

A B S T R A C T

The thesis describes the isolation and characterization of the complexes of Ru(III) and Ru(II), Rh(III) and Rh(I), Os(VI), Os(IV) and Os(II) and Ir(I) with the thioligands (HL) namely amidinothiourea (HATU) and its N-methyl (HNMATU) and S-ethyl (HSEATU) derivatives. A number of mixed ligands carbonyl complexes of Ru(II), Rh(I) and Ir(I) containing these thioligands have also been prepared and their structures discussed.

Both tris- and bis (ligand) complexes of the type ML_3 and $ML_2L'_2$ ($M = Ru^{III}, Rh^{III}$; HL = thioligand molecule, $L' = H_2O, py$) respectively were isolated by direct reaction between the appropriate metal halide and the respective ligand in nonaqueous medium. The ligands HATU, and HSEATU behave either as SN or NN donor ligands to Ru(III) in their complexes while HNMATU always behaves as SN donor under this condition. In other cases, the ligands behave as SN donors. The SN bonded Ru(III) and Rh(III) compounds could be protonated to yield the corresponding complex salts of composition $M(HL)_3^{3+}$ or $[M(HL)_2L'_2]^{3+}$ depending on the starting materials. Some dinuclear complexes of Rh(III) with chloride bridge or Ru(III) complexes with S bridge have also been isolated. the ligand replacement reaction involving the exchange of L' with other monodentate ligand in $ML_2L'_2$ and bridge cleavage reactions in the dinuclear complexes have been performed successfully.

The Ru(II) and Rh(I) complexes were prepared either by direct reaction of the corresponding metal halide with the ligand in presence of reducing agents or by ligand exchange reactions

involving Ru(II) or Rh(I) complexes and the thioligands. Reactions of IrCl_3 with the thioligands led to the isolation of Ir(I) complexes where the thioligands themselves behaved as reducing agent.

The Os^{VI} complexes are the nitrido complexes while Os^{IV} complexes prepared either from K_2OsCl_6 or KOsBr_5 always contained two SN donor ligands in the coordination zone. The group trans to $\text{Os} \equiv \text{N}$ bond in OsNL_2X ($\text{X} = \text{H}_2\text{O}$) are easily replaceable by other monodentate neutral groups.

The physical and chemical properties of these complexes have been discussed in detail.

The carbonylating agents used for the preparation of Ru(II), Rh(I) and Ir(I) mixed ligand carbonyl complexes was the refluxing DMF. In some cases, the compounds were prepared by ligand exchange reaction using some metal carbonyl complexes containing other ligands.

Ru(II) produces both mono and dicarbonyl complexes and both cis- and trans- dicarbonyl complexes were isolated. Only the mono carbonyl complexes of Rh(I) and Ir(I) containing one thioligand per molecule were possible to isolate. The stabilities of these complexes towards various chemical attacks were investigated.

The tentative structures of these complexes were suggested on the basis of analytical results, chemical properties and vibrational, electronic and pmr spectral analysis. The results indicate distorted octahedral structures for all these complexes except those of Rh(I) and Ir(I), which are suggested to have square planar geometries.
