Studies of Monothiomalonamide and its Palladium(II) and Platinum(II) Complexes

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A project related to the crystal engineering of hydrogen bonded coordination complexes has been initiated and our first results are presented here. The \textit{cis} and \textit{trans} forms of monothiomalonamide (LH\textsubscript{2}) have been fully characterized by vibrational spectroscopy, thermal techniques and single-crystal X-ray diffraction. The \textit{cis} form crystallizes in the monoclinic space group \textit{P}2\textsubscript{1}/\textit{c} and the \textit{trans} form in the monoclinic space group \textit{C}2\textsubscript{1}/\textit{c}. The respective lattice constants are \(a = 5.602(3), b = 9.055(2), c = 10.945(5) \text{ Å}, \beta = 101.29(2)^\circ\) (\textit{cis}-LH\textsubscript{2}) and \(a = 20.336(7), b = 4.317(1), c = 12.432(5) \text{ Å}, \beta = 92.16(1)^\circ\) (\textit{trans}-LH\textsubscript{2}). The new complexes \([\text{Pd(LH}_2)_2]X_2\) (X = Cl, Br), \([\text{Pt(LH}_2)_2]X_2\) (X = Cl, Br, I) and \([\text{PtX}_2(LH}_2)_2\) (X = Cl, I) were prepared and characterized by elemental analyses and spectroscopic (IR, far-IR, Raman) studies. All data are discussed in terms of the nature of bonding in conjunction with assigned structures. The LH\textsubscript{2} molecule behaves as a monodentate ligand binding through the sulfur atom. Monomeric square planar structures are assigned for the metal complexes in the solid state; the 1:2 complexes have the \textit{trans} geometry. A detailed comparison of the new complexes with the corresponding monothiooxamide complexes is also presented.