N-ethanoldithiocarbamate anion; dipdtc$^-$, diisopropyldithiocarbamate anion; pipdtc$^-$, piperidinecarbodithioate anion; mdtc$^-$, morpholinecarbodithioate anion; dnpdtc$^-$, di-n-propyldithiocarbamate anion; L = PPh_3, triphenylphosphine; P-P = dppm, bis(diphenylphosphino)methane; 1,3-dppp, (1,3-bis(diphenylphosphino)propane; 1,4-dppp, (1,4-bis(diphenylphosphino)butane; X= ClO_4^- ,BPh_4^-) were synthesized and characterized by C,H,N analyses, IR, UV-Visible, magnetic and conductivity measurements. Infra red spectra of the complexes show the contribution of the thioureide form to the dithiocarbamates. Thermal studies show that chelated phosphine complexes are more stable than free phosphine complexes. All the complexes are diamagnetic and 1:1 electrolytes. The bond valence sum (BVS) analysis shows that the observed BVS values are higher than the expected formal oxidation state of +2.

Keywords: Dithiocarbamate, triphenylphosphine, 1,3-bis(diphenylphosphino) propane, thioureide, bond valence sum analysis.

INTRODUCTION

Dithiocarbamate complexes are of great interest due to their chemical and biological properties and widely used in industries of agriculture, pharmaceutical, medicine and rubber [1,2]. Dithiocarbamate complexes have been used as a precursor for the synthesis of metal sulfide nanoparticles [3,4]. Divalent nickel complexes of dithiocarbamates with different substituents contain planar diamagnetic MS_4 chromophores [5, 6]. The planar nickel dithiocarbamates prefer to react with soft lewis bases such as phosphines rather than hard nitrogenous bases such as NH_3 and pyridine due to symbiotically induced softness.[7,8]

Spectral, electrochemical and single crystal x-ray structural studies were made on more number of mixed ligand complexes involving nickel dithiocarbamates and free, chelated phosphines [9-18]. The X-ray 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. The X-ray photoelectron spectroscopy (XPS) and cyclicvoltammetric studies on NiS_4,

NiS_2PCl and NiS_2P_2 chromphores in different nickel complexes have been reported [11]. XPS studies show that the decrease of electron density on nickel atoms in the phosphine complexes compared to parent Ni(II)dithiocarbamates. Cyclic voltammetry studies also support the observations from XPS studies with respect to the obtained lower reduction potential for the mixed ligand complexes compared with parent $Ni(dtc)_2$ [9,13,14] . NMR spectral studies on Ni(II) dithiocarbamates with NiS_2PN, NiS_2PC, NiS_2P_2 chromophores were reported[12]. ^1H NMR spectra of the complexes showed the deshielding of α-CH_2 protons on complexation. The S_2–^{13}C N< chemical shifts of the three complexes indicating the influence of PPh_3, NCS, CN respectively on the mesomeric drift of electron density towards nickel. NMR spectra of the complexes also show very large ^{31}P chemical shifts in all the compounds. The Bond Valence Sum (BVS) calculations were made on some mixed ligand complexes [15,19]. The BVS data support the highly covalent nature of the Ni–S interaction.

In continuation of our interest in planar NiS_2P_2 chromophores the present study was under taken. Since the single crystal X-ray structures for some of the complexes have been reported earlier by our research group [10,12], in this paper we report the detailed results obtained from the spectral and thermal characterization studies on NiS_2P_2 chromophores. In addition the results of the bond valence sum (BVS) calculations are also reported in this paper. The BVS values are calculated for a number of complexes whose crystal structures have been reported from our laboratory and a few others reported from other laboratories.

EXPERIMENTAL

Preparation of the complexes

Preparation of $[Ni(dtc)(PPh_3)_2]ClO_4$(dtc- = nmedtc, dnpdtc). A mixture of $Ni(dtc)_2$ (1 mmol), PPh_3 (2 mmol), $NiCl_2.6H_2O$ (0.5 mmol) and $NaClO_4$(1 mmol) in methanol – dichloromethane (1:1) solvent mixture (50 cm^3) was refluxed for about 3 hours followed by concentration to ca 25cm^3 and was then allowed to settle for 2 days. The precipitated purple red compound was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray work were obtained after recrystallization from dichloromethane-methanol solvent mixture (yield 70%).

$$Ni(dtc)_2 + 4PPh_3 + NiCl_2 + 2NaClO_4 \xrightarrow{MeOH/CH_2Cl_2} 2\,[Ni(dtc)(PPh_3)_2]ClO_4 + 2\,NaCl \qquad .....(1)$$

