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Synthesis and Spectroscopic Studies of Ru(II) Complexes of 1,2,4-Triazoles, 1,2,4-Triazines and Pyrimidine Derivatives

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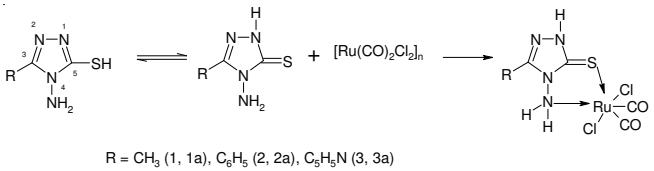
Treatment of the dichlorodicarbonyl ruthenium(II) $[Ru(CO)_2Cl_2]_n$ with bidentate 1,2,4-triazoles, 1,2,4-triazines and pyrimidine derivatives in refluxing ethanol or in THF yielded stable, octahedral yellow or pale-yellow solids. All the complexes have been characterized by IR, ^1H NMR spectroscopy and elemental analyses.

Key Words: Ruthenium(II), Triazoles, Triazines, Pyrimidine.

INTRODUCTION

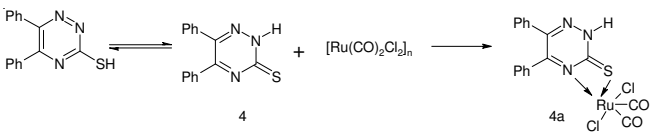
Coordination modes of metal complexes with organic ligands with heteroatom N, S or O are well known. The usefulness of metal complexes with such ligands exhibit remarkable biological activity against certain microbes, viruses and tumors[1-3]. The presence of heteroatom in such ligands play a key role when coordinated with transition metal atom for example 1,2,4-triazine derivative of Pd(II) and Pt(II) show mono-dentate or bidentate behaviour[4]. Similarly derivatives of 1,2,4-triazoles and 1,2,4-tiazine act as bidentate and exhibit tautomerism or ambidentate nature on coordination with metal atom. For example 3-alkyl-4-amino-5-thiol derivative of 1,2,4-triazole show a 5-membered ring complex on coordination with Co(II) or Ni(II)[5]. We have previously reported that Ru(II) forms very stable six membered complexes with ligands containing heteroatom N, S and O. These heteroatom's act as an electron donor to metal[6,7]. Now we report the preparation of Ru(II) complexes with 1,2,4-triazoles, 1,2,4-triazines and pyrimidine derivatives (**Scheme I-IV**). Ruthenium(II) in these complexes acts as an electron acceptor. This enhanced its ability to coordinate with electron donor ligand to yield a stable and electron rich compound of low ionization energy. The complexes (**1a**), (**2a**), (**3a**), (**4a**), (**6a**) show their tautomeric nature on coordination with metal Ru(II) while in complex **5a** the ligand acts as an ambidentate nature (**Scheme-IV**).

The IR spectra of all these complexes show only two metal terminal (Ru-CO) band near 2000 cm^{-1} and are in *cis* disposition[6,7,9]. All the ligands form a six membered ring structure around the metal Ru(II). IR and ^1H NMR spectra of complexes are shown in Tables 1 and 2, respectively. The elemental analyses are given in experimental section are consistent with proposed structures and formulations.

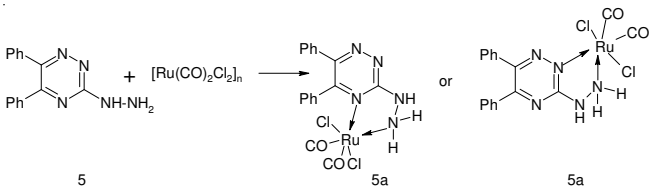


R = CH_3 (1, 1a), C_6H_5 (2, 2a), C_5H_5N (3, 3a)

Scheme-I: Complex (**1a**), (**2a**), (**3a**) tautomeric nature of thiol/thione of 3-methyl/phenyl/pyridine-4-amino-5-thiol 1,2,4 triazole



