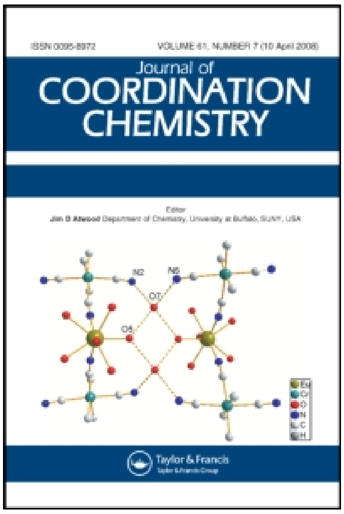

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MIXED LIGAND COMPLEXES OF NICKEL(II) AND COBALT(II)

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Complexes of Nickel(II) and Cobalt(II) containing triphenylphosphine and *N, N*-dimethylformamide (DMF) or dimethylsulphoxide (DMSO) are reported. These are of the type $Ni(PPh_3)L_2X_2$ (L = DMF or DMSO, and X = Cl or Br) and $CoX_2(PPh_3)L$ (L = DMF or DMSO, and X = Cl or Br). These have been synthesised by two different methods and characterised with the help of elemental analyses and various physical data, including infrared and electronic spectra, magnetic measurements, conductivity measurements and thermogravimetric analyses.

INTRODUCTION

Ligands such as *N, N*-dimethylformamide (DMF) or dimethylsulphoxide (DMSO) have a weak coordinating ability towards transition metal ions compared to tertiary phosphines or arsines.[1] Complexes of transition metal ions with DMF and DMSO have been fairly well studied. Complexes of DMF and DMSO with nickel(II) and cobalt(II) reported are of the type ML_nX_2 (where M = Ni or Co, L = DMF or DMSO, n = 2 to 6, X = Cl, Br, I, ClO_4, NO_3, NCS).[2-14] Complexes of nickel(II) and cobalt(II) with strong donor ligands, such as triphenylphosphine are also well known. These are generally of the type $M(PPh_3)_2X_2$ (M = Ni or Co, X = Cl, Br, I, NO_3, SCN).[15-17] Complexes of Ni(II) or Co(II) containing mixed neutral ligands with both weak and strong donor abilities have been very little studied.[18]

No compound containing a weak donor ligand such as DMF or DMSO and a strong donor ligand as triphenylphosphine is reported. Here, complexes of nickel(II) and cobalt(II) containing DMSO or DMF and triphenylphosphine are reported. The compounds presented here are of the type $Ni(PPh_3)L_2X_2$ and $Co(PPh_3)LX_2$ (L = DMF or DMSO, X = Cl or Br). These compounds were prepared by two different methods and have been characterized by their elemental analyses and various physical methods. Possible geometries of the complexes have been suggested on the basis of the studies.

EXPERIMENTAL

The solvents, DMF and DMSO were purified and dried according to standard methods. Carbon, hydrogen and nitrogen analyses were carried out at the Australian Mineral Development Laboratories, Australia, and at the Microanalytical Section, Indian Institute of Technology, Kanpur. Sulphur, halogen and metal estimations were carried out using standard methods after decomposition of the complexes using concentrated nitric acid. Infrared spectra were recorded on Perkin-Elmer 297 infrared spectrophotometer in nujol mull and potassium bromide. Some infrared spectra were recorded on a Perkin-Elmer 580 spectrophotometer. Electronic spectra were recorded in acetonitrile using a Beckman 26

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spectrophotometer. Magnetic measurements were carried out by the Gouy method. Conductivity measurements were carried out in acetonitrile using a Systronic conductivity bridge.

Preparation

The compounds were prepared according to the following methods.

Solution Method

$MX_2 \cdot xH_2O$ (M = Ni or Co, X = Cl or Br) (0.002 mole) was dissolved in 20 cm^3 of the solvent (DMF or DMSO). The mixture was heated to ~ 100° for about one hour, when a clear solution was obtained. Triphenylphosphine (0.004 mole) dissolved in 10 cm^3 of the solvent was added to the solution of the metal salt which was refluxed for about an hour. The solution was concentrated under vacuum at 50-60° to about 8 cm^3 and cooled. To the cold solution, ~ 100 cm^3 of dry ether was added and the complex (blue or green in colour) precipitated. It was filtered and washed several times with dry ether and dried under vacuum.

