

Some Possible New Internal Pressure Calibrants^{*†}

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Nickel dimethylglyoxime ($\text{Ni}(\text{DMG})_2$) has been extensively used for calibration of high pressure equipment.¹⁻² Davies² has constructed a pressure calibration curve relating the spectral shift of the $\text{Ni}(\text{DMG})_2$ visible absorption band to known freezing pressures of 14 liquids. A recent study³ 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 $\text{Ni}(\text{DMG})_2$ for use as internal pressure calibrants. The complexes are of the type $[\text{NiLX}]\text{Y}$, 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 $33\text{-}71 \text{ cm}^{-1}/\text{kbar}$. Table I summarizes the pressure behavior of $\text{Ni}(\text{DMG})_2$ and the $[\text{NiLX}]\text{Y}$ complexes. The $[\text{NiLX}]\text{Y}$ band, in most cases, becomes more symmetrical, and shows little change in peak intensity with pressure and has a higher plastic flow than $\text{Ni}(\text{DMG})_2$. 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 $\text{Ni}(\text{DMG})_2$ and Trigonal-Bipyramidal $\text{Ni}(\text{II})$ Complexes of the Type $[\text{NiLX}]_2\text{Y}$

$[\text{NiLX}]_2\text{Y}$ Complexes	$\text{Ni}(\text{DMG})_2$
$\epsilon = 1 \times 10^3$ to 4.5×10^3	$\epsilon = \sim 3 \times 10^3$
Blue shift	Red shift
$\sim 33\text{-}71 \text{ cm}^{-1}/\text{kbar}$	$\sim 80 \text{ cm}^{-1}/\text{kbar}$
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

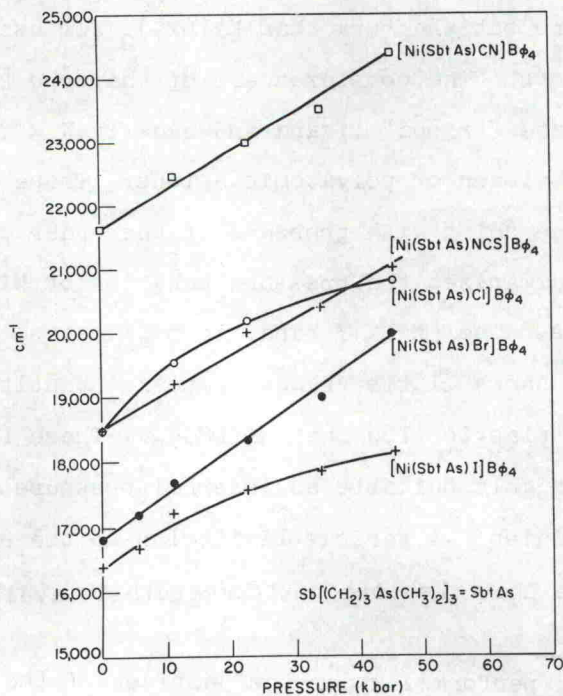


Fig. 1. Pressure Dependencies of the Ligand-Field Absorption in Several $[\text{Ni}(\text{SbtAs})\text{X}]\text{Y}$ Complexes.