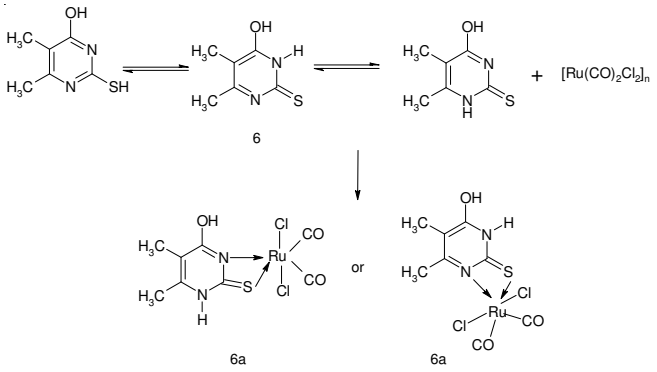
Scheme-II: Complex **2a** tautomeric nature of 3-thiol-5,6-diphenyl-1,2,4-triazine



Scheme-III: Complex **5a** ambidentate nature of 3-hydrazino-5,6-diphenyl-1,2,4-triazine

EXPERIMENTAL

The salt $RuCl_3 \cdot xH_2O$ was purchased from FLUKA Inc. and $[Ru(CO)_2Cl_2]_n$ was prepared by the procedure reported in literature[8,9].



Scheme-IV: Complex **6a** tautomeric nature of 4-hydroxy-2-thio/5,6-dimethyl pyrimidine

The ligand 3-alkyl-4-amino-5-thiol-1,2,4 triazole and its aryl or pyrimidine derivatives were prepared by method as reported in the literature[10]. While the ligand 3-hydrazino-5,6-dipheniyl-1,2,4-triazine was prepared as reported in literature[11].

Physical measurements: IR spectra were measured on Perkin-Elmer FTIR spectrometer. ^{1}H NMR were recorded on BRUCKER-AVANCE-111 600MHz. Elemental analyses were carried out by the Microanalysis Laboratory of King Abdulaziz University, Jeddah.

Preparation of the compounds

Typical reaction is described: In a small 100 mL round bottom 2-necked flask fitted with N_2 gas inlet and water condenser was added $[Ru(CO)_2Cl_2]_n$ and the corresponding ligand of 1,2,4-triazole in (1:1) mole ratio in ethanol or THF (20 mL). The solution was refluxed for 2 h. The solvent was reduced in volume which on cooling gave a yellow or pale yellow crystallized solid **1a-6a**. The complex was washed with pet. ether at 30-40 ºC and dried in vacuum.

TABLE-1
IR SPECTRAL BANDS (cm^{-1})[a]

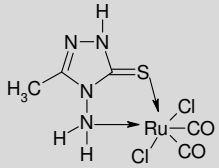
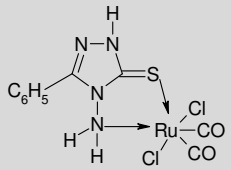
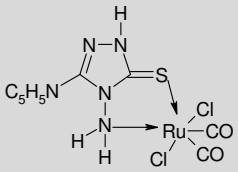
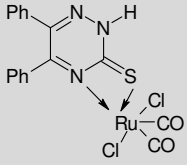
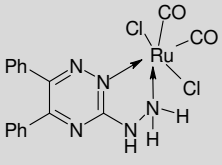
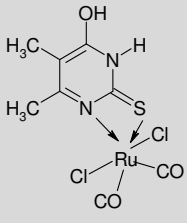
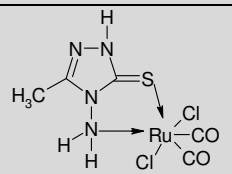
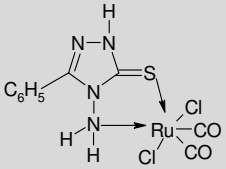
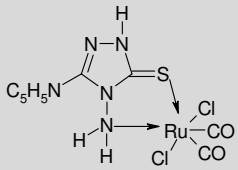
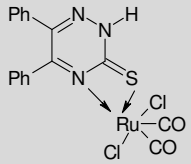
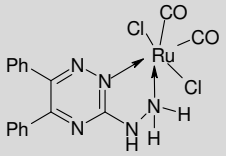
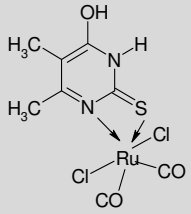
Compound	ν(N-H)	ν(Ru-CO)	ν(C=S)	Other bands
 **1a**	3319 (3264)[a], 3070(3102)[a]	2066, 2004	1102	2950, 1574, 1454,1374, 1314, 1981, 914, 756, 734
 **2a**	3250, 3140	2066, 2007	1076	1611. 1565, 1424, 1180, 1003, 772, 690
 **3a**	3350, 3142	2064, 2000	1043	1622, 1481, 1406, 1234, 835, 729, 678
 **4a**	3240	2063, 2010	1121	1633, 1554, 1515, 1427, 1351, 1121, 1060, 965, 762, 694.
 **5a**	3230, 3180	2068, 2006	–	1634, 1536, 1445, 1374, 1171, 1098, 1067, 926, 876, 764, 701, 694
 **6a**	3250	2067, 2001	1190	2901, 2887, 1672, 1557, 1442, 1445, 1042, 947, 835

