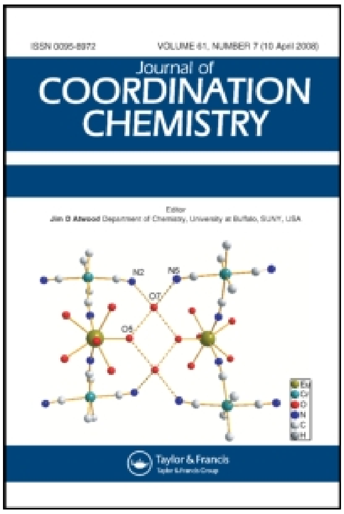

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SYNTHESIS AND STRUCTURAL INVESTIGATION OF METAL COMPLEXES OF 1-AMIDINO-2-THIOUREAS

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SYNTHESIS AND STRUCTURAL INVESTIGATION OF METAL COMPLEXES OF 1-AMIDINO-2-THIOUREAS

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Some new metal complexes of 1-amidino-2-thioureas† and its *S*- and *N*-alkyl derivatives have been isolated and characterized by electronic, vibrational and pmr spectral studies, magnetic and conductance measurements and thermal analysis. The ligands behave as SN or NN donors depending mainly on the pH of the medium and the nature of the metal atom. Protonation at the central nitrogen atom of the chelate ring converts the inner complexes to cationic ones and vice-versa. Electronic and pmr spectral data confirm the presence of strong ring currents in these chelates. Probable structures of the complexes have been suggested on the basis of their physicochemical properties.

INTRODUCTION

Few investigations on the synthesis and structure of metal complexes of 1-amidino-2-thioureas have been made so far.[1–6] Earlier workers suggested nonplanar chelate ring structures for them.[2,4–6] The ligands possess nitrogen and sulphur donors and the relative coordinating abilities of these donor atoms should depend on experimental conditions and the nature of the metal atoms. As SN donors, they stabilize lower oxidation states of metal atoms[8] and lower and electron density on NO in metal nitrosyls.[7] The structures of metal complexes of similar ligands like biguanide and dithiobiuret[9–16] suggests similar π-electron delocalized structures for these metal complexes. In the present paper we report the isolation of some new complexes and propose most probable structures on the basis of their physico-chemical properties.

EXPERIMENTAL

Analytical grade reagents and pure distilled solvents were generally used throughout the work. The ligands and the known compounds were prepared according to literature.[1–3,6,12] Vibrational (in KBr mull), electronic and pmr spectral studies, magnetic and conductance measurements and thermal analysis were carried out using Beckman IR-12, Cary 17D and EM 390 90 MHz spectrophotometers, a Gouy balance, a Phillips conductivity bridge and derivatograph, and a Paulik and Erdey instrument, respectively.

Preparation of the Complexes

The numbers used in this section refer to corresponding complexes in Table 1.

Synthesis of NN Bonded Complexes

Nickel(II) Complexes

Ni(HSEATU)$_2$X$_2$; (X = Cl, Br, I). Saturated ammonium halide solution was added

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† HATU = 1-amidino-2-thiourea, HMNATU = N-methyl-1-amidino-2-thiourea, HNEATU = N-ehtyl-1-amidino-2-thiourea, HSEATU = S-ethyl-1-amidino-2-thiourea.

TABLE 1
Analytical and conductance data for the complexes.[a]

Compound	Colour	M(%)	N(%)	C(%)	S(%)	Anion (%)	Λ1024 ($cm^2 mol^{-1}$)
1. $Ni(HSEATU)_2Cl_2$	Orange	14.07 (13.98)	26.75 (26.68)	22.70 (22.76)	15.35 (15.24)	16.99 (16.91)	250
2. $Ni(HSEATU)_2Br_2$	Orange	11.65 (11.55)	22.09 (22.01)	18.70 (18.79)	12.70 (12.58)	31.70 (31.45)	248
3. $Ni(HSEATU)_2I_2$	Orange	9.60 (9.73)	18.40 (18.58)	15.73 (15.87)	10.82 (10.61)	42.25 (42.44)	250
4. $Ni(HSEATU)_2SO_4H_2O$	Orange	12.80 (12.88)	24.35 (24.20)	20.52 (20.65)	13.95 (13.83)	20.84 (20.74)	
5. $Cu(ATU)_2$	Rose red	21.49 (21.34)	37.52 (37.64)	16.09 (16.13)	21.65 (21.51)		
6. $Cu(HSEATU)_2Cl_2$	Rose red	14.95 (14.88)	26.39 (26.26)	22.40 (22.50)	15.21 (15.00)	16.72 (16.64)	250
7. $Cu(HSEATU)_2Br_2$	Rose red	12.39 (12.31)	21.79 (21.72)	18.53 (18.62)	12.31 (12.41)	31.21 (31.03)	255
8. $Cu(HSEATU)_2SO_4H_2O$	Rose red	13.59 (13.52)	23.97 (23.85)	20.32 (20.44)	13.85 (13.63)	20.60 (20.44)	
9. $[Cu(HSEATU)(H_2O)_2]Cl_2$	Blue	20.19 (20.06)	17.85 (17.69)	15.10 (15.16)	10.25 (10.11)	22.43 (22.41)	255
10. $[Cu(HSEATU)(H_2O)_2]Br_2$	Blue	15.79 (15.65)	13.92 (13.81)	18.71 (11.83)	7.95 (7.89)	39.52 (39.45)	255
11. $Co(ATU)_3 1.5H_2O$	Orange	13.60 (13.49)	35.72 (35.69)	16.30 (16.36)	21.81 (21.96)		
12. $[Co(ATU)_2(H_2O)_2]Cl$	Orange	16.11 (16.18)	30.69 (30.72)	13.10 (13.16)	17.62 (17.55)	9.81 (9.73)	
13. $Co(SEATU)_2(OH)(H_2O)$	Orange	15.41 (15.36)	29.25 (29.16)	24.85 (25.00)	16.52 (16.66)		

Table 1 cont.

