

Complexes of Oxovanadium(IV), Chromium(III), Manganese(II), Iron(III) & Cobalt(II) with 1-Amidino-2-thioureas

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Complexes of Co(II), oxovanadium(IV), Fe(III), Cr(III) and Mn(II) with 1-amidino-2-thioureas have been prepared and characterized by different physicochemical techniques. The ligands behave as NN donors towards Cr(III) and SN donors towards Co(II), Fe(II), oxovanadium(IV) and Mn(II). Probable structures have been assigned to the complexes on the basis of their physicochemical properties.

The ligand 1-amidino-2-thiourea and its N- or S-alkyl derivatives are capable of acting both as NN and SN donors in their metal complexes¹⁻⁶; the former type of bonding is operative in alkaline medium while the latter type occurs in neutral or slightly acidic medium. As SN donors, these ligands stabilize lower oxidation states of the central metal ions⁶ and decrease the electron density on NO in mixed ligand metal nitrosyls⁵. As NN donors, their behaviour is similar to that of biguanides and amidinoisoureas. The results of structural investigation of some of the complexes were reported in one of our earlier communications⁷. This paper describes the synthesis, characterization and probable structures of oxovanadium(IV), Cr(III), Mn(II), Co(II) and Fe(III) complexes with the above mentioned ligands.

Materials and Methods

Analytical grade reagents and pure distilled solvents were used throughout the present work. Metal, halogen and sulphur were analysed by standard classical methods and C and N were analysed by semimicro methods. Vibrational and electronic spectral studies, magnetic, conductance and molecular weight measurements were carried out on Beckman IR-12, Cary 17D, Gouy balance, Philips conductivity bridge and Knauer, Dampdruk osmometer respectively.

Syntheses of the complexes†:

(i) $VO(HATU)_2SO_4 \cdot H_2O$, (ii) $VO(HNMATU)_2SO_4 \cdot H_2O$, (iii) $VO(HNEATU)_2SO_4 \cdot 2H_2O$, (iv) $VO(HATU)_2Cl_2$, (v)

$VO(HNMATU)_2Cl_2$, and (vi) $VO(HNEATU)_2Cl_2$

Addition of methanolic solution of $VOSO_4$ (0.01 mol, 50 ml) to that of the appropriate ligand (0.04 mol, 100 ml) at 20°C produced the deep green solution of the sulphate complexes (i - iii). Deep green crystals of the respective compounds separated out from the solution within two hours. The chloride complexes (iv - vi) were obtained by metathesis of the corresponding sulphates with $BaCl_2$. The sulphate and chloride complexes were crystallized from methanol and acetone respectively. The compounds were dried *in vacuo*.

(vii) $[Cr(ATU)_2(OH)]_2$, (viii) $Cr(ATU)_3$

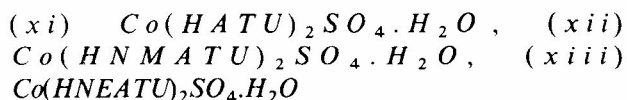
The solutions of chrome alum (0.01 mol) and the ligand (0.06 mol) in 40% aqueous sodium hydroxide (100 ml) were mixed and magnetically stirred for 12 hr at 20°C when a deep red colour was produced. Red prismatic crystals of (vii) separated out from the solution at 0°C after 30 days. These were carefully hand-picked and washed with water. For the preparation of (viii), a mixture of $CrCl_3$ (0.01 mol), ligand (0.1 mol) and sodium hydroxide pellets (5g) in methanol (100 ml) was magnetically stirred for 12 hr at 10°C to get a red solution. The filtrate was evaporated quickly to dryness and the mass was dissolved in ethanol (50 ml) containing $(NH_4)_2SO_4$ (5g). The filtrate produced red crystals on evaporation which were recrystallised from ethanol.

(ix) $[Mn(HATU)(ATU)Cl]_2$, (x) $[Fe(ATU)_2Cl]_2$

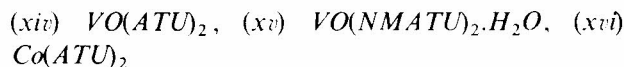
The green solution formed on addition of HATU (0.04 mol) to the methanolic solution of $MnCl_2 \cdot 2H_2O$ (0.01 mol, 100 ml) was filtered. The filtrate produced, on standing, fine yellow green crystals of (ix) within 2 hr. Brick red crystals of (x) were obtained within 1 hr on keeping at 0°C the mixture of anhydrous $FeCl_3$ (0.01 mol) and HATU (0.05 mol) in

†Abbreviations: HATU = 1-amidino-2-thiourea; HNMATU = N-methyl-1-amidino-2-thiourea; and HNEATU = N-ethyl-1-amidino-2-thiourea

acetone (100 ml). Both the compounds were washed with the respective solvents and dried *in vacuo*.