TABLE-2
PROTON MAGNETIC RESONANCE SPECTRUM ppm (δ)

Compound	Chemical shift (δ)	Relative intensity	Multiplicity	Multiplicity
 **1a**	10.8 (11.0)[a] 4.4 (4.6)[a] 1.5 (1.7)[a]	1 2 3	1 Broad 1	NH/SH NH_2 CH_3
 **2a**	7.3 (7.6)[a] 3.8 (3.65)[a] 14.0 (14.6)[a]	5 2 1	D Broad Broad	C_6H_5 NH_2 SH/NH
 **3a**	7.7 (8.0-8.8)[a] 3.2 (3.3)[a] 13.8 (14.0)[a]	2,2 2 1	dd Broad s	C_5H_5 NH_2 SH/NH
 **4a**	10.8 (13.8)[a] 8.1 (8.1)[a] 7.4-7.6 (7.5-8,0)[a]	1 2 5	Broad s d,d	NH NH_2 C_6H_5
 **5a**	14.8 (15.1)[a] 7.0-7.2 (7.3-7.6)[a]	1 5	Broad d,d	SH/NH C_6H_5
 **6a**	2.2 (2.1)[a] 3.8 (2.5)[a] 5.9 (5.7)[a] 12.8 (12.3)[a]	3 3 1 1	1 1 1 1	CH_3 CH_3 CH_3 CH_3

a = (Free ligand).

All the complexes shown in **Scheme I-IV** were prepared according to this general method using (1:1) mole ratio of the salt $[Ru(CO)_2Cl_2]_n$ and the corresponding ligand.

Preparation of dichorodicarbonyl-3-methyl-4-amino-5-thio-1,2,4-triazole ruthenium (II) (1a): The salt $[Ru(CO)_2Cl_2]_n$ (0.2 g) and the ligand (0.11 g) were refluxed in 20 mL THF for 1 h. The solution was worked out as described above which gave reddish yellow solid. Anal. calcd. (%) for $[C_5H_6N_4O_2SCl_2]Ru$: C, 16.7, H, 1.6, N, 15.6, Found (%): C, 16.1, H, 1.7, N. 15.2.

Preparation of dichorodicarbonyl-3-phenyl-4-amino-5-thio-1,2,4 triazole ruthenium(II) (2a): The salt $[Ru(CO)_2Cl_2]_n$ (0.2 g) and the ligand (0.11 g) were refluxed in 20 mL THF for 1 h. This gave yellow solid. Anal. calcd. (%) for $[C_{10}H_8N_4O_2SCl_2]Ru$: C, 28.5, H, 1.9, N, 13.3, found (%): C, 28.1, H, 1.7, N. 13.9.