14.	$[Co(HSEATU)_2(H_2O)_2]Cl_3$	Reddish-yellow	11.80 (11.94)	22.90 (22.69)	19.38 (19.45)	12.70 (12.99)	21.91 (21.58)	330
15.	$[Co(HSEATU)_2(H_2O)_2]Br_3$	Reddish-yellow	9.30 (9.39)	17.99 (17.86)	15.25 (15.31)	10.00 (10.20)	38.60 (38.28)	325
16.	$Ni(HATU)_2Cl_2 1.5H_2O$	Red	14.87 (14.94)	28.40 (28.52)	12.15 (12.22)	16.39 (16.29)	18.21 (18.01)	130^b
17.	$Ni(HATU)_2Br_2. H_2O$	Red	12.52 (12.41)	23.65 (23.69)	10.01 (10.15)	13.59 (13.53)	33.76 (33.84)	130^b
18.	$Ni(HATU)_2(NO_3)_2H_2O$	Red	13.52 (13.44)	25.67 (25.64)	10.91 (10.99)	14.76 (14.65)	28.47 (28.39)	125^b
19.	$Ni(ATU)_2$	Red	20.17 (20.05)	38.40 (38.26)	16.31 (16.39)	21.78 (21.86)		
20.	$Ni(HNMATU)_2Cl_2$	Red	14.98 (14.90)	28.56 (28.44)	18.30 (18.38)	16.40 (16.25)	18.15 (18.03)	260
21.	$Ni(HNMATU)_2Br_2$	Red	12.05 (12.16)	23.40 (23.20)	14.85 (14.91)	13.37 (13.25)	33.05 (33.14)	258
22.	$Ni(HNEATU)_2Cl_2$	Red	13.79 (13.91)	26.59 (26.55)	22.75 (22.87)	15.28 (15.17)	16.97 (16.88)	254
23.	$Ni(HNEATU)_2Br_2$	Red	11.56 (11.49)	21.82 (21.93)	18.73 (18.87)	12.65 (12.53)	31.41 (31.22)	253
24.	$Ni(HNMATU)_2SO_4 1.5H_2O$	Red	13.51 (13.44)	25.70 (25.64)	16.10 (16.15)	14.72 (14.65)	21.90 (21.78)	
25.	$Ni(NMATU)_2$	Red	18.35 (18.30)	34.87 (34.92)	22.37 (22.45)	19.81 (19.95)		
26.	$Ni(NEATU)_2$	Red	16.87 (16.83)	31.19 (31.12)	27.48 (27.53)	18.45 (18.35)		
27.	$Cu(HNMATU)_2F_2$	Bluish	17.39 (17.46)	30.70 (30.81)	19.69 (19.80)	17.71 (17.60)	10.51 (10.45)	
28.	$Cu(HNMATU)_2SO_4 1.5H_2O$	Bluish-pink	14.11 (14.17)	24.88 (24.97)	16.12 (16.05)	21.51 (21.40)	21.31 (21.40)	

Table 1 cont.

29.	Co(NMATU)$_3$	Chocolate	13.11 (13.05)	37.10 (37.16)	23.81 (23.89)	21.33 (21.23)		
30.	Co(NEATU)$_3$	Chocolate	11.81 (11.94)	34.11 (34.00)	29.19 (29.14)	19.52 (19.43)		
31.	Pd(HATU)$_2$Cl$_2$H$_2$O	Light brown	24.75 (24.66)	25.87 (25.96)	11.01 (11.12)	14.92 (14.83)	16.55 (16.45)	215
32.	Pd(HATU)$_2$Br$_2$H$_2$O	Light brown	18.62 (18.45)	19.39 (19.43)	9.14 (9.22)	11.21 (11.10)	27.89 (27.75)	217
33.	Pd(HNMATU)$_2$Cl$_2$H$_2$O	Light brown	23.40 (23.26)	24.60 (24.48)	15.58 (15.67)	14.07 (13.99)	15.63 (15.52)	210
34.	Pd(HNMATU)$_2$Br$_2$H$_2$O	Light brown	19.60 (19.47)	20.61 (20.49)	13.00 (13.12)	11.62 (11.71)	29.35 (29.28)	208
35.	Pt(HNMATU)$_2$Cl$_2$	Light yellow	36.72 (36.79)	21.19 (21.13)	13.62 (13.58)	12.21 (12.07)	13.49 (13.39)	220
36.	Pt(HNMATU)$_2$Br$_2$	Light yellow	31.62 (31.50)	17.21 (18.09)	11.51 (11.63)	10.42 (10.33)	25.91 (25.84)	215
37.	Pd(HSEATU)Cl$_2$2H$_2$O	Orange yellow	29.70 (29.49)	15.41 (15.58)	13.41 (13.35)	8.79 (8.96)	19.85 (19.75)	
38.	Pd(HSEATU)Br$_2$2H$_2$O	Orange yellow	23.91 (23.72)	12.57 (12.48)	10.59 (10.70)	7.19 (7.10)	35.79 (35.68)	
39.	Pt(HSEATU)Cl$_2$	Orange	45.39 (45.34)	13.20 (13.22)	11.53 (11.65)	7.61 (7.44)	16.62 (16.51)	
40.	Pt(HSEATU)Br$_2$	Orange	38.80 (38.92)	11.20 (11.17)	19.63 (9.58)	6.35 (6.38)		