Green brown precipitates of the respective compounds separated out almost immediately on mixing the methanolic solution of $CoSO_4 \cdot 7H_2O$ with that of the appropriate ligand under nitrogen. The precipitates were washed with methanol and dried *in vacuo* over fused $CaCl_2$.



The neutral oxovanadium(IV) complex separated out as light green precipitate on treating the methanolic solutions of the corresponding chloride complexes with methanolic sodium hydroxide at $0^\circ C$. Dropwise addition of methanolic solution of $CoCl_2 \cdot 6H_2O$ to the ligand solution in 40% aqueous sodium hydroxide at $0^\circ C$ with constant stirring under nitrogen produced yellow precipitate of (xvi). The compounds were thoroughly washed with methanol and dried *in vacuo*.

Results and Discussion

The oxovanadium(IV) and $Cr(ATU)_3$ complexes are soluble in common polar solvents. The former complexes behave as 1:2 electrolytes in water while the latter is a nonelectrolyte. Sulphate complexes of cobalt(II) are 1:2 electrolytes in methanol under nitrogen and change to a polymeric brown compound of indefinite composition in presence of oxygen. Complexes of iron(III), manganese(II) and $[Cr(ATU)_2OH]_2$ are soluble and nonelectrolytes in DMF and DMSO. The neutral complexes of oxovanadium(IV) and cobalt(II) (compounds xiv-xvi) are insoluble in all common solvents. All these compounds are decomposed by acids to produce free ligands. Manganese(II), iron(III) complexes and greenish-brown cobalt(II) complexes are converted to the corresponding metal sulphides by hot concentrated alkalis indicating the presence of SN bonding in them⁷ while chromium(III) and yellow cobalt(II) complexes do not undergo any such change. The ligand anion ATU^- , produced in strong alkaline medium, probably behaves as NN donor in the latter two metal complexes.

Iron(III), manganese(II) and $[Cr(ATU)_2OH]_2$ complexes exhibit subnormal magnetic moments (Table I). Cryomagnetic studies were done only with $[Cr(ATU)_2OH]_2$ for which the θ value was determined to be 120° . Similar measurements could not be done

for other compounds due to instrumentation difficulties. The compounds are most probably dimeric through chlorine or hydroxide bridging, and the superexchange interaction occurs through the bridging system⁹⁻¹¹. The molecular weights of the complexes were determined in DMF solution; the low molecular weights of $[Cr(ATU)_2OH]_2$ (~ 360) and $[Fe(ATU)_2Cl]_2$ (~ 400) suggest the cleavage of the bridge bonds in solution. The molecular weight of $[Mn(HATU)(ATU)Cl]_2$ was almost normal (~ 650). $Cr(ATU)_2OH \cdot DMF$ was isolated from the DMF solution of $[Cr(ATU)_2OH]_2$. The high magnetic moments of cobalt(II) complexes are in accordance with their tetrahedral geometries while the low magnetic moment of $Co(ATU)_2$ suggests it to be square planar. The oxovanadium(IV) complexes have normal magnetic moments. The manganese(II) complex contains both protonated and deprotonated ligands as has been found in other cases^{12,13}.

The recognizable IR bands of these complexes have been assigned according to literature reports^{1,2,4,14}. Very broad bands in the region $3,500$ to $3,200\text{ cm}^{-1}$ are assigned to hydrogen bonded νNH_2 and νOH modes. Hydrated compounds exhibit bands in the region 1680 to 1700 cm^{-1} due to δH_2O mode. In chromium(III) and yellow $Co(ATU)_2$ complexes, the asymmetric and symmetric $\nu N-C-N$ modes of the free ligand (observed at 1625 and 1615 cm^{-1}) are split and appreciably shifted to lower frequency region (~ 1570 , ~ 1540 and $\sim 1520\text{ cm}^{-1}$) while the $\nu N-C-S(2)$ band (1320 cm^{-1}) is split up and shifted to both higher and lower frequency sides. These and a new band in the region $400-500\text{ cm}^{-1}$ (due to $\nu M-N$) suggest the presence of MN bonding in these complexes⁷. In other complexes, the bands due to $\nu N-C-S(3)$ and $\nu C-S$ undergo considerable negative frequency shift of nearly ~ 100 and $\sim 50\text{ cm}^{-1}$ respectively. Peaks at 500 cm^{-1} (due to $\nu M-N$) and 300 cm^{-1} (due to $\nu M-S$) are also observed in these complexes. Hence the presence of SN bonding has been suggested in them⁷. Vanadyl complexes exhibit peaks at $\sim 950\text{ cm}^{-1}$ due to $\nu V=O$ ¹⁵.

