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Complexes of Ditertiary Phosphine and Ditertiary Arsine Oxides with Metal Ions. IV. Nickel(II) Complexes with Oxides of 1,2-ethylenebisdiphenylphosphine and 1,4-butylenebisdiphenylphosphine (or Arsine)

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The ditertiaryphosphine/arsine oxide $(C_6H_5)_2M(O)$-$(CH_2)_n(O)M(C_6H_5)_2$ *(L) forms three types of complexes with nickel(II) salts; (a)* NiX_2L *(b)* $NiBr_2L_{1.5}$ *and (c)* $Ni(ClO_4)_2 . L_2 . 2H_2O$*. Molar conductance, spectral and magnetic data for the complex of type (b), where M is P and n is 2, indicate the presence of an octahedral and tetrahedral species. However, in case of the complexes of type (a) (where M is P, n is 2 and X is Cl or* NO_3*) and (c) (where M is As; n is 4 when M is P, n is 2 or 4) these measurements support a pseudo-octahedral stereo-chemistry.*

Introduction

Complexes of nickel(II) with monotertiary phosphine (or arsine) oxides have been assigned tetrahedral, square pyramidal and D_{2d} symmetry with the help of magnetic and spectral data.[1-4] Inspite of the observation that a bulky ligand favours tetrahedral configuration, the complex $[Ni(Bu_3PO)_4](ClO_4)_2$ acquires hexacoordination on solvolysis in organic solvents.[5] Complexes of 1,1-methylenebisdipropoxyphosphine oxide (L′) 1,1-methylenebisdibutylphosphine oxide (L″) with nickel(II) having the empirical formulae, $[Ni((L')_3](ClO_4)_2$ and $NiCl_2L''_{1.5}$ have been reported.[6] In continuation of our studies,[7] the complexes of nickel(II) halides, nitrate and perchlorate with 1,2-ethylenebisdiphenylphosphineoxide (EDPO), 1,4-butylenebisdiphenylphosphine oxide (BDPO) and 1,4-butylenebisdiphenylarisne oxide (BDAO) have been prepared.

Experimental Section

The ligands were prepared as described earlier.[8]

Preparation of Complexes

1. *Dichloro(ethylenebisdiphenylphosphine oxide)-nickel(II).* 1,2-ethylenebisdiphenylphosphine oxide (0.63 g) and nickel(II) chloride hexahydrate (0.24 g) were dissolved in 30 ml and 5 ml of absolute alcohol. The two solutions were mixed and kept in a desiccator for about 15 days. The residue was redissolved in hot absolute alcohol and again kept in the desiccator for 10 days. The green crystals were picked up, washed with absolute alcohol and dried under vacuum. Yield 0.21 g, M.P. 288°. Found: C, 55.41; H, 4.47; P, 10.93; Ni, 10.28; Cl, 12.50. $C_{26}H_{24}O_2$-P_2Cl_2Ni requires C, 55.71; H, 4.28; P, 11.07; Ni, 10.53; Cl, 12.67%.

2. *Tris(ethylenebisdiphenylphosphine oxide)nickel-(II) tetrabromonickelate(II).* The ligand (0.43 g) was dissolved in hot n-butanol (5 ml) and mixed with nickel(II) bromide (0.21 g) in 50 ml of hot n-butanol. The light green complex separated out after about 30 minutes. It was filtered, washed with n-butanol, dry ether and dried under vacuum. Yield, 0.25 g, M.P. 330°. Found: C, 53.66; H, 4.45; P, 10.68; Ni, 6.70; Br, 18.43. $C_{39}H_{36}O_3P_3Br_2Ni$ requires C, 54.16; H, 4.17; P, 10.77; Ni, 6.82; Br, 18.50%.