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[a]Theoretical values given in parentheses. [b]In methanol. All other conductance measurements in H_2O at 25°.

dropwise to a suspension of $Ni(SEATU)_2$[3] (5 g) in water (100 cm^3) at 80° with continuous stirring. When most of the suspension had dissolved, the mixture was filtered and the filtrate produced orange crystals of the subject compounds on aerial evaporation. *$Ni(HSEATU)_2SO_4H_2O$* separated out in the form of fine crystals on treating the aqueous solution of the complex chloride with sodium sulphate. The complexes were washed with water and dried over $CaCl_2$.

Copper(II) Complexes

$Cu(ATU)_2$. A methanolic solution of $CuCl_2$ (0.01 mole, 25 cm^3) was slowly added to that of HATU (0.04 mole, 100 cm^3) containing sodium hydroxide pellets (1.5 g) at 0°. At first, a brown precipitate appeared which dissolved slowly on shaking, producing a rose-red solution. It was filtered quickly and the filtrate produced rose-red crystals within half an hour. *$Cu(HSEATU)_2X_2$ (X = Cl, Br)* and *$Cu(HSEATU)_2SO_4H_2O$* were isolated following the method of preparation of the corresponding nickel(II) complexes.

$[Cu(HSEATU)(H_2O)_2]X_2$ (X = Cl, Br). Dropwise addition of appropriate haloacides (1:1) to an aqueous solution of $Cu(HSEATU)_2X_2$ (X = Cl, Br) turned the rose-red colour of the solution slowly to blue. The addition of the haloacid was continued until the blue colour of the solution became most intense (pH $\approx$ 4.0). The clear filtrate was allowed to evaporate in an atmosphere of the corresponding hydrogen halide in a desiccator. Blue crystals of $[Cu(HSEATU)(H_2O)_2]X_2$ (X = Cl, Br) separated out from the solution within 4 days. These were washed with methanol and dried over $CaCl_2$.

Cobalt(III) Complexes

Orange $Co(ATU)_3 1.5H_2O$ (compound 11). A saturated aqueous solution of $[Co(NH_3)_6]Cl_3$ (0.01 mole) was mixed with a saturated methanolic solution of the ligand (0.05 mole). A brown precipitate of $Co(ATU)_3$ (SN bonded) appeared within 30 minutes. The mixture was then treated with sodium hydroxide pellets (4 g) and kept for 24 hrs. During this time most of the brown precipitate dissolved to produce a deep orange solution. It was heated at 60° on water bath for 20 minutes and filtered quickly. The filtrate produced orange crystals of the compound on concentration in a vacuum dessiccator. The diaquo-complex (compound 12) was obtained by heating a saturated aqueous solution of $Co(ATU)_3 1.5H_2O$ (0.01 mole) with NH_4Cl (0.05 mole) at 80° on water bath for 30 minutes. This was filtered hot and the filtrate produced orange crystals of the subject compound on cooling.

$[Co(SEATU)_2(OH)(H_2O)]$. Passage of air through an aqueous suspension (100 cm^3) of $Co(SEATU)_2$[3] (0.01 mole) for 6 hrs produced an orange solution. This was filtered and the filtrate produced orange crystals of $[Co(SEATU)_2(OH)(H_2O)]$ on vacuum evaporation. For the preparation of complex halides (compounds 14 and 15), saturated aqueous solutions of $[Co(SEATU)_2(OH)(H_2O)]$ (0.01 mole) were heated with the appropriate ammonium halide (0.05 mole) on a water bath for 30 minutes. The solution gave crystals of the complex halides on aerial evaporation.

Synthesis of SN bonded complexes.

Nickel(II) Complexes

$Ni(HATU)_2X_2$ (X = Cl, Br, NO_3). Saturated acetone solutions of the appropriate nickel(II) salts (0.01 mole) were thoroughly mixed with those of HATU (0.04 mole) at 0°. The mixture was filtered immediately and the filtrate produced red crystals of

the subject compounds within 30 minutes. The crystals were washed with acetone and dried over $CaCl_2$. *Ni(ATU)$_2$* (compound 19) was prepared by treating a methanolic solution of $Ni(HATU)_2Cl_2$ with dilute sodium hydroxide in methanol. The mixture was filtered immediately and the filtrate produced silky red crystals of the subject compound within 5 minutes.

NiL_2X_2 (L = HNMATU, HNEATU, X = Cl, Br). Aqueous solutions of the appropriate nickel(II) halide 50 cm^3, 0.01 mole) and the ligand (50 cm^3, 0.04 mole) were mixed together and heated at 80° on a water bath for 15 minutes. The clear filtrates produced red crystals of the desired compounds on vacuum evaporation. The complex sulphate (compound 24) and the innter complexes (compounds 25 and 26) precipipated out in the form of fine crystals on treating aqueous solutions of the corresponding complex chlorides with sodium sulphate and sodium hydroxide solutions, respectively. The precipitates were thoroughly washed with water and dried over $CaCl_2$.