The remarkable similarities of $d-d$ band positions of chromium(III) and $Co(ATU)_2$ complexes with those of the corresponding biguanide complexes suggest the presence of similar bonding pattern in them²³. For chromium(III) compounds, the bands in the region $20,000-21,000\text{ cm}^{-1}$ and $26,000-27,000\text{ cm}^{-1}$ are assigned to the transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ respectively. The spectra of the oxovanadium(IV) complexes are different from those of the corresponding biguanide complexes²³ and exhibit three major bands in the regions $11,000-13,500\text{ cm}^{-1}$, $14,000-17,000\text{ cm}^{-1}$ and $26,000-28,000\text{ cm}^{-1}$. They are tentatively assigned to ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ transitions respectively¹⁵. The

Table 1—Analytical, Magnetic and Molar Conductance Data of the Complexes

Compound	Colour	Found (Calc.), %					$\mu_{\text{eff.}}(\text{B.M.})$ at 300 K	Λ_{1024} ($\text{S cm}^{-1} \text{mol}^{-1}$)
		M	N	C	S	Anion		
$[\text{Cr}(\text{ATU})_2\text{OH}]_2$	Red	17.30 (17.16)	36.68 (36.96)	15.90 (15.84)	21.85 (21.12)	—	3.5	—
$\text{Cr}(\text{ATU})_3$	Red	12.68 (12.90)	41.47 (41.69)	17.75 (17.86)	23.90 (23.82)	—	3.85	—
$\text{VO}(\text{HATU})_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Green	12.15 (12.23)	26.77 (26.85)	11.42 (11.51)	15.81 (15.34)	23.10 (23.02)	1.73	140 ^a
$\text{VO}(\text{HNMATU})_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Green	11.32 (11.46)	25.92 (25.16)	16.17 (16.18)	14.28 (14.38)	21.70 (21.57)	1.71	135 ^a
$\text{VO}(\text{HNEATU})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Green	10.26 (10.38)	22.56 (22.81)	19.40 (19.55)	12.92 (13.03)	19.48 (19.55)	1.72	140 ^a
$\text{VO}(\text{HATU})_2\text{Cl}_2$	Green	13.65 (13.63)	30.20 (29.95)	12.85 (12.83)	17.32 (17.11)	19.05 (18.98)	1.74	140 ^a
$\text{VO}(\text{HNMATU})_2\text{Cl}_2$	Green	12.69 (12.68)	28.05 (27.89)	18.07 (17.96)	15.86 (15.92)	17.82 (17.66)	1.76	146 ^a
$\text{VO}(\text{HNEATU})_2\text{Cl}_2$	Green	11.76 (11.86)	26.12 (26.04)	22.16 (22.32)	14.65 (14.88)	16.32 (16.51)	1.74	148 ^a
$\text{Co}(\text{HATU})_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Greenish brown	14.28 (14.42)	27.32 (27.38)	11.60 (11.74)	15.75 (15.64)	23.41 (23.47)	4.65	160 ^b
$\text{Co}(\text{HNMATU})_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Greenish brown	13.41 (13.50)	25.75 (25.62)	16.28 (16.47)	14.45 (14.66)	21.80 (21.96)	4.72	165 ^b
$\text{Co}(\text{HNEATU})_2\text{SO}_4 \cdot \text{H}_2\text{O}$	Greenish brown	12.61 (12.70)	24.12 (24.08)	20.58 (20.64)	13.84 (13.76)	20.72 (20.64)	4.61	165 ^b
$[\text{Fe}(\text{ATU})_2\text{Cl}]_2$	Brick red	17.31 (17.20)	34.52 (34.40)	14.85 (14.74)	19.80 (19.66)	10.79 (10.90)	3.62	—
$[\text{Mn}(\text{HATU})(\text{ATU})\text{Cl}]$	Yellowish green	17.15 (17.20)	34.26 (34.40)	14.75 (14.74)	19.45 (19.66)	10.68 (10.90)	4.72	—
$\text{Co}(\text{ATU})_2$	Yellow	19.96 (20.13)	38.14 (38.22)	16.26 (16.38)	21.72 (21.81)	—	2.4	—
$\text{VO}(\text{ATU})_2$	Green	16.81 (16.94)	37.11 (37.20)	15.84 (15.94)	21.28 (21.26)	—	1.74	—
$\text{VO}(\text{NMATU})_2 \cdot \text{H}_2\text{O}$	Green	14.56 (14.69)	32.18 (32.27)	20.56 (20.74)	18.32 (18.44)	—	1.74	—
$\text{Cr}(\text{ATU})_2\text{OH} \cdot \text{DMF}$	Red	13.64 (13.82)	33.46 (33.51)	22.46 (22.32)	17.15 (17.02)	—	3.70	—