3. *Dinitrato(ethylenebisdiphenylphosphine oxide)-nickel(II).* The ligand (2.9 g) was dissolved in n-butanol (50 ml) and nickel(II) nitrate hexahydrate (2.0 g) in 10 ml of n-butanol. The two solutions were mixed, concentrated for about 15 minutes and volume reduced to about 25 ml. A yellow complex separated out which was filtered, washed with n-butanol, dry ether and dried at 120°. Yield, 3.5 g, M.P. 284°. Found: C, 50.70; H, 4.14; P, 9.95; N, 4.30; Ni, 9.7. $C_{26}H_{24}O_8N_2P_2Ni$ requires C, 50.90; H, 3.91; P, 10.11; N, 4.56; Ni, 9.58%.

4. *Diaquobis(ethylenebisdiphenylphosphine oxide)-nickel(II) perchlorate.* The ligand (0.43 g) and nickel (II) perchlorate hexahydrate (0.36 g) were dissolved in a little excess of absolute alcohol. The metal perchlorate solution was added to the hot ligand solution

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Table I. Molar conductance and infrared data.

Complex/ligand	Molar conductance (ohm^{-1}cm^{2}mol^{-1})	Position of bands in cm^{-1} P=O/As=O	 P—C/As—C	 Water	 Nitrate/Perchlorate
EDPO		1180s,sp	1115m		
BDPO		1178s,sp	1117m		
BDAO		879s,br	1084m		
$NiCl_2(EDPO)$	0.8	1170s,sp	1115m		
$[Ni(EDPO)_3][NiBr_4]$	30.09	1170m,sp	1115m		
$Ni(NO_3)_2(EDPO)$	2.9	1170s,sp	1122m		705w, 805sh, 810m, 1015m, 1250sh, 1270vs, 1430vs, 1480vs, 1525m
$[Ni(EDPO)_2(H_2O)_2](ClO_4)_2$	43.3	1170s,sp	*	1620sp, 3400br	1080-1117s,br
$[Ni(BDPO)_2(H_2O)_2](ClO_4)_2$	48.1	1143s,sp z	*	1600sp, 3300br	1082-1118s,br
$[Ni(BDAO)_2(H_2O)_2](ClO_4)_2$	55.2	850s,br	*	1650sp, 3300br	900vw, 110s,br

* Indicates region obscured by absorption of perchlorate. vs, very strong; s, strong; sp, sharp; m, medium; br, broad; sh, shoulder; and vw, very weak.

and kept in a desiccator for 5 days when a yellow complex separated out. The complex was filtered washed with absolute alcohol and dried under vacuum. Yield, 0.32 g, M.P. 294°. Found: C, 53.96; H, 4.97; P, 10.51; Ni, 5.07; Cl, 6.19. $C_{52}H_{52}O_{14}P_4Cl_2Ni$ requires C, 54.07; H, 4.50; P, 10.74; Ni, 5.11; Cl, 6.15%.

5. *Diaquobis(butylenebisdiphenylphosphine oxide)-nickel(II) perchlorate.* The ligand (0.45 g) and nickel(II) perchlorate hexahydrate (0.36 g) were dissolved in absolute alcohol, mixed and kept in a desiccator for 2 days. The pale yellow complex was filtered, washed with absolute alcohol and dried under vacuum. Yield, 0.48 g, M.P. 268°. Found: C, 55.10; H, 5.55; P, 10.10; Ni, 4.53; Cl, 6.03. $C_{56}H_{60}O_{14}P_44Cl_2Ni$ requires C, 55.53; H, 4.95; P, 10.24; Ni, 4.87; Cl, 5.87%.

6. *Diaquobis(butylenebisdiphenylarsine oxide) nickel(II) perchlorate.* The ligand (0.55 g) in 40 ml of hot absolute alcohol was mixed with nickel(II) perchlorate hexahydrate (0.36 g) in 5 ml of absolute alcohol and kept in a desiccator for 5 days. The yellow complex was filtered, washed with absolute alcohol and dried under vacuum. Yield, 0.30 g. It decomposes at 160-65°. Found: C, 48.43; H, 4.96; Cl, 4.85; Ni, 3.90. $C_{56}H_{60}O_{14}As_4Cl_2Ni$ requires C, 48.48; H, 4.33; Cl, 5.12; Ni, 4.25%.

