

Some Possible New Internal Pressure Calibrants^{*†}

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(Received 1 July 1970)

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 $\text{Ni}(\text{II})$ 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 $X \neq Y$ 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.

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

† Presented at the 21st Mid-America Symposium on Spectroscopy, June 2-5, 1970, Chicago, Illinois.