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Octahedral Nickel(II) Complexes of a Stibene–Phosphine Ligand

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As part of a study[1] of the nickel(II) complexes of a range of bidentate ligands with *o*-phenylene backbones and group VB donors, o-$C_6H_4(EPh_2)(E'Ph_2)$ (E, E′ = P, As, Sb) we prepared $Ni(sbp)X_2$ (sbp = *o*-diphenylphosphinophenyldiphenylstibine, o-$C_6H_4(SbPh_2)(PPh_2)$; X = Br, I). Unlike the planar 1:1 complexes of the other ligands in the series the $Ni(sbp)X_2$ were paramagnetic and had anomalous electronic spectra which we tentatively suggested might be due to planar ⇌ tetrahedral isomerism.[1] More detailed studies reported here have shown this tentative suggestion to be erroneous.

The $Ni(sbp)X_2$ complexes, obtained[1] by reaction of excess NiX_2 with sbp in boiling *n*-butanol, are insoluble in all common solvent in which they do not decompose. Attempts to prepare analogues with X = Cl, NCS, or CN in a variety of solvents were unsuccessful. The green $Ni(sbp)I_2$ has μ_{eff} = 3.02 B.M., the moment being temperature independent and following the Curie Law (Table). A study of its reflectance spectrum reveals that in addition to the absorption reported previously (27.3, 24.7, 17.8, 12.7 × 10^3 cm^{-1}) there is a weak broad absorption at ~ 8.3 × 10^3 cm^{-1}. Thus, the magnetic and electronic spectral data are consistent with a pseudo-octahedral nickel(II) environment.

The brown $Ni(sbp)Br_2$ has μ_{eff} = 2.16 B.M., also temperature independent, and exhibits ϵ_{max} (diffuse reflectance) at 27.0, 20.6, 17.6sh, 14.7, 8.8 × 10^3 cm^{-1}, which can be interpreted as due to a 1:1 mixture of planar and pseudo-octahedral molecules.[2] Although ligand absorptions partially obscure the infrared region where ν(Ni–Br) is expected, the tentative identification of Ni–Br stretches at 260, 215 cm^{-1} is consistent with two different coordinated environments.

TABLE. Magnetic Data.

T °K	$\chi_M^{corr} \times 10^6$ cgs	$1/\chi_M^{corr}$	μ_{eff} B.M.
$Ni(sbp)Br_2$			
333.1	1737	575.7	2.16
313.1	1814	551.3	2.14
293.1	1905	524.9	2.12
253.1	2134	468.6	2.09
213.1	2500	400.0	2.07
173.1	3080	324.7	2.07
133.1	4056	246.5	2.09
93.1	6085	164.3	2.14
$Ni(sbp)I_2$			
333.1	3393	295	3.02
293.1	3860	259	3.02
253.1	4319	231	2.97
213.1	5033	199	2.94
163.1	6522	153	2.93
123.1	8914	112	2.97
103.1	10899	91.8	3.00

The occurrence of pseudo-octahedral geometry in heavy group VB donor ligand complexes of nickel(II) is rare, the known examples being $Ni(F\text{-}das)_2X_2$ [3] (F-das = o-$C_6F_4(AsMe_2)_2$), $Ni(dasp)X_2$ [4] (dasp = $PhMeAs(CH_2)_3AsPhMe$), and possibly $[Ni(cis\text{-}edas)Cl_2]_n$ [5] (*cis*-edas = $Me_2AsCH{=}CHAsMe_2$). The tendency of sbp to promote six-coordination is a further example of the ability of antimony ligand to produce a higher coordination number than do similar phosphines or arsines.[1,6]

The analytical, spectroscopic, and magnetic measurements reported here are highly reproducible.

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