Physical measurements:

Toshniwal conductivity bridge type CLOI/OI, Perkin-Elmer infrared spectrophotometer Models 21 and 337 and UNICAM spectrophotometer SP 700C were used. Hexachlorobutadiene was used for the preparation of mull for recording ir spectra of nitrate complex in the region obsecured by nujol. The magnetic susceptibility measurements were made on Gouy balance[9]. The diamagnetic correction due to ligands was found experimetally (EDPO, 226; BDPO, 233 and BDAO, 270).

Discussion

Molar condustances in nitrobenzene indicate that chloro and nitrato complexes are non-electrolytes, the bromo complex is uni-univalent electrolyte, and the perchlorate complexes are uni-bivalent electrolytes. The infrared spectra of ligands and the complexes have been recorded in the range 600-4000 cm^{-1}. The most significant stretching frequencies in the ligands and complexes are due to P=O or As=O bond. The lowering of phosphoryl and arsenyl stretching frequencies in the i.r. spectra of all the nickel(II) complexes indicate that ligands are coordinated through the oxygen atoms although $\nu(P=O)$ lowering in some cases is very small[1,8,10] (10 cm^{-1}). However, in case of nickel(II) perchlorate complexes with EDPO and BDPO, the assignment of P=O stretching frequency has been made tentatively because of strong absorption by the perchlorate ion in the 1100 cm^{-1} region[10](Table I). The presence of coordinated nitrate, water and uncoordinated perchlorate ion has been indicated by the i.r. spectra[11-13].

All the nickel(II) complexes obey curie-weiss law in the temperature range 85-300°K and θ values are given in table II. The magnetic moment of octahedral nickel(II) and tetrahedral nickel(II) complexes are expected to lie in the range 2.9-3.3 B.M. and 3.6-4.2 B.M respectively. The magnetic moment of $NiCl_2(EDPO)$ has been calculated to be 2.90 ± 0.05 at different temperatures (table II). The independence of magnetic susceptibility of temperature is a charateristic feature of octahedral nickel(II) complexes. Thus the observed magnetic moment favours psendo octahedral stereochemistry[14]. The low magnetic moment may be due to metal-metal interaction since the hexacoordination is achieved by bridging through halogen[15]. Octahedral nickel(II) complexes show three spin allowed electronic transitions which occur in the range 7000-13000, 11000-20000 and 19000-27000 cm^{-1} with low intensities. The assignment of psendo octahedral structure is also supported by reflectance spectra[16,18] (Table III).

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Table II. Magnetic susceptibility data

S.No.	Complex	Temp/K	$10^6 . \chi_g$ cgsu	$10^6 . \chi_m$ cgsu	$10^6 . \chi_{m'}$ cgsu	$\mu_{eff} = 2.828(\chi_{m'} . T)^{1/2}$	θ
1.	$NiCl_2(EDPO)$	86.6	20.43	11440	11719	2.85	−8
		125.4	14.04	7862	8141	2.85	
		227.4	7.6	4257	4536	2.88	
		296.0	6.085	3404	3683	2.95	
2.	$[Ni(EDPO)_3][NiBr_4]$	84.5	22.4	19354	19766	3.66	−16
		136.8	13.12	11336	11748	3.62	
		263.0	6.84	5910	6322	3.66	
		294.5	5.98	5166	5578	3.61	
3.	$Ni(NO_3)_2(EDPO)$	85.0	25.32	15774	16051	3.30	−12
		136.0	15.83	9704	9981	3.30	
		256.0	8.60	5272	5549	3.36	
		294.5	7.21	4419	4696	3.32	
4.	$[Ni(EDPO)_2(H_2O)_2](ClO_4)_2$	86.0	13.20	15230	15785	3.29	6
		133.5	8.29	9566	10121	3.27	
		256.0	4.01	4627	5182	3.25	
		293.2	3.54	4085	4640	3.28	
5.	$[Ni(BDPO)_2(H_2O)_2](ClO_4)_2$	85.0	12.13	14677	15246	3.21	8
		133.5	7.19	8699	9268	3.14	
		263.5	3.25	4053	4622	3.13	
		294.1	2.93	3545	4114	3.10	
6.	$[Ni(BDAO)_2(H_2O)_2](ClO_4)_2$	83.5	11.32	15689	16332	3.29	−6
		133.2	6.66	9230	9873	3.22	
		258.5	3.23	4476	5119	3.21	
		282.1	2.94	4074	4717	3.22	