Preparation of dichorodicarbonyl-3-pyridine-4-amino-5-thio-1,2,4 triazole ruthenium(II) (3a): Take the salt $[Ru(CO)_2Cl_2]_n$ (0.1 g, 0.438 mmol) and the ligand (0.116 g 0.438 mm) in 20 mL EtOH were refluxed for 1.5 h and worked as above. This gave light orange solid. Anal. calcd. (%) for $[C_9H_8N_4O_2SCl_2]Ru$: C, 25.5, H, 1.8, N, 16.5, found (%): C, 25.1, H, 1.6, N. 16.1.

Preparation of dichlorodicarbnyl-3-thiol-5,6-diphenyl-1,2,4-triazine ruthenium (II) (4a): The salt $[Ru(CO)_2Cl_2]_n$ and the ligand were refluxed in 20 mL THF for 1 h. The solution was worked out as described above and it gave yellow solid. Anal. calcd. (%) for $[C_{17}H_{10}N_3O_2SCl_2]Ru$: C, 41.4, H, 2.0, N, 8.5, found (%): C, 42.0, H, 2.2, N. 8.3.

Preparation of dichlorodicarbnyl-3-hydrazino-5,6-diphenyl-1,2,4-triazine ruthenium (II) (5a): The salt $[Ru(CO)_2Cl_2]_n$ and the ligand in (1:1) mole ratio were refluxed

in 20 mL EtOH for 1.5 h. Which gave yellow solid. Anal. calcd. (%) for $[C_{17}H_{13}N_5O_2Cl_2]Ru$: C, 41.5, H, 2.6, N, 14.2, Found (%): C, 41.9, H, 3.0, N. 14.4.

Preparation of dichlorodicarbnyl-2-mercapto-4-hydroxy 5,6-dimethyl pyrimidin ruthenium (II) (6a): The salt $[Ru(CO)_2Cl_2]_n$ (0.15 g) and the ligand (0.1 g) were refluxed in 20 mL THF for 2 h. The solution was reduced in vol. and addition of pet.ether 30-40 ºC gave yellow solid in good yield. Anal. calcd. (%) for $[C_8H_8N_2O_2SCl_2]Ru$: C, 26.0, H, 2.1, N, 7.6, found (%): C, 26.4, H, 2.0, N. 8.0.

RESULTS AND DISCUSSION

The structure of complex (**1a**) dichlorodicarbonyl-3-methyl-4-amino-5-thione ruthenium (**II**) as shown in **Scheme-I** and other structures (**2a**), (**3a**), (**4a**) and (**6a**) show S=C-N-N unit which acts as bidentate to the metal Ru(II) through (N) amine and (S) thione to give very stable crystallized solid six membered ring with tautomeric structure while complex (**5a**) may be represented as having ambidentate character. On comparing the IR spectra of these complexes with their free ligands clearly show that there is ν(N-H) asym and sym symetrical stretching frequencies in the region of 3200-3100 cm^{-1} and a band δ NH near 1600 cm^{-1} while ν(C-H) for CH_3, C_6H_5 and C_5H_5-N group are at 2900-2800 cm^{-1}. A band for ν(C=S) around 1100-1130. All these complexes show very distinct two sharp bands around 2070 and 2004 cm^{-1} which are metal terminal-carbonyl (Ru-CO) and are in *cis* disposition[6,7,9]. These bands in the salt $[Ru(CO)_2Cl_2]_n$ are at 2145, 2075 and 2020 cm^{-1} [8,9]. ^1H NMR spectrum of complex (**1a**) shows a single band at 1.7 δ (NH_2) and a single band at 3.8 δ(N-H) which may be due to tautomeric NH/SH protons of phenyl groups around 7.0-7.5 δ while the (**5a**) shows protons of hydrazine (NH-NH_2) very clearly, see Table-2. It is note worthy that proton magnetic resonance of all the complexes show a slight down field compared to free ligand as a result of coordination to the metal Ru(II) ion which acts as electron acceptor from the ligand to the metal Ru(II) that causes down field shift in all the complexes.

^1H NMR spectra of all complexes show a slight down field shift that may be due to the coordination between ligands and the electron deficient metal Ru(II).

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