Copper(II) Complexes

$Cu(HL)_2X_2$ (L = NMATU; X = F, ½SO_4). An aqueous solution (50 cm^3) of HNMATU (0.04 mole) was rapidly added to a well-stirred aqueous solution of the corresponding Cu(II) salt at room temperature. Bluish-pink crystalline precipitates were obtained in both cases. These were filtered, washed and dried as usual.

Cobalt(III) complexes.

CoL_3 (L = NMATU, NEATU). A saturated aqueous solution of $Co(NH_3)_6Cl_3$ (0.01 mole) was mixed with a saturated methanolic solution of the ligand (0.06 mole) at room temperature. The solution was made alkaline (pH ≈ 12) with sodium hydroxide and kept in a desiccator for 3 days. The colour of the solution became deep brown. It was filtered, and the filtrate on evaporation produced deep brown crystals of the desired compound. These were purified by recrystallization three times from methanol.

Palladium(II) and Platinum(II) complexes.

The Palladium(II) complexes (compounds 31-34) were obtained by adding an aqueous solution of the ligand (0.01 mole) to that of PdX_2 (0.001 mole, X = Cl, Br) at 50 to 60°. The resulting solution was filtered and the filtrate produced light brown crystals of the desired compound on evaporation. Other complexes of palladium(II) and platinum(II) (compounds 35-40) were isolated in 1:1 haloacid medium following the above procedure.

RESULTS AND DISCUSSION

Different types of complexes with these ligands have been synthesized both in aqueous and nonaqueous media. The ligands behave both as NN and SN donors depending on the experimental conditions and the pH of the medium. NN bonded complexes were isolated under alkaline conditions while the SN bonded complexes were obtained at neutral or slightly acidic pH. Palladium(II) and platinum(II) always form SN bonded complexes.

NN bonded complexes.

The colours and properties of these complexes are comparable to those of the corresponding biguanides.[20] Inner complexes of nickel(II), copper(II) and cobalt(III) with HATU were isolated from aqueous or methanolic solutions under highly alkaline conditions. The complexes are stable towards water or cold alkali, but are decomposed by hot strong base. The ligands themselves, however, decompose under these conditions. Attempts to convert the inner complexes to the corresponding cationic ones by the addition of dilute HX or NH_4X (X = Cl, Br, 1/2SO_4) under different experimental conditions were unsuccessful and led to metal-ligand bond rupture. Warm NH_4Cl solutions convert $Co(ATU)_3$ to $[Co(ATU)_2(H_2O)_2]Cl$ and the latter forms $[Co(ATU)_2(OH)(H_2O)]$ with dilute alkali.

Inner and cationic complexes of HSEATU were synthesized in ammoniacal and slightly acid solutions, respectively. Attempts to synthesize $[Co(HSEATU)_3]X_3$ (X = Cl, Br, ½SO_4) or $Co(SEATU)_3$ in the presence of excess ligand under different experimental conditions were unsuccessful and led to the isolation of bis-chelate complexes. A pH dependent equilibrium (*1*) operates in the case of the copper(II) complexes and mono- and bis-chelates were isolated at ph ≈ 3 and ≈ 7 respectively. Their properties are comparable to those of corresponding copper(II) biguanides.[20]

$$Cu(HSEATU)_2X_2 \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [Cu(HSEATU)(H_2O)_2]X_2 + H_2SEATU^+ \qquad (1)$$

SN bonded complexes.

The physicochemical properties of these complexes are different from those of the NN bonded species. The conductances of the deep red diamagnetic complexes $Ni(HATU)_2X_2$ (X = Cl, Br) in methanol indicate them to be 2:1 electrolytes. HNMATU and HNEATU also form red diamagnetic nickel(II) complexes in water which are more stable than $Ni(HATU)_2X_2$.

The pink complexes $Cu(HNMATU)_2X_2$ (X = F, ½SO_4) were prepared in neutral aqueous solution. Isolation of these complexes was possible due to their high insolubilities. Preparation of copper(II) complexes with X = Cl, Br was not possible due to reduction of Cu(II) to Cu(I) by these thioligands.[8] The water-insoluble reddish-brown complex, $Co(ATU)_3.3H_2O$ was converted to the corresponding cationic one, $Co(HATU)_3(SO_4)_{3/2}$. DMSO by $(NH_4)_2SO_4$ in DMSO. These two compounds are, however, decomposed to CoS by hot alkali. The inner complexes $Co(NMATU)_3$ and $Co(NEATU)_3$ were converted to their corresponding complex chlorides by dilute ammonium chloride solution.

Complexes $M(HL)_2X_2$ (M = Pd, Pt; L = ATU, NMATU, X = Cl, Br) are soluble in water and stable towards dilute acid. They are decomposed to metal sulphides by warm alkali. Their conductances in water show them to be 2:1 electrolytes. The mono-chelates $M(HSEATU)X_2$ (M = Pd, Pt; X = Cl, Br) were isolated from acid solution. Attempts to synthesize the corresponding bis-chelate or inner complexes in the presence of excess ligand under different experimental conditions were unsuccessful.