Melt Method

MX_2L_n (M = Ni or Co, X = Cl or Br, n = 3 or 4) was prepared according to the methods reported in the literature.[1,4] A melt of MX_2L_n (0.002 mole) was prepared by heating the compound to 80° in a small round bottom flask fitted with a guard-tube on a water bath and triphenylphosphine (0.004 mole) was added to it. Heating was continued for about 15 minutes when coloured crystalline compound separated out. The mixture was cooled and washed several times with dry ether to remove unreacted triphenylphosphine and DMSO or DMF. The compounds were dried under vacuum.

The compounds obtained by the above methods are $Ni(PPh_3)L_2X_2$ (X = Cl or Br, L = DMF or DMSO) and $Co(PPh_3)LX_2$ (L = DMF or DMSO, X = Cl or Br). However, $Ni(PPh_3)(DMSO)_2Br_2$ and $Co(PPh_3)(DMSO)Cl_2$ could not be isolated by the solution method. The compounds, except $Co(PPh_3)LBr_2$ (L = DMF or DMSO), were recrystallised from dry acetonitrile. The cobalt bromo-complexes were recrystallised from dry acetone. Attempts to prepare the triphenylarsine compounds analogous to the above mentioned triphenylphosphine ones were unsuccessful using either of the methods and only the compounds containing the solvent as ligands were obtained.

RESULTS AND DISCUSSION

$NiX_2(PPh_3)L_2$ (X = Cl or Br; L = DMF or DMSO)

On the basis of the analytical data the empirical formula for the nickel complexes is found to be $NiX_2(PPh_3)L_2$ (X = Cl or Br, L = DMF or DMSO). The physical data for these complexes, as reported in Tables I and II, suggest that the metal is in the oxidation state II. The magnetic moment data (μ_{eff} = 3.4 to 3.6 B.M.) are characteristic of high-spin nickel (II). These pentacoordinated complexes may have a distorted trigonal-bipyramidal geometry in the solid state. In solution, most probably, a tetrahedral geometry is obtained by the liberation of one of the coordinated DMF or DMSO molecule as evidenced by electronic spectra (*vide-infra*). Examples of nickel(II) complexes with distorted trigonal-bipyramidal structures in the solid state and tetrahedral structures in solution are known.[19] Conductivity measurements in acetonitrile show that all the complexes are non-electrolytes.

TABLE I

Physical properties and analytical data for the complexes[a]

Compound	Colour	M.P.(°)	μ_{eff}(B.M.)	%C	%H	%Halogen	%Metal	% N or S
$NiCl_2(DMSO)_2(PPh_3)$	Blue	175-8d	3.63	48.38 (48.15)	5.15 (4.92)	13.27 (12.95)	11.21 (10.70)	11.83 (11.67)
$NiBr_2(DMSO)_2(PPh_3)$	Green	115-8d	3.58	41.54 (41.43)	4.13 (4.23)	25.32 (25.10)	9.38 (9.21)	10.21 (10.04)
$NiCl_2(DMF)_2(PPh_3)$	Dark blue	140-5d	3.40	53.59 (53.51)	5.43 (5.38)	13.39 (13.19)	11.25 (10.90)	5.65 (5.20)
$NiBr_2(DMF)_2(PPh_3)$	Dark green	123-5d	3.42	45.78 (45.91)	4.43 (4.62)	25.83 (25.51)	9.78 (9.35)	4.42 (4.46)
$CoCl_2(DMSO)(PPh_3)$	Blue	70-5d	4.88	51.10 (51.03)	4.39 (4.46)	15.33 (15.09)	12.74 (12.52)	6.29 (6.80)
$CoBr_2(DMSO)(PPh_3)$	Light blue	112-5d		42.76 (42.91)	3.69 (3.75)	28.35 (28.60)	10.42 (10.53)	5.38 (5.72)
$CoCl_2(DMF)(PPh_3)$	Dark blue	135-40d	4.86	53.85 (54.15)	4.95 (4.72)	15.32 (15.25)	12.34 (12.65)	3.34 (3.00)
$CoBr_2(DMF)(PPh_3)$	Blue	145-8d		45.23 (45.46)	3.89 (3.96)	29.01 (28.86)	10.54 (10.62)	2.72 (2.52)

[a] d = decomposes. Figures in brackets indicate the calculated percentages of the elements present in the compounds.

