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

ABDULLAH M. ASIRI, A.O. BAGHLAF, R.M. ABDEL-RAHMAN, SALMAN A. KHAN* and M. ISHAQ

Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah-21589, Saudi Arabia

*Corresponding author: Tel: +966 2 0598337050; E-mail: sahmah_phd@yahoo.co.in

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Treatment of the dichlorodicarbonyl ruthenium(II) $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ 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 tumors¹⁻³. 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 behaviour⁴. Similarly derivatives of 1,2,4-triazoles and 1,2,4-triazine 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

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

analyses are given in experimental section are consistent with proposed structures and formulations.

EXPERIMENTAL

The salt $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was purchased from FLUKA Inc. and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ 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 literature¹⁰. While the ligand 3-hydrazino-5,6-diphenyl-1,2,4-triazine was prepared as reported in literature¹¹.

Physical measurements: IR spectra were measured on Perkin-Elmer FTIR spectrometer. ¹H 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 N₂ gas inlet and water condenser was added [Ru(CO)₂Cl₂]_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 °C and dried in vacuum.

TABLE-1
IR SPECTRAL BANDS (cm⁻¹)^a

Compound	$\nu(\text{N-H})$	$\nu(\text{Ru-CO})$	$\nu(\text{C=S})$	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 ₆ H 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 ₅ H 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 ₆ H ₅
5a	14.8 (15.1) ^a 7.0-7.2 (7.3-7.6) ^a	1 5	Broad d,d	SH/NH C ₆ H 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 $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ and the corresponding ligand.

Preparation of dichlorodicarbonyl-3-methyl-4-amino-5-thio-1,2,4-triazole ruthenium (II) (1a): The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (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 $[\text{C}_5\text{H}_6\text{N}_4\text{O}_2\text{SCl}_2]\text{Ru}$: C, 16.7, H, 1.6, N, 15.6, Found (%): C, 16.1, H, 1.7, N, 15.2.

Preparation of dichlorodicarbonyl-3-phenyl-4-amino-5-thio-1,2,4 triazole ruthenium(II) (2a): The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (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 $[\text{C}_{10}\text{H}_8\text{N}_4\text{O}_2\text{SCl}_2]\text{Ru}$: C, 28.5, H, 1.9, N, 13.3, found (%): C, 28.1, H, 1.7, N, 13.9.

Preparation of dichlorodicarbonyl-3-pyridine-4-amino-5-thio-1,2,4 triazole ruthenium(II) (3a): Take the salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (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 $[\text{C}_9\text{H}_8\text{N}_4\text{O}_2\text{SCl}_2]\text{Ru}$: C, 25.5, H, 1.8, N, 16.5, found (%): C, 25.1, H, 1.6, N, 16.1.

Preparation of dichlorodicarbonyl-3-thiol-5,6-diphenyl-1,2,4-triazine ruthenium (II) (4a): The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ 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 $[\text{C}_{17}\text{H}_{10}\text{N}_3\text{O}_2\text{SCl}_2]\text{Ru}$: C, 41.4, H, 2.0, N, 8.5, found (%): C, 42.0, H, 2.2, N, 8.3.

Preparation of dichlorodicarbonyl-3-hydrazino-5,6-diphenyl-1,2,4-triazine ruthenium (II) (5a): The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ 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 $[\text{C}_{17}\text{H}_{13}\text{N}_3\text{O}_2\text{Cl}_2]\text{Ru}$: C, 41.5, H, 2.6, N, 14.2, Found (%): C, 41.9, H, 3.0, N, 14.4.

Preparation of dichlorodicarbonyl-2-mercapto-4-hydroxy 5,6-dimethyl pyrimidin ruthenium (II) (6a): The salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (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 °C gave yellow solid in good yield. Anal. calcd. (%) for $[\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{SCl}_2]\text{Ru}$: 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 $\text{S}=\text{C}-\text{N}-\text{N}$ 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 $\nu(\text{N}-\text{H})$ asym and sym symmetrical stretching frequencies in the region of $3200-3100\text{ cm}^{-1}$ and a band $\delta\text{ NH}$ near 1600 cm^{-1} while $\nu(\text{C}-\text{H})$ for CH_3 , C_6H_5 and $\text{C}_3\text{H}_5-\text{N}$ group are at $2900-2800\text{ cm}^{-1}$. A band for $\nu(\text{C}=\text{S})$ around $1100-1130$. All these complexes show very distinct two sharp bands around 2070 and 2004 cm^{-1} which are metal terminal-carbonyl ($\text{Ru}-\text{CO}$) and are in *cis* disposition^{6,7,9}. These bands in the salt $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ are at 2145 , 2075 and 2020 cm^{-1} ^{8,9}. ^1H NMR spectrum of complex (**1a**) shows a single band at 1.7δ (NH_2) and a single band at 3.8δ ($\text{N}-\text{H}$) which may be due to tautomeric NH/SH protons of phenyl groups

around $7.0-7.5\delta$ while the (**5a**) shows protons of hydrazine ($\text{NH}-\text{NH}_2$) 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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REFERENCES

1. S. Padhye and G.B. Kaufman, *Coord. Chem. Rev.*, **63**, 127 (1985).
2. A.M. Asiri and S.A. Khan, *Molecules*, **15**, 4784 (2010).
3. E. Bermego, R. Carballo, A. Castimeiras, R. Domingues, C.M. Mossmer, J. Strahle and D.X. West, *Polyhedron*, **18**, 3695 (1999).
4. M. Ghassemzadeh, M.M. Aghayan and B. Neumuller, *Inorg. Chim. Acta*, **358**, 2057 (2005).
5. C.M. Menzies and P.J. Squattrito, *Inorg. Chim. Acta*, **314**, 194 (2001).
6. A.O. Baghlaf, M. Ishaq and A.K.A. Rashed, *Polyhedron*, **6**, 837 (1987).
7. A.O. Baghlaf, M. Ishaq, S.A. Rahman, A.B. Al-Tahir, A. Zaidan and R.A. Kabli, *Polyhedron*, **7**, 219 (1988).
8. R. Colton and R.H. Farthing, *Aust. J. Chem.*, **20**, 1283 (1997).
9. M.J. Cleare and W.P. Griffith, *J. Chem. Soc. (A)*, 372 (1969).
10. R.M. Abdel-Rahman, *Pharmazie*, **56**, 18 (2001).
11. C. Ma, G. Tian and R. Zhang, *Inorg. Chem. Commun.*, **9**, 882 (2006).