General characteristics of the complexes.

Except the NN bonded complexes of HATU and SN bonded complexes of HSEATU with Pd(II) and Pt(II), all species can be obtained both in inner and cationic forms according to equation (*2*).

$$MLn \underset{n(OH^-)}{\overset{nH^+}{\rightleftharpoons}} [M(HL)_n]^{n+} \qquad (2)$$

The complexes are decomposed by strong acids or alkalies. The inner complexes are insoluble in water, methanol etc., while the corresponding cationic ones are soluble in these solvents. Conductance data, conductometric titrations and magnetic moments of these compounds agree with their formulae as given in Table 1. The SN bonded complexes are decomposed easily to metal sulphides by alkali while the NN bonded complexes are decomposed to metal hydroxide under the same conditions. *N*-alkyl-l-amidino-2-thioureas were always found to behave as SN donors. Isolation of their NN bonded complexes was not possible.

Infrared spectra

The assignment of some important ir bands of these complexes have been made (Table 2) after due consideration to similar compounds.[3,4,6,18-19] Absence of any bands in the region 2600 to 2000 cm^{-1} in neutral or monobasic salts of the ligands probably indicates the absence of the —SH group. The ν_{N-C-N} bands are split in the NN bonded complexes (compounds 2-4 and 12-14; Table 2) but not in the SN bonded ones (compounds 5, 6, 8-10; Table 2). The most characteristic differences between the spectra of NN and SN bonded complexes are that, in the former, the bands due to ν_{N-C-S} (3) and ν_{C-S} remain almost unchanged relative to those in the free ligands and only one new band appears at ~ 500 cm^{-1} due to ν_{M-N}. In the latter, the first two bands i.e. ν_{N-C-S} (3) and ν_{C-S} undergo appreciable lower frequency shifting and two new bands at ~ 500 cm^{-1} (due to ν_{M-N}) and ~ 350 cm^{-1} (due to ν_{M-S}) appear. The positions of the bands appear to be insensitive to the nature of the metal atoms. In $M(HSEATU)Cl_2$ (M = Pd, Pt), the ν_{C-S} band shows an appreciable red shift and two new bands at ~ 490 (ν_{M-N}) and ~ 360 cm^{-1} (ν_{M-S}) are observed. All these observations suggest SN bonding in these complexes.

Electronic spectra

Electronic spectral data for the complexes in the solid state and in solution are presented in Table 3. The striking resemblance of the d-d band positions of the nickel(II) (compounds 1-6), copper(II) (compounds 19-25) and cobalt(III) complexes (compounds 28-31) to those of the corresponding metal biguanides suggests 12, 24[12,24] the presence of NN bonding and strong chelate ring currents. The spectra of the other nickel(II) (compounds 7-12), copper(II) (compounds 26,27), cobalt(III) (compounds 32-34) and palladium(II) complexes (compounds 15-18) are completely different from those of the NN bonded ones and indicate SN bonding. The spectra of the NN bonded nickel(II) complexes are consistent with the energy level diagram for square-planar complexes with delocalized π-electron systems[17] as only two d-d bands are observed in compounds 1-6. In the SN bonded complexes (compound 7-12, 14-16), the appearance of three d-d bands may be due to a lower symmetry of coordination. Assigning the first band to the $^1A_{1g} \rightarrow {}^1B_{1g}$ ($xy \rightarrow x^2-y^2$) in-plane transition, the orbital splitting parameters were calculated assuming a correction factor[21] ($F_2 = 10F_4 = 800$ cm^{-1} for nickel(II) and 600 cm^{-1} for palladium(II)) for both SN and NN types of complexes. The results show $\Delta_1(NN) > \Delta_1(SN)$ for nickel(II) and $\Delta_1(Pd) > \Delta_1(Ni)$ for the SN bonded complexes. For L → M charge transfer bands, the relation CT(Pd) > CT(Ni) also holds good.[22,23] The Δ_1 values for SN donor complexes of nickel(II) (~ 21,000 cm^{-1}) and palladium(II) (~ 23,000 cm^{-1}) place these ligands in the following SN donor spectrochemical series: dithiooxamide > *N*, *N*-dimethyldithiooxamide > HATU > HNMATU > dithiomalonamide > diphenyldithiomalonamide.[23]

For $Pd(HSEATU)X_2$ and $Pt(HSEATU)X_2$ (X = Cl, Br), higher Δ_1 values for X = Cl then X = Br are in accordance with the relative positions of the halogens in the spectrochemical series and support the presence of coordinated halogen in the complexes.

For the orange cobalt(III) complexes, relatively high values of 10 Dq and low values of β indicate the presence of extensive metal ligand π-bonding. The splitting of the

TABLE 2
Infrared spectral data for selected complexes; cm^{-1}.