The infrared spectra (Table II) of the DMF complexes show a very strong band around 1645 cm^{-1} besides other bands due to DMF and triphenylphosphine. The band at 1645 cm^{-1} can be assigned to ν_{CO} of the amide, bound to the metal through the oxygen atom. ν_{CO} of amides on coordination with metals *via* oxygen is shifted towards lower energies (ν_{CO} in free DMF is observed at 1670 cm^{-1}).[20] A band of medium intensity around 385 cm^{-1} observed in the complexes can be assigned to ν_{Ni-P}.[21] The infrared spectra of the DMSO complexes show a band around 995 cm^{-1} of medium intensity besides other bands due to DMSO and triphenylphosphine. The band at 995 cm^{-1} can be assigned to ν_{SO} of an oxygen-bound DMSO. A shift of ν_{SO} to a lower frequency upon coordination of DMSO through its oxygen atom is reported for many compounds (ν_{SO} for free DMSO is observed at 1040 cm^{-1}).[2,6] The absence of bands at 1670 cm^{-1} and 1040 cm^{-1} in the DMF and DMSO complexes, respectively, suggests the absence of uncoordinated DMF or DMSO.

The reflectance data (Table II) of the Ni(II) complexes seem to support a distorted trigonal-bipyramidal structure in the solid state. The reflectance spectra of the nickel(II) compounds show absorptions around 10,600, 13,000, 14,500, 23,000 and 25,500 cm^{-1}. Energy-level diagram for high-spin trigonal-bipyramidal Ni(II) complexes with a D_{3h} symmetry have been reported by Ciampolini.[22] Hence the above absorptions may be assigned as follows:

$$10{,}600\ cm^{-1} : {}^3E'(F) \longrightarrow {}^3A_2''(F)$$
$$13{,}000\ cm^{-1} : {}^3E'(F) \longrightarrow {}^1E''(D)$$
$$14{,}500\ cm^{-1} : {}^3E'(F) \longrightarrow {}^3A_2'(F)$$
$$23{,}000\ cm^{-1} : {}^3E'(F) \longrightarrow {}^3E''(P)$$
$$25{,}500\ cm^{-1} : {}^3E'(F) \longrightarrow {}^3A_2'(P)$$

Similar observations have been reported for $[Ni(Me_6tren)Br]Br$, a pentacoordinated trigonal-bipyramidal compound.[23]

The visible spectral studies of the complexes in acetonitrile reflect their tetrahedral nature in the solution. An assymetrical broad band in the region 14,000-17,000 cm^{-1} is observed in all of the complexes of nickel(II) reported here. On resolution this gives two bands, separated by about 1000 cm^{-1} (Table II). The molar extinction coefficient (between 70 to 100 $M^{-1} cm^{-1}$) is in the range for tetrahedral nickel(II) complexes. The broad band around 15,500 cm^{-1} may be assigned to the ${}^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ transition of the tetrahedral system. The splitting of this band could be due to lower symmetry of the ligand field around the central nickel atom. The ${}^3T_{1(P)}$ term may be split into one component of two-fold orbital degeneracy of one energy and another non-degenerate component of a different energy.[24]

From the thermogravimetric analysis of $NiBr_2(PPh_3)(DMF)_2$ in static air, the complex is found to start losing weight at about 120° and the complete loss of the triphenylphosphine molecule is observed at 300°. A static weight, corresponding to $NiBr_2(DMF)_2$ is observed between 320-360°. The loss of one DMF molecule gives an inflection at 420° and another inflection at 560° corresponds to the loss of the second DMF molecule.

