

SUMMARY

This thesis reports the syntheses, characterization and probable structures of metal complexes of 1-amidino-2-thiourea (HATU), S-ethyl-1-amidino-2-thiourea (HSEATU) and N-methyl- and N-ethyl-1-amidino-2-thiourea (HNMATU/HNEATU). Simple complexes of Cu^{II} , Ni^{II} , Co^{II} , Co^{III} , Pd^{II} and Pt^{II} , nitrosyl complexes of Co^{III} , Ru^{II} and Fe^{I} and Cu^{I} , Ag^{I} and Zn^{II} complexes with these ligands have been described.

The first chapter gives a brief review of the metal complexes with SN donor ligands. The synthesis, characterization, reactions and structures of metal complexes with bidentate and polydentate sulphur and nitrogen donor ligands have been described.

The most probable structures of the present thioligands and their metal complexes in relation to those of biguanides and dithiobiurets have been suggested in Chapter II. The following structures having delocalized π -electron system throughout the chelate ring have been presented for the thioligands.

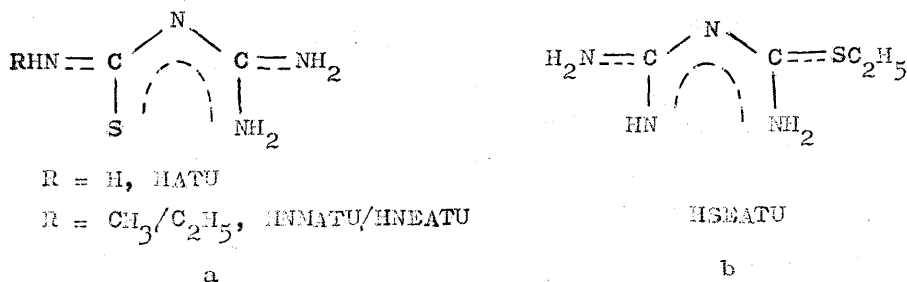


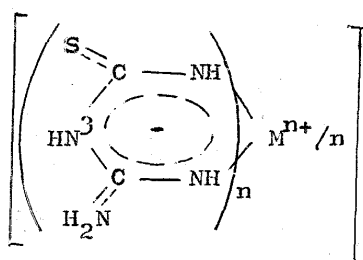
Fig. I

The dependence of the mode of coordination of these ligands on the pH of the reaction medium has been discussed. In alkaline medium, HATU and HSEATU behave as NN donors while in neutral or



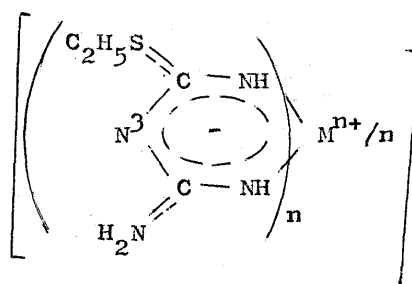
slightly acidic medium they act as SN donors. Like metal complexes of biguanides and dithiobiurets, the protonation of the central nitrogen atom (i.e. N^3 atom) during the conversion of inner to cationic complexes has been suggested. Following structures have been thought to be most probable for these metal complexes.

1. NN bonded complexes.



$M(ATU)_n$

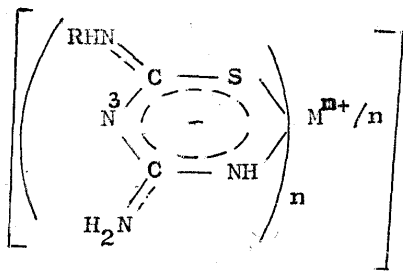
a



$M(SEATU)_n$

b

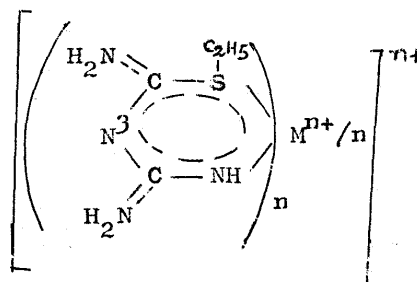
2. SN bonded complexes.



$R = H, M(ATU)_n$

$R = CH_3/C_2H_5, M(NMATU/NEATU)_n$

c



$[M(HSEATU)_n]^{n+}$

d

Fig. 2

In the case of inner metallic complexes, the presence of protonated N^3 atom in 2a and deprotonated ones in 2b and 2c suggest the existence of only inner metallic complexes for the former and both inner metallic and cationic complexes for the latter pairs. Again the structure 2d for cationic complexes excludes the formation of corresponding inner metallic complexes.