Table III. Assignment of electronic transition

Electronic transition	$NiCl_2(EDPO)$	$[Ni(EDPO)_3]$-$[NiBr_4]$	$Ni(NO_3)_2$-(EDPO)	$[Ni(EDPO)_2(H_2O)_2]$-$(ClO_4)_2$	$[Ni(BDPO)_2(H_2O)_2]$-$(ClO_4)_2$	$[Ni(BDAO)_2(H_2O)_2]$-$(ClO_4)_2$
$^3T_{2g}(F) \leftarrow {}^3A_{2g}$	7400	8600	7400	7400	7300	8200
$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	14100	13100 [a]	12400	12500	12600	13000
$^1E_g \leftarrow {}^3A_{2g}$	15100	13900	14000sh	14650	15000sh	14600sh
$^3T_{1g}(P) \leftarrow {}^3A_{2g}$	22850	22900	22500	23600	23800	24100
		27000 [b]				
$^3A_2 \leftarrow {}^3T_1$		6800				
		(6950)				
$^1E \leftarrow {}^3T_1$		10500				
		(11630)				
$^3T_1(P) \leftarrow {}^3T_1$		13100 [a]				
		(13230)				
$^1T_2 \leftarrow {}^3T_1$		18000				
		(21190)				
Calculated						
Dq	739	862	742	742	748	775
Dq/B	0.85	1.175	0.883	0.805	0.805	0.84
B	870	736	841	921	928	922

[a] This band may result due to the overlap of bands of the anion as well as cation. [b] Most likely charge transfer band. The values in parentheses are the bands reported for $[NiBr_4]^{2-}$ ion.

The bromo complex, $[Ni(EDPO)_3][NiBr_4]$ has magnetic moment of 3.52±0.05 B.M which is quite close to the root mean square value of octahedral $[Ni(EDPO)_2(H_2O)_2]^{2+}$ and tetrahedral $[NiBr_4]^{2-}$ ions. The independence of magnetic susceptibility together with bands in the reflectance spectrum support that the complex is a mixture of octahedral and tetrahedral species[6,16,17]. The bands at 13000 and 13900 cm^{-1} in the reflectance spectrum has been assigned to $^3T_{1g}$ (F)$\leftarrow {}^3A_{2g}$ and $^1E_g \leftarrow {}^3A_{2g}$ respectively since Dq/B is 1.175. It appears that the former band has mixed up with spin allowed $^3T_1$ (P)$\leftarrow {}^3T_1$, transition of tetrahedral nickel(II) species[16]. This assignment takes into consideration, the spectrum of $[NiBr_4]^{2-}$ which has been reported in literature[15].

The magnetic moments of nitrate and perchlorate complexes are of the order 3.10-3.30 B.M and suggest an octahedral stereochemistry, also supported by their reflectance spectra(Table III). It is of interest to note that in the two nickel(II) perchlorate complexes with EDPO and BDPO, the Dq value is lower than that of analogous BDAO complex. This supports the view that ditertiaryphosphine oxides are weaker ligands than ditertiaryarsine oxides. Hexacoordination in the perchlorate complexes appear to have been achieved by coordination of two bidentate ligands and two water molecules.

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