Preparation of $[Ni(dtc)(P\text{-}P)]ClO_4$ (dtc- = nmedtc, dnpdtc, pipdtc, dipdtc, mdtc, P-P = dppm, dppp, dppb). A mixture of $Ni(dtc)_2$ (1 mmol), dppm (or) dppp (or) dppb (1mmol) and $NiCl_2.6H_2O$ (0.5 mmol) and $NaClO_4$ or $NaBPh_4$ (1 mmol) in CH_3CN – MeOH (2:1, 75 cm^3) was refluxed for about 3 hours. Resulting red organge solution was filtered and left for evaporation. After two days red orange crystals were obtained directly(yield 70%).

$$Ni(dtc)_2 + 2L + NiCl_2 \xrightarrow[2NaClO_4\text{ (or) }2NaBPh_4]{MeOH/CH_3CN} [Ni(dtc)(L)]X + 2NaCl(X = ClO_4 \text{ or } BPh_4) \;.....(2)$$

L = dppm, 1,3-dppp, 1,4-dppb)

The parent dithiocarbamate complexes were prepared by literature method [20-24].

Materials and Methods

All the reagents and solvents employed were commercially available, high-grade purity materials(E-merck) used as supplied without further purification.IR spectra were recorded on a JASCO IR-700 spectrophotometer (range 4000 – 400cm^{-1}) as KBr pellets. The UV-Visible spectra in CH_2Cl_2 were recorded in a JASCO UVIDEC-340 double beam spectrophotometer. The room temperature magnetic susceptibility was measured using Faraday method with $Co[Hg(NCS)_4]$ as calibrant. Conductivities were measured with an OK 102/1 conductivity meter at 25°C. Elemental analyses(C,H,N) were carried out with an Heraeus Erba 1108 instrument. STA 1500 PL and Perkin – Elmer TGA7 Thermal Sciences instruments were used for the thermal analysis. The heating rate of the furnace was fixed at 10°C per minute. About 5 mg of the sample was taken in porcelain crucible for each thermogravimetric experiment.

RESULTS AND DISCUSSION

Infrared Spectra.

Important absorptions in the dithiocarbamate complexes are due to νC-N and νC-S stretching modes. The νC-N band has been used as a measure of the contribution of the thioureide form to the structure of the dithiocarbamate compound. For all the complexes strong bands appeared around 1500 and 1000 cm^{-1} due to νC-N (thioureide) and νC-S vibrations, respectively. Shift in νC-N values to higher wave numbers compared with the parent Ni(dtc)$_2$ complexes is due to the mesomeric drift of electrons from the dithiocarbamate moiety towards the metal centre, increasing the contribution of the thioureide form. The νC-S bands appear without any splitting supporting the bidentate coordination of the dithiocarbamate moiety [25]. In addition to νC-N and νC-S bands, the spectra showed strong band around 1100 and 1434 cm^{-1} due to ClO_4^- and BPh_4^- ions, respectively [26]. Important IR bands and analytical data for the complexes are given in Table 1. IR spectra of (a)Ni(mdtc)$_2$, (b) [Ni(mdtc)(1,3-dppp)$_2$]ClO_4 and (c) [Ni(mdtc)(1,4-dppb)]ClO_4 are given in Fig.1.

