

Some Possible New Internal Pressure Calibrants<sup>\*†</sup>

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Nickel dimethylglyoxime ( $\text{Ni}(\text{DMG})_2$ ) has been extensively used for calibration of high pressure equipment.<sup>1-2</sup> Davies<sup>2</sup> 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 study<sup>3</sup> of pressure effects on the ligand-field spectra of five-coordinate, trigonal-bipyramidal  $\text{Ni}(\text{II})$  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  $\text{X} \neq \text{Y}$  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.

\* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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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  $[\text{NiLX}]\text{Y}$

$[\text{NiLX}]\text{Y}$ Complexes	$\text{Ni}(\text{DMG})_2$
$\epsilon = 1 \times 10^3$ to $4.5 \times 10^3$	$\epsilon = \sim 3 \times 10^3$
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

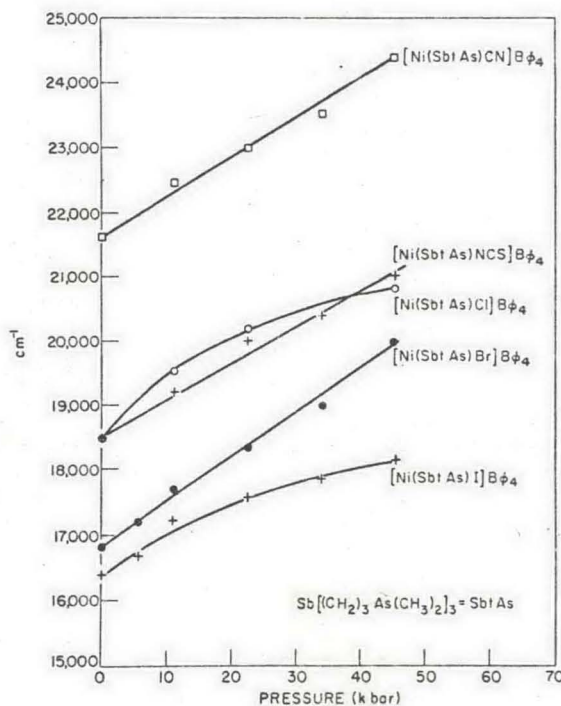


Fig. 1. Pressure Dependencies of the Ligand-Field Absorption in Several  $[\text{Ni}(\text{SbAs})\text{X}]\text{Y}$  Complexes.

Figure 1 shows the effects of pressure on the  $[\text{Ni}(\text{SbtAs})\text{X}]\text{Y}$  complexes, where  $\text{SbtAs} = \text{Sb}[(\text{CH}_2)_2\text{As}(\text{CH}_3)_2]_3$ .

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#### References

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