Compound		δH_2O	δNH_2	$\nu_{N\text{-}C\text{-}N}$	$\nu_{N\text{-}C\text{-}S(1)}$	$\nu_{N\text{-}C\text{-}S(2)}$	$\nu_{N\text{-}C\text{-}S(3)}$	$\nu_{C\text{-}S}$	$\nu_{M\text{-}N}$	$\nu_{M\text{-}S}$
1.	HATU		1645vs	1615vs 1525vs	1440ms	1370ms	935s	800ms		
2.	$Ni(ATU)_2.1.5H_2O$	1710vs	1640vs	1610vs 1570vs 1520s	1440ms	1370s	930s	810ms	490ms	
3.	$Cu(ATU)_2$		1645vs	1615vs 1575vs 1520vs	1435ms	1380s	930s	815ms	480ms	
4.	$Co(ATU)_2.1.5H_2O$	1715s	1640vs	1610vs 1580vs 1510vs	1440s	1370s 1325s	930s	805	510s	
5.	$Ni(ATU)_2$		1650vs	1610vs 1580vs	1440ms	1360s 1335ms	870w 820s	760s	460s	335w
6.	$Co(ATU)_2.3H_2O$	1715	1645vs	1610vs 1520vs	1430ms	1350ms 1350ms	840s	715s	500s	360w
7.	HNMATU		1660vs	1620vs 1510vs	1425ms	1340s	960w	770ms		
8.	$Ni(HNMATU)_2Cl_2$		1655vs	1610vs 1535vs	1450s	1360s 1336s	850ms	710ms	460s	340w
9.	$Cu(HNMATU)_2F_2$		1650	1615vs 1530vs	1440s	1360s 1340s	840ms	715ms	850s	340w
10.	$Pd(HNMATU)_2Cl_2H_2O$	1700s	1660vs	1620vs 1550vs	1450s	1350s 1300s	840w	700s	470w	365w
11.	$H_2SEATUBr$		1645vs	1590s 1535s				675s		
12.	$Ni(HSEATU)_2Cl_2$	1615vs	1560s	1500s				670w	510s 500s	
13.	$Cu(HSEATU)_2Cl_2$		1640vs	1590 1570s 1520s				670	485s	
14.	$Cu(HSEATU(H_2O)_2Cl_2$	1670s	1040vs	1600s 1580s 1520s				675	890w 480s	
15.	$Pd(HSEATU)Cl_2.2H_2O$			1550s 1530vs				645ms	490s	

TABLE 3
Electronic spectral data for the complexes.[a]

	Compound	d-d bands ($cm^{-1} \times 10^{-3}$)	Charge transfer bands ($cm^{-1} \times 10^{-1}$)	gl(cm-1) ν_1 (cm^{-1})
1.	Ni(Hbg)$_2$Cl2	21.74(2.05), 24.10(2.0)sh	35.71(3.4)	24,540
2.	Ni(ATU)2	22.47(2.08), 24.39(2.02)sh	35.71(3.48)	25,270
3.	Ni(SEATU)$_2$^{b}	20.15(2.05), 23.81(2.32)	34.84(3.47), 37.04(3.85)	22,950
4.	Ni(HSEATU)$_2$Cl$_2$	20.16(2.09), 23.69(2.32)	33.78(3.48), 38.46(3.89)	22,960
5.	Ni(HSEATU)$_2$Br$_2$	20.16(2.04), 23.63(2.33)	33.68(3.45), 38.21(3.81)	22,960
6.	Ni(HSEATU)$_2$I$_2$	20.08(2.04), 23.58(2.32)	33.68(3.46), 38.12(3.85)	22,880
7.	Ni(ATU)$_2$^{b}	17.86(1.83), 20.41(1.94), 22.73(1.97)	35.71(3.31)	20,660
8.	Ni(HATU)$_2$Cl$_2$	18.00(1.76), 20.01(1.92), 23.25(1.95)	31.02(3.34), 35.71(3.92)	20,800
9.	Ni(HATU)$_2$Br$_2$	18.04(1.78), 20.01(1.93), 23.25(1.92)	31.05(3.35), 35.82(3.86)	20,840
10.	Ni(NMATU)$_2$^{b}	18.12(1.84), 20.06(1.99), 22.73(2.00)	31.75(3.33), 36.36(3.48)	20,920
11.	Ni(HNMATU)$_2$Cl$_2$	18.02(1.82), 20.16(2.00), 22.72(1.99)	31.25(3.31), 36.36(3.52)	20,820
12.	Ni(HNMATU)$_2$Br$_2$	18.02(1.84), 20.06(2.00), 22.68(2.00)	31.25(3.34), 36.36(3.50)	20,820
13.	Pd(bg)$_2$^{d}	24.39 28.27		26,490
14.	Pd(ATU)$_2$^{d}	21.06 24.40 27.78	32.72 37.76	23,160
15.	Pd(HATU)$_2$Cl$_2$	21.00 24.38 27.81	32.71 37.82	23,100
16.	Pd(HNMATU)$_2$Cl$_2$^{d}	21.02 24.33 27.40	32.29	23,120
17.	Pd(HSEATU)Cl$_2$^{d}	21.04 24.39 27.78	37.08	23,140

Table 3 cont.