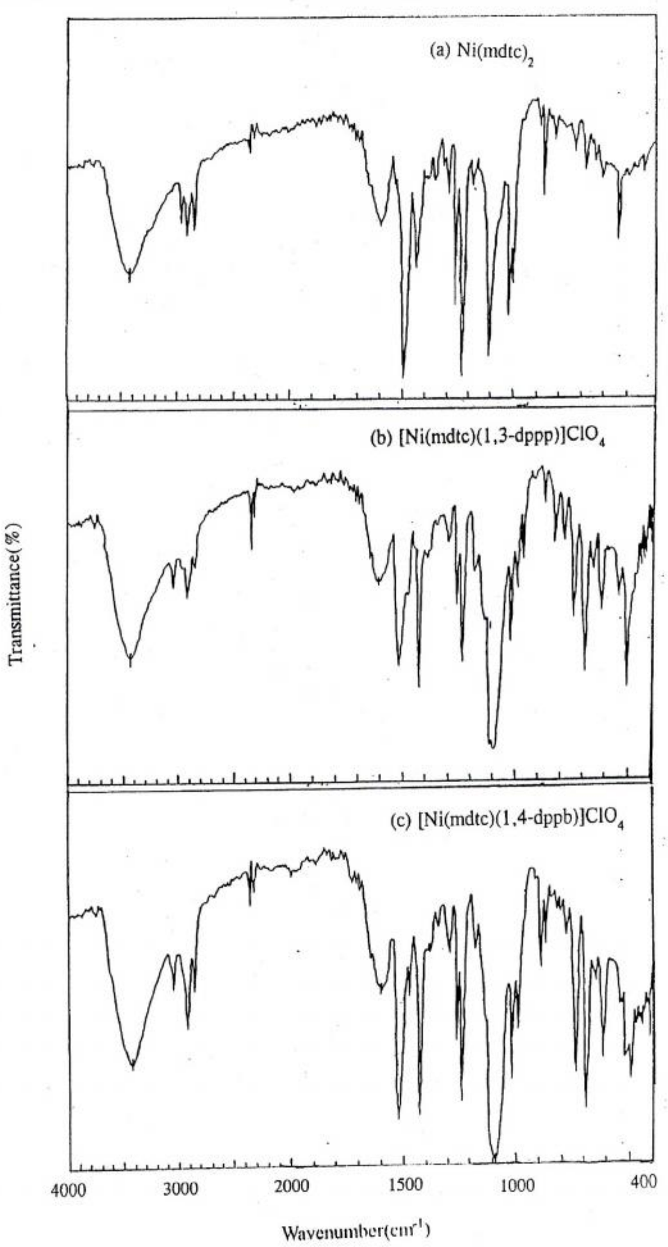

Fig.1: IR spectra of (a)Ni(mdtc)$_2$, (b) [Ni(mdtc)(1,3-dppp)$_2$]ClO_4 and (c) [Ni(mdtc)(1,4-dppb)]ClO_4

Electronic Spectra

In electronic spectra the bands below 350nm are due to intra ligand π- π * transitions, mainly associated with N-C=S and S-C = S groups in all the nickel(II) complexes. The intense bands observed in the 390-450 nm region are due to either metal- ligand or ligand - metal charge transfer [27]. The bands at 650 nm and 490 nm correspond to the $dxy \rightarrow dx^{2}-y^{2}$ and $dz^{2} \rightarrow dx^{2}-y^{2}$ transitions respectively. UV-Visible spectra of phosphine complexes show bands at ca 400, 440, 450,, 470, 480, 550 and 570 nm. Very intense bands which appear at 400, 440 and 450 nm are attributed to the charge transfer processes [9], other bands are due to $dz^{2} \rightarrow dx^{2-}y^{2}$(470 and 480 nm),$dxz \rightarrow dx^{2}-y^{2}$(550 nm) and $dxy \rightarrow dx^{2}-y^{2}$(570 nm)transitions. All the complexes are diamagnetic and behave as electrolytes of the 1:1 type [28,29].

Thermogravimetric studies

All the free and chelated phosphine complexes are showing similar course of thermal decomposition. The thermal degradation pattern of the free phosphine complexes shows the initial mass loss corresponds to the loss of PPh_3 and is followed almost simultaneously by the dithiocarbamate moiety. The final residue above 650°C were analyzed as $NiSO_4$. The chelated phosphine analogues show a multistep decay process which are converted into $NiSO_4$ at 750 °C. Chelated phosphine complexes are thermally more stable than free phosphine complexes with respect to their initial decomposition temperatures. The degradation of dithiocarbamate proceeds through the formation of $Ni(SCN)_2$ *ca.* 500 °C, as is evident in the parent dithiocarbamate complexes. The present study indentifies the formation of planar chromophores *viz.*, NiS_2P_2 and NiS_2P_2(chelated phosphines) with different dithiocarbamate ligands. The NiS_2P_2 chromophore structure is given in Fig.2.

