

^1H , ^{13}C , ^{15}N NMR AND IR SPECTROSCOPIC STUDIES OF A Rh(II) COMPLEX OF THIOUREA

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A rhodium(II) complex of thiourea (Tu), $\text{Rh}_2(\text{OAc})_4\text{Tu}_2$, has been prepared from $\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ and characterized. A shift of the $\nu(\text{N}-\text{H})$ vibration towards higher frequencies in the IR spectrum is consistent with sulfur coordination to rhodium(II). ^{13}C NMR spectra recorded in $\text{DMSO}-d_6$ reveal that thiourea is replaced by $\text{DMSO}-d_6$ solvent, followed by replacement of acetate ions by free thiourea. ^{15}N NMR indicates some nitrogen involvement in coordination to form an S–N chelate.

Keywords: Rhodium acetate; Thiourea; NMR; IR; Exchange phenomena

INTRODUCTION

The ability of thiourea (Tu) to form stable adducts with a variety of transition metals (Cu, Ag, Au and Pt) is well established and the structures of several such complexes have been determined [1–6]. Fatima *et al.* [7] studied the reactions of mono-, di- and tri-substituted thiourea with chloride salts of Pd(II), Pt(IV), Rh(III) and Ir(III) and on the basis of IR data suggested S coordination in all Tu derivatives. Daniele and co-workers [8] investigated the behaviour of substituted thioureas with rhodium(I) and reported the crystal structure of a dinuclear, sulfur-bridged rhodium(I) complex. In 1993 Carlos and co-workers [9] studied the reaction of thiocyanate and thiourea with rhodium(III) aqua ions. However, it was Mal'kova and Shafranskii [10] who first reported infrared spectroscopic and thermogravimetric studies of thiourea compounds of dirhodium(II) tetraacetate. Structural studies [2–5] using spectroscopic techniques (IR and NMR) of thiourea complexes of silver(I), $[\text{Ag}(\text{Tu})_2\text{Cl}]$, $\text{Ag}(\text{Tu})_2\text{SCN}$ and $\text{Ag}(\text{Tu})_3\text{ClO}_4$ have shown that Tu can act both as a bridging and terminal ligand (Scheme 1).

In order to observe the coordination behaviour of Tu with rhodium(II) acetate, we have prepared the Rh(II)–Tu complex. Additionally, we have also investigated exchange phenomenon of the Tu ligand with acetate ion in dimethylsulfoxide using ^1H , ^{13}C and ^{15}N NMR spectroscopy. The complexes were characterized by elemental

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