Synthesis, Characterization, and Biological Studies of Some Schiff Base Complexes

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Received July 14, 2006

Abstract—The synthesis of a new Schiff base derived from 2-hydroxy-5-chloroacetophenone and 4-amino-5-mercapto-3-methyl-1,2,4-triazole and its coordination compounds with Ti(III), VO(IV), Cr(III), Mn(III), Fe(III), Zr(IV), MoO₂(VI), and UO₂(VI) are described. The ligand and the complexes have been characterized on the basis of analytical, electrical conductance, molecular weight, IR and electronic spectra, magnetic susceptibility measurements, and thermogravimetric analysis. The ligand acts as a dibasic tridentate molecule. Antibacterial activities of the ligand and its metal complexes have been determined by screening the compounds against E. coli, S. typhi, P. aeruginosa, and S. aureus. The solid state dc electrical conductivity of the ligand and its complexes have been measured over 313–403 K, and the complexes were found to be of semiconducting nature.

DOI: 10.1134/S1070328407100077

Metal complexes of Schiff bases have been widely studied due to their unusual magnetic properties, novel structural features, and relevance to biological systems [1]. A number of Schiff base complexes [2, 3] have been tested for antimicrobial activities, and they have found to exhibit bacteriostatic and fungistatic activities. The formation of stable complexes is facilitated by the presence of functional groups, such as SH and/or OH sufficiently near to the azomethine moiety. Although there has been considerable interest in Schiff base complexes of the first transition series metal ions [4, 5], little work has been reported on such complexes with higher valent metal ions.

It was, therefore, of interest to synthesize and characterize a Schiff base derived from 2-hydroxy-5-chloroacetophenone and 4-amino-5-mercapto-3-methyl-1,2,4-triazole and its metal complexes with tri-, tetra-, and hexavalent metal ions.

EXPERIMENTAL

4-amino-5-mercapto-3-methyl-1,2,4-triazole, manganese(III) acetate dihydrate, bis(acetylacetonato)dioxo-molybdenum(VI), zirconium acetate, and 2-hydroxy-5-chloroacetophenone were synthesized according to published procedures [6–8]. Chromium chloride hexahydrate, ferric chloride (anhydrous), titanium trichloride (anhydrous), and uranyl nitrate hexahydrate (S.D.’s fine chemicals) were used for synthesis.

**Synthesis of ligand (HCASTZ).** An ethanolic solution (25 ml) of 4-amino-5-mercapto-3-methyl-1,2,4-triazole (2.6 g, 0.02 mol) was added with stirring to an ethanolic solution (25 ml) of 2-hydroxy-5-chloroacetophenone (3.4 g, 0.02 mol). The mixture was refluxed for 5 h in the presence of few drops of piperidine. The solvent was then partially evaporated, and the yellow crystalline product obtained was dried under vaccum, yield 70%, mp 218°C. 1H NMR: 12.10 (1H, s., phenolic OH); 11.58 (1 H, s., imino NH); 2.80 (3 H, s., methyl); 2.3 (3 H, s., triazole–CH₃); 7.1, 7.4, and 8.3 ppm (3 H, m., phenyl). The schematic representation of the synthesis of HCASTZ and its tautomeric forms is shown below:

![Diagram of ligand and complexes](image)
Synthesis of complexes. Equimolar quantities of the Schiff base and appropriate metal acetate/metal chloride were dissolved separately in DMF (25 ml) and ethanol, respectively, and mixed under hot conditions. The mixture was refluxed for 3–5 h with constant magnetic stirring using CaCl₂ guard tube. On cooling to room temperature, the solid product was obtained. The product was filtered off, washed with hot water, alcohol, DMF, and petroleum ether, and finally dried under vacuum at room temperature. The yield was 70–80%.

Physical measurements. Elemental analysis was carried out at the microanalytical laboratory (CDRI, Lucknow). Sulfur was estimated as barium sulfate by the Messengers method. The molecular weights were determined by the Rast Camphor method. Metal contents of the complexes were analyzed using standard methods. IR spectra were recorded on a Perkin-Elmer RX–1 spectrophotometer using KBr pellets.

IR spectra. The infrared spectrum of 2–1 Cl–1 Elemental analysis was stretches at 1634 and 1545 cm⁻¹. The IR spectrum of the complexes was recorded on a Cary–2390 spectrophotometer using MgO as reference. The VO(IV) complex displays a strong band at 969 cm⁻¹ due to ν(C=O) modes, respectively. The separation of these peaks by ~200 cm⁻¹ indicates the monodentate coordination of the acetato group to the Mn³⁺ ion. It further exhibits a band at 651 cm⁻¹ due to δ(C=O), which is considered as a diagnostic band for a monodentate ligand. The VO(IV) complex displays a strong band at 969 cm⁻¹ due to the ν(C=O) band in the spectrum of the zirconium(IV) complex, the absence of ν(C=O) (Zr = O) favors the formation of Zr(OH)$_3$ and not Zr = O. The new band at 1140 cm⁻¹ has been assigned to the δ(Zr–OH). The MoO$_2$(VI) and UO$_2$(VI) complexes exhibit a single band at 935 and 920 cm⁻¹ due to ν$_{as}$(O=Mo=O) and ν$_{as}$(O=U=O) stretching, indicating trans structures. The presence of coordinated water in the complexes, except for VO(IV), is indicated by a broad band in the region 3450–3367 cm⁻¹ and two weaker bands in the regions 840–820 and 726–700 cm⁻¹ assigned as the OH rocking and wagging vibrations, respectively [10].

Electronic spectra and magnetic measurements. The reflectance spectrum of the Ti(III) complex exhibited a broad band in the range 18552–20449 cm⁻¹ due to $^3T_{2g} \rightarrow ^3E_g$ transition in an octahedral symmetry. The Cr(III) complex exhibits three bands at 16207, 21880, and 35842 cm⁻¹ due to the $^4A_{2g} \rightarrow ^4T_{2g}$, $^4A_{2g} \rightarrow ^4T_{1g}$, and $^4A_{2g} \rightarrow ^4T_{1g}(P)$ transitions, respectively, suggesting an octahedral geometry around the Cr³⁺ ion. The reflectance spectral parameters for Cr(III) are found to be $D_q = 1620$ cm⁻¹, $B = 606$ cm⁻¹, $\beta = 0.66$, $\beta^0 = 34.0$, and CFSE = 193 kJ mol⁻¹. The reduction of the Racah parameter ($B$) from the free ion value of 918 to 606 cm⁻¹ and $\beta^0$ value of 34% indicates the covalent nature of the Cr(III) complex [11]. The reflectance