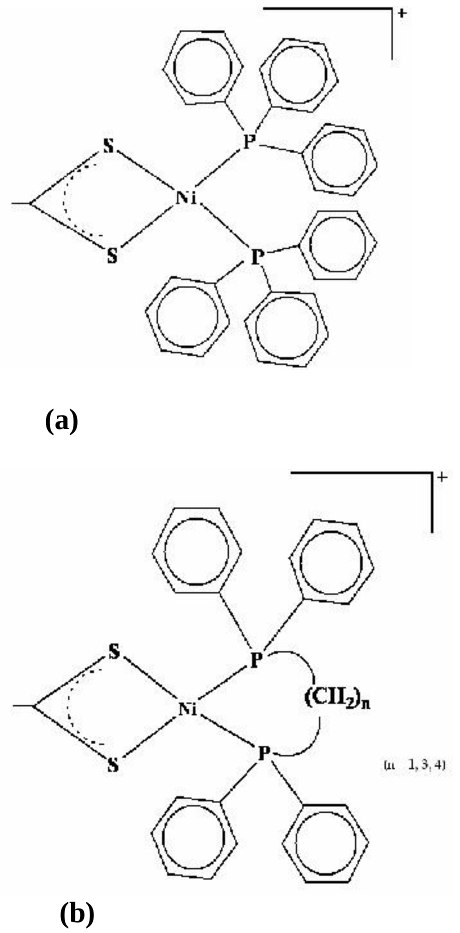

Fig.2 Structure of NiS_2P_2 chromophore in (a) $[Ni(dtc)(PPh_3)_2]^+$ And (b) $[Ni(dtc)(P\text{-}P)]^+$

Bond Valence Sum (BVS) Analysis.

The bond valence sum method is popular method in coordination chemistry to estimate the oxidation states of atoms. In a signifcant number of cases the information based on BVS analysis is sufficient to make accurate predictions about the real crystal structure of the compound. The chemist wishing to estimate an unknown bond length in a molecule or crystal is confronted with an intimidating array of covalent radii, ionic radii, metallic radii etc., from which to choose[30]. The bond valence method [31,32] has recently had considerable success in predicting and interpreting bond lengths in 'ionic solids'. As it can be applied to estimate the bond lengths, *vice-versa* the sum of these bond lengths should give information about the valence of the central ion. In the present study, the BVS method is applied on some mixed ligand complexes of nickel to estimate the effective valence of the nickel ion from the bond lengths reported from their crystal structures.The V_{ij} of a bond between two atoms i and j is defined so that the sum of all the bond valences from a given atom i with valence V_i obeys [33]-

$$\sum v_{ij} = V_i$$

where:

$v_{ij} = \exp[(R_{ij} – d_{ij}/B]$,

$R_{ij} = r_i + r_j – [r_i r_j (\sqrt{c_i}-\sqrt{c_j})^2] / [c_i r_i + c_j r_j]$

and B is a universal constant equal to 0.37. The parameter R_{ij} is the bond valence parameter.The R_{ij} parameters reported by two groups of authors are used in the present calculations. R_{ij}(OK/B) is defined as [34]: $R_{ij} = r_i+r_j-[r_i r_j(\sqrt{c_i}-\sqrt{c_j})^2]/[c_i r_i+c_j r_j]$, where r_i and r_j are size parameters of the atom i and j involved in bonding and c_i, c_j are additional parameters associated with atoms i and j.

Use of R_{ij} values determined from homoleptic extended solids in the calculations of BVS 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 d^{10} metal ions. Using the crystallographic distances, the BVS calculations were made on a series of zinc, cadmium dithiocarbamate complexes whose crystal structures have been reported by our research group [35-37].