18.	Pd(HSEATU)Br$_2$^{d}	19.23	25.00	27.77		37.08	21,330
19.	Cu(bg)$_2$^{d}	17.84sh	20.40				
20.	Cu(Hbg)$_2$Cl$_2$	18.76					
21.	Cu(HSEATU)$_2$Cl$_2$	18.69			28.22		
22.	Cu(ATU)$_2$	18.69			28.22		
23.	Cu(Hbg)(H$_2$O)$_2$Cl$_2$	15.25					
24.	Cu(HSEATU) (H$_2$O)$_2$Cl$_2$	15.38			28.56		
25.	Cu(HSEATU) (H$_2$O)$_2$Br$_2$	15.38			28.56		
26.	Cu(HNMATU)$_2$F$_2$^{d}	16.52	18.34		27.03		
27.	Cu(HNMATU)$_2$SO$_4$^{d}	16.66	18.18		27.03		
28.	Cu(Hbg)$_3$Cl$_3$		20.80(1.87),	27.00(2.01)			*10Dq*^{g}
29.							22,350
29.	Co(ATU)$_3$^{e}		21.05(1.82),	28.16(2.04)	33.33(3.01)		22,830
30.	Co(Hbg)$_2$(H$_2$O)$_2$Cl$_3$	16.66(0.18)	21.05(1.98),	28.17(2.05)			25,580
31.	Co(ATU)$_2$(H$_2$O)$_2$Cl^f	16.64(0.17)	20.60(1.92),	28.15(1.98)	33.33(3.02)		25,610
32.	Co(ATU)$_3$^{e}		20.10(1.89)		29.41sh(2.98)		
33.	Co(NMATU)$_3$		20.15(1.92)		29.62sh(3.10)		
34.	Co(NEATU)$_3$		20.16(1.95)		29.62sh(3.15)		

[a] Figures in the parentheses indicate log ϵ values. The spectra were recorded in methanol unless mentioned otherwise. [b] in DMSO. [c] in isobutanol. [d] reflectance spectra. [e] in DMF. [f] in H_2O. [g] calculated assuming $C = 4B$, and $E({}^1A_{1g} \rightarrow {}^3T_{2g}) = 10D_q + 8B - 3C$.

$^1A_{1g} \rightarrow {}^1A_{1g}$ band due to *trans*-H_2O molecules was not observed. The bands at ~ 16,650 cm^{-1} for compounds 30–31 are assigned to $^1A_{1g} \rightarrow {}^3T_{2g}$ transitions due to their very low intensity. In $Co(ATU)_3$, the $^1A_{1g} \rightarrow {}^1T_{2g}$ absorption is masked by intense charge transfer bands.

Nmr studies.

The pmr spectral data of some of the nickel(II) and cobalt(III) complexes are presented in Table 4 and the assignments have been made with reference to $Ni(Hbg)_2Cl_2$.[12] The spectra can be explained on the basis of the suggested structures in Figure 1. The signals appearing in the range of 0–2.5 τ in compounds 1, 2, 4, 6 and 8 are due to the H_γ protons. This indicates the planarity of the metal-ligand ring and the presence of strong chelate ring currents in these complexes. In the orange inner complexes of nickel(II) and cobalt(III) (compounds 2 and 8 respectively) the presence of signals in this range is in accordance with their NN bonded structures (Fig. 1c). The absence of this signal (H_γ) in the inner complexes of $Ni(ATU)_2$ (compound 3), $Ni(SEATU)_2$ (compound 5) and $Co(ATU)_3$ (compound 7) and its presence in their corresponding cationic complexes (compounds 4 and 6) support the suggested structures shown in Fig. 1e for compounds 3 and 7, Fig. 1g for compound 5, Fig. 1d for compound 4 and Fig. 1h for compound 6 (Table–4). Splitting of the H_β proton signals in compounds 3 and 7 is due to their unsymmetrical structures (Fig. 1e). Protons corresponding to β_2, being nearer to less electronegative ring sulphur atoms will be slightly more shielded than β_1 protons. Similar splittings of the NH_α protons and upfield shifting of $H(\alpha_2)$ relative to $H(\alpha_1)$ in compounds 2 and 8 can be explained by the inductive effect of the sulphur group (Fig. 1e). This splitting does not occur in symmetric structures of $Ni(Hbg)_2Cl_2$.[12] The pmr signals of $Pd(HSEATU)Cl_2$ and $Pd(HNMATU)_2Cl_2$ could not be properly assigned due to over-

TABLE 4
Pmr spectral data for selected complences[a]

Compound	CH_3	CH_2	H_α	H_β	H_γ
1. $Ni(Hbg)_2Cl_2$	–	–	5.35(2) broad	3.4(4) narrow	0.12(1) broad
2. $Ni(ATU)_2$	–	–	4.8(α_1,1) 5.2(α_2,1)	4.2(2) narrow	0.8(1) broad
3. $Ni(ATU)_2$	–	–	5.8(1) broad	3.4(β_1,2) 4.4(β_2,2) narrow	–
4. $Ni(HATU)_2Cl_2$	–	–	5.6(1) broad	3.4(β_1,2) 4.0(β_2,2) narrow	0.6(1)
5. $Ni(SEATU)_2$	8.7(t,3)	6.8(q,2)	4.9(2) broad	4.0(2) narrow	–
6. $Ni(HSEATU)_2Cl_2$	8.8(t,3)	6.8(q,2)	4.8(2) broad	3.6(2.1) narrow	2.1(0.8) broad
7. $Co(ATU)_3$	–	–	5.6(1) Very broad	3.4(β_1,2) 3.9($\beta_2$2)	–
8. $Co(ATU)_3$	–	–	4.8(α_1,1) broad 5.4(α_2,1) narrow	3.8(2) narrow	1.2(1) broad

[a] Recorded in d^6-DMSO; Figure in parentheses indicate relative intensities; t = triplet, q = quartet.