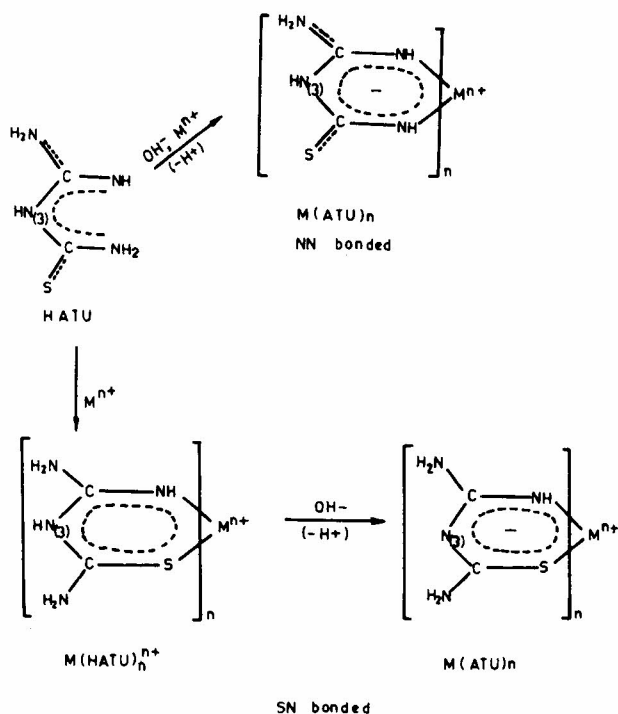
^aConductance in methanol, ^bconductance in water.

dependence of the peak positions of the solution spectra on the nature of the solvent indicates loose solvent coordination to the square pyramidal oxovanadium(IV) giving rise to near octahedral configuration. According to the energy difference between the second and the first bands, the solvents may be placed in the following sequence regarding their strengths as ligands: $\text{H}_2\text{O} > \text{MeOH} > \text{DMF}$. Both the solid state and solution spectra (in methanol under nitrogen) of cobalt(II) complexes revealed peaks at $\sim 18,000$ and $\sim 7,500 \text{ cm}^{-1}$, consistent with ${}^4A_2 \rightarrow {}^4T_1(P)$ and ${}^4A_2 \rightarrow {}^4T_1(F)$ transitions in tetrahedral complexes^{17,18}. For iron(III) complexes, two shoulders at $\sim 17,800$ and $\sim 20,200 \text{ cm}^{-1}$, assigned to the transitions ${}^6A_{1g} \rightarrow {}^4A_{2g}(B)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$ respectively¹⁰, appear on the intense charge transfer band at $28,170 \text{ cm}^{-1}$. The difference in the solid state and DMF solution spectra is probably due to cleavage

of $\text{Fe} \begin{smallmatrix} \text{Cl} \\ \diagup \diagdown \\ \text{Cl} \end{smallmatrix} \text{Fe}$ bridge in DMF solution. The spectra of manganese(II) complexes show only weak bands in the region $17,000\text{--}27,000 \text{ cm}^{-1}$. These bands are due to spin forbidden transition from the ground sextet to the first excited quartet states, and the complex is suggested to be octahedral by comparison¹⁹.

Endothermic loss of water molecules from the hydrated compounds in the temperature range $110\text{--}120^\circ\text{C}$ suggests the presence of lattice water. Exothermic decomposition of all the compounds occurred above 250°C with the liberation of NH_3 . Residues left at 500°C were the corresponding metal oxides.

The presence of extensive π -electron delocalization in metal-amidinothiureas has been proved from their physicochemical properties and PMR spectral studies⁷. From the physicochemical properties



SCHEME 1

discussed above, the ligand anion, ATU^- , is suggested to act as NN donor in chromium(III) and $Co(ATU)_2$ complexes. Their cationic complexes could not be prepared as N(3) atom was already protonated. All other compounds are believed to contain SN donor

ligands and hence both cationic and inner complexes could be prepared for them (Scheme 1).

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