The isolation, characterization and probable structures of chelates having NN or SN donor ligands have been described in Chapter III. HNMATU always forms SN bonded while HATU and HSEATU form both SN and NN coordinated compounds depending on the nature of the metal atom and the experimental conditions.

NN bonded complexes : The complexes ML_n , $[CrL_2(OH)]_2$, ($M = Ni^{2+}$, $n = 2$, $M = Co^{3+}/Cr^{3+}$, $n = 3$ and $L = ATU^-$), NiL'_2 , $M(HL')_2X_2$, $[M'(HL')_n(H_2O)_2] X_{n+1}$ ($M = Cu^{2+}/Ni^{2+}$, $M' = Cu^{2+}$, $n = 1$, $M' = Co^{3+}$, $n = 2$, $HL' = HSEATU$, $X = \text{halide, } NO_3^-, \frac{1}{2} SO_4$) are of this type. The physico-chemical properties of these complexes are comparable to those of corresponding metal biguanides. The metal complexes with HATU are all inner metallic type and isolated in strongly alkaline medium. The cationic complexes could not, however, be isolated.

The inner metallic complexes of HSEATU were prepared in slightly alkaline medium and are converted to the corresponding cationic complexes by treatment with NH_4X solution. The properties of these complexes are comparable to those of biguanides and N' -amidinoisoureas and suggest the structure 2b for the inner metallic compounds. The red $[Cr(ATU)_2(OH)]_2$ is suggested to be

dimeric with hydroxy bridging from its high insolubility, spectral data and subnormal magnetic moments ($\mu_{\text{eff}} = 3.30 \text{ BM}$). The addition of HX (X = Cl/Br) to rose red $\text{Cu}(\text{HSEATU})_2\text{X}_2$ produced the blue diaquocomplexes $[\text{Cu}(\text{HSEATU})(\text{H}_2\text{O})_2]\text{X}_2$ having properties similar to those of the corresponding metal biguanides.

The values of Δ_1 for Ni^{II} , 10 Dq and β for Co^{III} and Cr^{III} and Z value for Cr^{III} complexes suggest the presence of NN coordination in them. I.r. spectral data also support this. Pmr spectra of Ni^{II} complexes indicate the presence of strong chelate ring current and confirm the structure 2a for HATU and 2b for HSEATU complexes.

SN bonded complexes : All metal complexes with HNMATU, Pd^{II} and Pt^{II} complexes with HATU and HSEATU, red Ni^{II} and brown Co^{II} and Co^{III} complexes with HATU are in this class. For HATU and HNMATU, both inner metallic and cationic complexes have been isolated, the formers being converted to the latter by NH_4X and vice-versa by alkali. Only SN coordinated cationic mono chelates of Pd^{II} and Pt^{II} with HSEATU have been synthesized and attempts to isolate the corresponding bis(chelate) or innermetallic ones were unsuccessful.

These compounds generally decompose by warm alkali to the corresponding metal sulphides except $\text{Ni}(\text{HATU})_2\text{X}_2$ which, however, changes to NN bonded orange yellow complex, $\text{Ni}(\text{ATU})_2$ in presence of water or alkali. The infrared spectral data, Δ_1 values for d^8 metal complexes and 10 Dq and β values for Co^{III} compounds suggest the presence of SN bonding in these chelates.

On these basis, the structures 2c for inner metallic complexes of HATU and HNMATU and 2d for the cationic complexes of HSEATU have been suggested. These are also supported by pmr spectral data of Ni^{II} and Pd^{II} complexes.

The syntheses, characterization and probable structures of Co^{III}, Ru^{II} and Fe^I nitrosyls are reported in Chapter IV of this thesis. Cobalt nitrosyls contain either NN or SN donor ligands while ruthenium and iron nitrosyls contain only SN bonded ligands.