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

	Band			C%		H%		N%	
Complex	νC-N	νC-S	ClO_4^- (or)BPh_4^-	Calcd	Found	Calcd	Found	Calcd	Found
[Ni(nmedtc)$_2$]	1523	997	-	26.8	26.7	4.5	4.3	7.8	7.6
[Ni(nmedtc) (PPh$_3$)$_2$]$^+$	1550	997	1086	57.7	57.6	4.6	4.4	1.7	1.5
[Ni(nmedtc) (dppm)]$^+$	1537	975	1104	52.0	51.9	4.7	4.5	2.0	1.9
[Ni(nmedtc) (1,3-dppp)]$^+$	1532	971	1086	51.7	51.6	4.8	4.6	1.9	1.6
[Ni(nmedtc) (1,4-dppb)]$^+$	1542	997	1118	52.3	52.1	4.9	4.7	1.9	1.7
[Ni(dipdtc)$_2$]	1495	997	-	40.9	40.7	6.9	6.7	6.8	6.7
[Ni(dipdtc) (dppm)]$^+$	1509	975	1088	53.5	53.3	5.0	4.9	1.9	1.7
[Ni(dipdtc) (1,3-dppp)]$^+$	1512	970	1096	54.7	54.5	5.4	5.2	1.9	1.8
[Ni(dipdtc) (1,4-dppb)]$^+$	1510	997	1119	55.2	55.0	5.6	5.4	1.8	1.7
[Ni(pipdtc)$_2$]	1508	975	-	38.0	37.9	5.3	5.1	7.4	7.2
[Ni(pipdtc) (dppm)]$^+$	1531	1023	1118	53.0	52.8	4.6	4.4	2.0	1.9
[Ni(pipdtc) (1,3-dppp)]$^+$	1536	1001	1094	54.2	54.0	5.0	4.9	1.9	1.7
[Ni(pipdtc) (1,4-dppb)]$^+$	1535	1022	1096	54.8	54.6	5.1	5.0	1.9	1.6
[Ni(mdtc)$_2$]	1494	1010	-	31.3	31.1	4.2	4.0	7.3	7.2
[Ni(mdtc) (dppm)]$^+$	1524	997	1103	51.1	51.0	4.3	4.2	2.0	1.8
[Ni(mdtc) (1,3-dppp)]$^+$	1523	997	1104	52.4	52.2	4.7	4.5	1.9	1.7
[Ni(mdtc) (1,4-dppb)]$^+$	1527	997	1092	53.1	53.0	4.9	4.7	1.9	1.6
[Ni(dnpdtc)$_2$]	1509	1031	-	40.9	40.6	6.9	6.7	6.8	6.7
[Ni(dnpdtc) (PPh$_3$)$_2$]$^+$	1520	1020	1089	60.1	60.0	5.2	5.0	1.6	1.4
[Ni(dnpdtc) (dppm)]$^+$	1522	995	1088	53.5	53.3	5.0	4.7	1.9	1.7
[Ni(dnpdtc) (1,3-dppp)]$^+$	1522	971	1086	54.7	54.5	5.4	5.2	1.9	1.7
[Ni(dnpdtc) (1,4-dppb)]$^+$	1526	997	1433	72.3	72.1	6.4	6.3	1.4	1.3

Table 2. Bond Valence Sums for Nickel complexes

Compound	Vi(OK/B)	Vi(B/OK)	Ref
$[Ni(dedtc)(PPh_3)_2]^+$	2.895	3.023	9
$Ni(dedtc)(dppe)]^+$	3.167	3.321	38
$[Ni(mdtc)(dppe)]^+$	3.162	3.316	39
$[Ni(mdtc)(1,3\text{-}dppp)]^+$	3.050	3.196	40
$[Ni(mdtc)(1,4\text{-}dppb)]^+$	2.967	3.104	40
$[Ni(mdtc)(dppf)]^+$	2.925	3.055	41
$[Ni(bzmedtc)(PPh_3)_2]^+$	2.833	2.956	42
$[Ni(4\text{-}mpipdtc)(PPh_3)_2]^+$	2.869	2.992	43

$dedtc^-$ = diethyldithiocarbamate anion, $mdtc^-$ = 4-morpholinecarbodithioate anion,
$bzmedtc^-$ = N-benzyl, N-methyldithiocarbamate anion,
$4\text{-}mpipdtc^-$ = 4-methyl piperazine dithiocarbamate anion,
PPh_3 = triphenylphosphine,
dppf = 1,1'- bis(diphenylphosphino)ferrocene,
dppe = 1,2-bis(diphenylphosphino)ethane,
1,3-dppp = 1,3-bis(diphenylphosphino)propane,
1,4-dppb = 1,4-bis(diphenylphosphino)butane.

In continuation of our interest to estimate the effective valence of the nickel ion in NiS_2P_2 chromophores, the BVS values are calculated on some mixed ligand nickel(II) complexes whose crystal structures have been reported from our laboratory and a few others reported from other laboratories. The calculated results show that the BVS values are higher than the expected formal oxidation state of +2. The trends support the fact that the Ni-S, Ni-P bonds are more covalent and the back bonding effects are very highly pronounced. The bond valence sums(BVS) of various Nickel complexes are given in Table 2.

CONCLUSIONS

Mixed ligand complexes involving bis (dithiocarbamato)nickel(II) and free, chelated phosphines such as PPh_3, dppm, dppe, dppp and dppb were synthesized and experimental results of the investigation are presented in this paper. The shifts in νC-N values to higher wave numbers compared with the parent dithiocarbamate are due to the mesomeric drift of electrons from the dithiocarbamate moiety to the metal center. Electronic spectra of the complexes contain charge transfer and d-d transition bands. All the complexes are diamagnetic and hence must be of square planar geometry. Conductivity measurements show that all the complexes behave as 1:1 electrolytes. Chelated phosphines are thermally more stable than the free phosphines. The BVS values are far higher than the expected formal oxidation state of nickel because of the highly pronounced covalent bonding and back bonding effects in NiS_2P_2 chromophores.

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