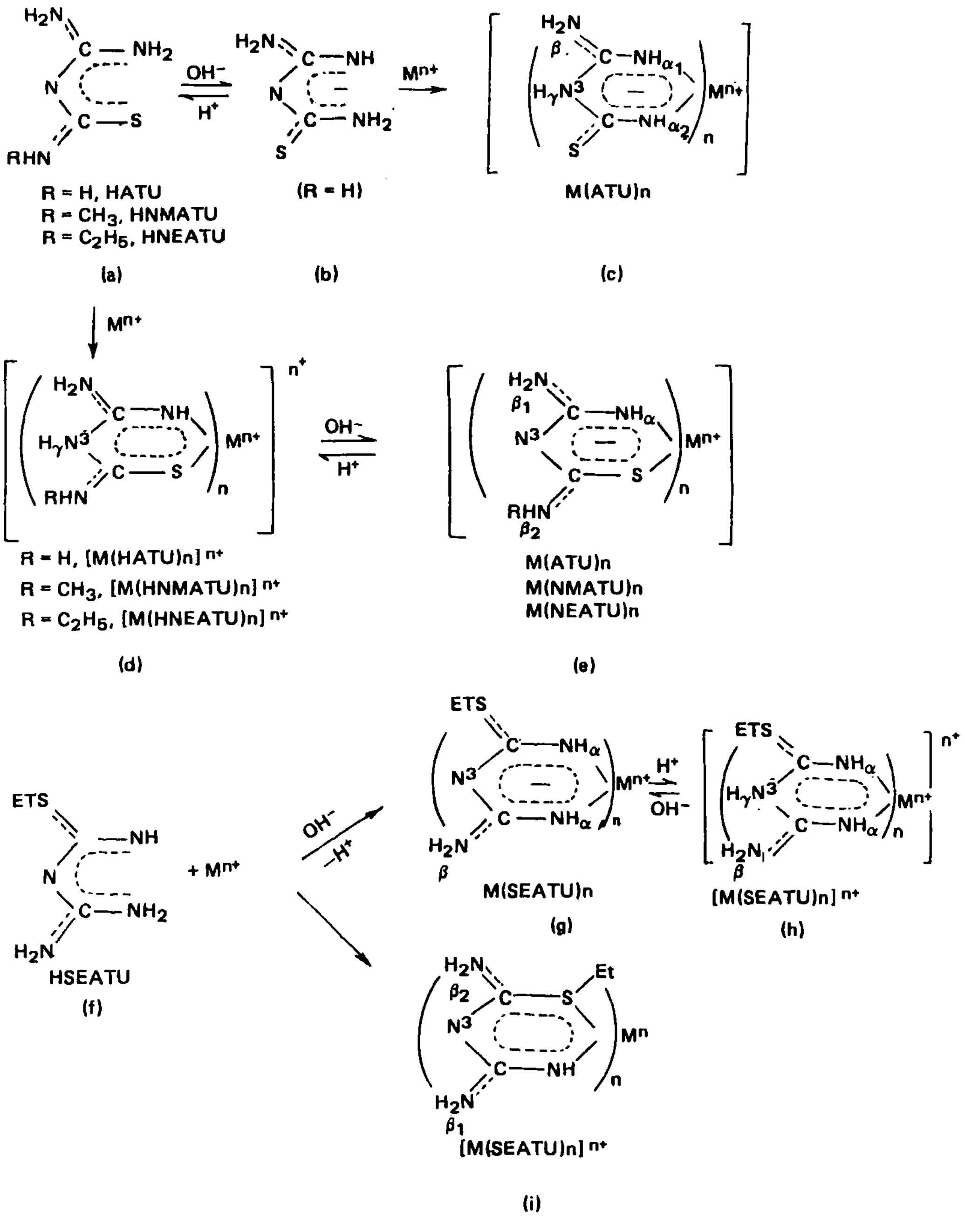

FIGURE 1

lapping and broad peaks. However, the absence of any proton signals in the range 0-3.0 τ in the former and their presence at 1.4 τ in the latter, supports the suggested structures, Fig. 1i and Fig. 1d, respectively.

Thermal analyses.

The lattice water molecules are generally lost in the temperature range 80 to 120°. Higher temperatures (120 to 150°) required for the dehydration of orange $Ni(ATU)_2.1.5H_2O$, orange $Co(ATU)_3.1.5H_2O$ and chocolate $Co(ATU)_3.3H_2O$ and the complex sulphates (Table 1) indicate the possibility of strong hydrogen bonding between H_2O and the ligand or sulphate ions as the case may be. The diaquo-complexes of copper(II) and cobalt(III) lose coordinated H_2O molecules in the temperature range 150-200° with partial decompositions.

The suggested structures of these complexes shown in Fig. 1 can explain all of their physicochemical properties. The presence of chelate ring currents in these complexes is responsible for their high stabilities. Conversion of the inner complexes to the corresponding complex salts *via* protonation of ligand nitrogen atoms is only possible if the π-electron delocalization is preserved. This happens through the protonation of the N_3 atom in case of metal complexes of HSEATU (Figs. 1e and 1d) and HNMATU (Figs 1g and 1h). NN bonded inner complexes of HATU, on the other hand, cannot be converted to the corresponding cationic ones because protonation of any ligand nitrogen atom destorys the π-electron delocalization either partially or completely (Fig. 1e). Non-existence of inner complexes such as $M(HSEATU)X_2$ (M = Pd, Pt; X = Cl, Br) must be due to absence of H_γ protons in their structures (Fig. 1i).

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