The violet cobalt nitrosyls of formula $[\text{CoL}_2(\text{NO})(\text{H}_2\text{O})]$, $[\text{Co}(\text{HL}')_2(\text{NO})(\text{H}_2\text{O})]\text{X}_2$, $[\text{Co}(\text{HL}'')(\text{NO})\text{SO}_4\text{Y}]$ (HL = HATU, HL' = HSEATU or $1/2 \text{H}_2\text{endbg}$, HL'' = Hbg, X = Cl, Br, OH, $1/2\text{SO}_4$, Y = H_2O , py) have been synthesized either in alkaline (for inner metallic) or in neutral medium (for cationic complexes). The complexes are stable towards nucleophilic reagents i.e. OH^- , NH_3 , $\text{NH}_2\text{-NH}_2$ etc. and the NO group undergoes oxidation by air or H_2O_2 to produce the corresponding NO_2 complexes. The thermal analysis and the splitting of ${}^1\text{A}_{1g} \longrightarrow {}^1\text{T}_{1g}$ band relative to that of orange $\text{Co}(\text{ATU})_3$ indicates the presence of transaquonitrosyl group^s. The ν NO band at $\sim 1600 \text{ cm}^{-1}$, the splitting of $\nu \bar{\text{N}}\text{-}\bar{\text{C}}\text{-}\bar{\text{N}}$ band, the diamagnetism of these complexes and the similarity of their electronic spectra with those of $[\text{Co}(\text{Hbg})_2(\text{NO})(\text{H}_2\text{O})]\text{X}_2$ and finally the pmr spectra of $[\text{Co}(\text{ATU})_2(\text{H}_2\text{O})(\text{NO})]$ suggest the following structure with bent nitrosyl having strong chelate ring current.

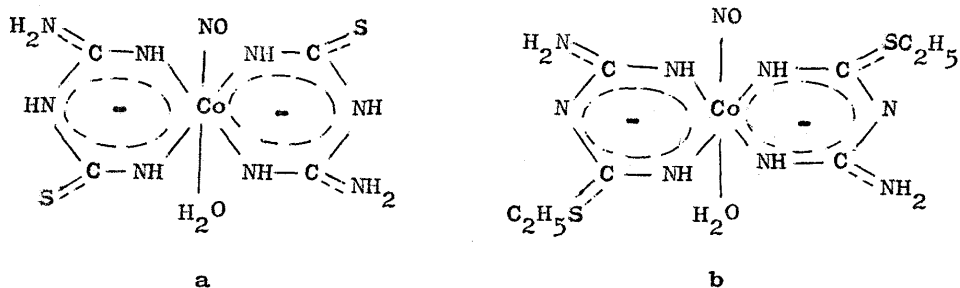


Fig. 3

The complexes, $[\text{CoL}_2(\text{NO})(\text{H}_2\text{O})]$ (green), $[\text{RuL}'(\text{H}_2\text{O})(\text{NO})\text{Cl}_2]$ (brown) and $[\{\text{FeL}'(\text{NO})\}_2\text{SO}_4]$ (light green) (HL = HNMATU, HL' = HATU) are suggested to contain SN bonded chelate. The green cobalt nitrosyls are less sensitive to electrophilic reagents and aerial oxidation relative to the corresponding violet compounds. Ruthenium and iron nitrosyls decompose by dilute alkali but not by dilute acids. The cobalt and ruthenium nitrosyls are diamagnetic while the iron nitrosyl is paramagnetic ($\mu = 2.2$ BM). The ν NO values observed at ~ 1650 , ~ 1800 and ~ 1850 cm^{-1} for Co^{III} , Ru^{II} and Fe^{I} complexes respectively suggest the presence of NO^- in the former and NO^+ in the latter pair of complexes. The vibrational and electronic spectral data suggest the presence of SN coordination in them.

Chapter V begins with a brief discussion on the compounds of Cu^{I} and Ag^{I} and deals with the preparation and properties of Cu^{I} , Ag^{I} and Zn^{II} complexes with these thioligands. Some mixed ligand complexes of Cu^{I} with triphenylphosphine have also been described. The dimeric structures for $[\text{Cu}(\text{HL})\text{X}]_2$ (HL = HATU, HNMATU and X = Cl, Br) have been suggested from their physico-chemical properties. The presence of NN coordination in $[\text{Ag}(\text{SEATU})(\text{H}_2\text{O})_2]$ and $\text{Zn}(\text{ATU})_2$ and SN coordination in all other

Ag^{I} and Cu^{I} complexes has been suggested from their ir spectral data. The mixed ligand complexes $[\text{CuL}(\text{PPh}_3)_2]$ ($\text{L} = \text{ATU}^-$, NMATU^-) are more stable than the corresponding simple complexes. Tetrahedral four coordination has been suggested for all these d^{10} metal complexes.

Chapter VI records the relevant references cited in the thesis.