$CoX_2(PPh_3)L$ (X = Cl or Br, L = DMF or DMSO)

On the basis of analytical data, the empirical formula for the cobalt complexes is found to be $CoX_2(PPh_3)L$ (X = Cl or Br, L = DMF or DMSO). The physical data for the complexes as reported in Table I and II suggest that the metal is in the oxidation state II.

TABLE II

Electronic Spectral, reflectance and important infrared data for the complexes.

Complexes	Electronic absorption $\bar{\nu}_{max}/cm^{-1}$ (ϵ^{a}_{max})	Reflectance $\bar{\nu}_{max}/cm^{-1}$	Infrared (cm^{-1})
$Ni(PPh_3)Cl_2(DMF)_2$	15,625(75), 16,800(70)	10,600, 13,000 14,200, 25,000	1640 1370 1100
$Ni(PPh_3)Br_2(DMF)_2$	14,600 sh[b], 15,625(81) 26,900(1100), 39,000(3150)	10,640, 13,000 sh, 14,700, 23,000 25,640	1645 1378 1110 385
$Ni(PPh_3)Cl_2(DMSO)_2$	15,500(95), 16,900(92) 27,400(1320)	10,640, 13,160, 14,700, 26,300	1640 1315 996
$Ni(PPh_3)Br_2(DMSO)_2$	14,300(75), 15,430(97), 16,400sh.		1630 1315 995
$Co(PPh_3)Cl_2(DMSO)$	14,700(580), 15,950(325), 16,340(330), 17,030(335), 17,480(335), 39,200(3200).		1630 1315 998
$Co(PPh_3)Br_2(DMSO)$	14,640(630), 15,380sh, 15,830(410), 16,220(380), 16,950sh.		1628 1318 995
$Co(PPh_3)Cl_2(DMF)$	14,700(460), 15,920(280), 16,340(310), 17,000(270), 17,480(310), 39,000(7400).	14,000, 15,150sh, 16,950, 18,180sh.	1640 1375 1110 377
$Co(PPh_3)Br_2(DMF)$	14,600(565), 15,380sh, 15,830(390), 16,220(345), 16,950sh.		1645 1378 1110 375

[a] $M^{-1}cm^{-1}$. [b] sh = shoulder.

The magnetic moment data (μ_{eff} = 4.9 B.M.), is characteristic of tetrahedral cobalt(II) complexes in a high-spin state. Conductivity studies in acetonitrile illustrate the non-ionic nature of the complexes.

Infrared studies give information similar to that obtained for the nickel complexes. A strong band around 1640 cm^{-1} and a medium band at 377 cm^{-1} can be assigned to ν_{CO} of the amide and $\nu_{Co\text{-}P}$ of the DMF complexes. The cobalt complexes contining DMSO show a strong band around 995 cm^{-1} assigned to ν_{SO} of an *O*-bound DMSO. The absence of bands at 1670 cm^{-1} and 1040 cm^{-1} in the DMF and DMSO complexes, respectively, confirm that the DMF or DMSO molecules are coordinated to the metal. The electronic spectra of these complexes indicate a distorted tetrahedral structure for the complexes. The bands in the region 14,700–17,500 cm^{-1} are due to the transition $^4A_{2(F)} \rightarrow {}^4T_{1(P)}$ in tetrahedral cobalt(II) systems. Here spin-orbit coupling is a smaller perturbation than the low symmetry field and the tetrahedral level $^4T_{1(P)}$ splits into the components $B_2 < A_2 < B_1$. Hence three absorption bands for transition from the $^4A_{2(F)}$ level to the three singly degenerate B_2, A_2 and B_1 states are expected to be observed.[25] However, spin-orbit coupling which mixes the $^4T_1$ and components of the ^2G state could be a reason for the type of band observed in the region 14,700-17,500 cm^{-1}. The electronic absorption spectral pattern of the cobalt complexes in the region 14,700-17,500 cm^{-1} is very similar to that of many other tetrahedral cobalt(II) complexes.[26] An absorption in the 39,000 cm^{-1} region with a very high molar extinction coefficient can be assigned to metal → ligand charge transfer.

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