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Some Possible New Internal Pressure Calibrants*†

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Nickel dimethylglyoxime ($Ni(DMG)_2$) has been extensively used for calibration of high pressure equipment.[1-2] Davies[2] has constructed a pressure calibration curve relating the spectral shift of the $Ni(DMG)_2$ visible absorption band to known freezing pressures of 14 liquids. A recent study[3] of pressure effects on the ligand-field spectra of five-coordinate, trigonal-bipyramidal Ni(II) complexes, has resulted in the observation that some of these complexes may be more satisfactory than $Ni(DMG)_2$ for use as internal pressure calibrants. The complexes are of the type [NiLX]Y, where L is a tetradentate "tripod" ligand and usually $X \neq Y$ and are halogen, pseudo-halogen or polyatomic anions. These complexes demonstrate a blue shift with pressure of the order of 33-71 cm^{-1}/kbar. Table I summarizes the pressure behavior of $Ni(DMG)_2$ and the [NiLX]Y complexes. The [NiLX]Y band, in most cases, becomes more symmetrical, and shows little change in peak intensity with pressure and has a higher plastic flow than $Ni(DMG)_2$. These features make these complexes highly suitable as internal pressure calibrants for high pressure studies. A serious limitation to the use of these calibrants may be that they are not commercially available as yet.

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TABLE I

Comparison of High Pressure Behavior of $Ni(DMG)_2$ and Trigonal-Bipyramidal Ni(II) Complexes of the Type [NiLX]Y

[NiLX]Y Complexes	$Ni(DMG)_2$
$\epsilon = 1 \times 10^3$ to 4.5×10^3	$\epsilon = \sim 3 \times 10^3$
Blue shift	Red shift
~ 33-71 cm^{-1}/kbar	~ 80 cm^{-1}/kbar
Little change in peak intensity	Decrease in intensity
Band more symmetrical	Band broadens
More plastic - easier to thin sample and obtain a parabolic distribution across diamond faces	Less plastic
Must be synthesized	Commercially available

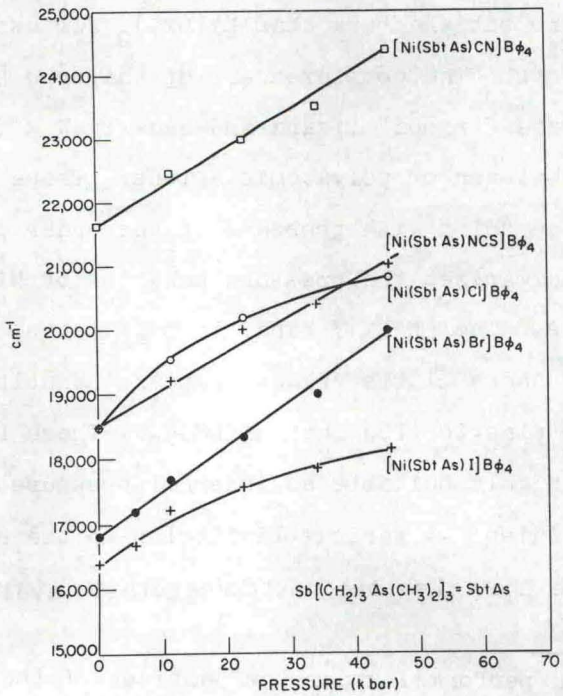

Fig. 1. Pressure Dependencies of the Ligand-Field Absorption in Several [Ni(SbtAs)X]Y Complexes.

Figure 1 shows the effects of pressure on the [Ni(SbtAs)X]Y complexes, where SbtAs = $Sb[(CH_2)_2As(CH_3)_2]_3$.

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