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Synthesis and spectral studies of iron(III), ruthenium(III) and rhodium(III) complexes with new tetraaza macrocyclic ligands

S.J. Swamy*, B. Veera Pratap, P. Someshwar, K. Suresh and D. Nagaraju

Department of Chemistry, Kakatiya University, Warangal – 506 009, India

Complexes of iron(III), ruthenium(III) and rhodium(III) with three new tetraaza macrocyclic ligands, oxo$_4$bzo$_3$[14]triene-N$_4$ [TBTAC14Tone], oxo$_4$bzo$_2$[14]diene-N$_4$ [DBTAC14Tone] and oxo$_4$bzo$_2$[15]diene-N$_4$ [DBTAC15Tone] have been prepared and characterised. The complexes are found to have the formulae [FeLCl$_2$]Cl. 2H$_2$O, [RuLCl$_2$]Cl. 3H$_2$O and [RhLCl$_2$]Cl. 2H$_2$O. The cations adopt a *trans*-dichloro configuration with the six-coordinated trivalent metal ions in a pseudo-octahedral geometry.

Keywords: macrocyclic ligands, tetraazatetraamide ligands, transition metal complexes, iron(III), ruthenium(III), rhodium(III)

The naturally occurring macrocyclic compounds, the tetrapyrrole derivatives, are found repeatedly in compounds carrying out extremely diverse functions, *e.g.* light harvesting (chlorophyll[1]), oxygen carriers (hemoglobin[2]) and electron transport (cytochromes[3]). To understand the biochemical activity of metalloenzymes, a number of synthetic analogues have been prepared and investigated.[4] In view of the interest and importance of nitrogen macrocycles, we have developed some new tetraaza macrocycles of variable ring sizes by non-template synthetic methods.[5] We present here the synthesis and characterisation of the complexes of trivalent transition metal ions, Fe(III), Ru(III) and Rh(III) with three ligands, tribenzo[*b,f,i*][1,4,8,11]tetraazacyclotetradecene-5,9,10,14-tetraone, TBTAC14Tone, dibenzo[*e,m*][1,4,8,11]tetraazacyclotetradecene-2,3,7,12-tetraone, DBTAC14Tone and dibenzo[*e,n*][1,4,8,12]tetraazacyclopentadecene-2,3,7,13-tetraone, DBTAC15Tone, using analytical, conductance, magnetic, thermal and spectroscopic (IR, UV-Vis, NMR, and mass) investigations. These three ligands can be named and abbreviated by following the rules suggested for naming the nitrogen macrocycles[6] as: 5,9,10,14-oxo$_4$-2,3:6,7:12,13-bzo$_3$[14]2,6,12-triene-1,4,8,11-N$_4$ {Oxo$_4$Bzo$_3$[14]triene-N$_4$}; 2,3,7,12-oxo$_4$-5,6:13,14-bzo$_2$[14]5,14-diene-1,4,8,11-N$_4$ {Oxo$_4$Bzo$_2$[14]diene-N$_4$} and 2,3,7,13-oxo$_4$-5,6:14,15-bzo$_2$[15] 5,14-diene-1,4,8,12-N$_4$ {Oxo$_4$Bzo$_2$[15]diene-N$_4$}.

Results and discussion

All the complexes are stable, non-hygroscopic and soluble in methanol, ethanol, DMF and DMSO. The analytical data of the metal chelates, presented in Table 1, indicate that the metal ions are coordinated to one ligand molecule and two chloride ions. The conductance data of all the complexes (20–30 ohm^{-1} cm^2 mol^{-1}) indicate that they are 1:1 electrolytes. The data confirmed that the metal ions are coordinated to a ligand molecule and two chloride ions and the third chloride ion is outside the coordination sphere. The analytical data further confirm that the Fe(III) and Rh(III) complexes have two water molecules, while the Ru(III) complexes analyse for the formula [RuLCl$_3$].3H$_2$O. The formulae and the tentative structures of the complexes have been confirmed with the help of thermal and spectral investigations. Heating the complexes in open capillaries has indicated that the complexes do not melt but decompose above 260 °C. This is confirmed by the absence of any endothermic peak above 200 °C in their thermograms.

The mass spectra of all the complexes exhibit fragments corresponding to the ion [MLCl$_2$]$^+$. Another ion that confirms the coordination of the ligand to the metal ion is the appearance of ML$^+$ fragment. The other ions detected in the mass spectra of the complexes are those of the ligands.[5]

Thermal analysis

The complexes are found to undergo three or four stage decomposition. The initial weight loss curve was found between 60° and 120 °C in all the complexes. The percentage loss accounts for two water molecules in the case of Fe(III) and Rh(III) complexes and to the three water molecules in Ru(III) complexes. An endothermic peak is found in the DTA curves of all the complexes between 60° and 120 °C. The loss of water molecules in this temperature range, indicates that the water molecules are lattice held.[7] The thermograms are parallel to the temperature axis up to 250 °C and then exhibit a mass loss curve that continues up to about 400 °C. The mass loss corresponded to three chloride ions. The final stage of decomposition starts after a break of 50–60 °C. The percentage of the residue left at the end was found to be respective metal oxide, Fe$_2$O$_3$[8], Ru$_2$O$_3$[9] and Rh$_3$O$_4$.[10]

IR spectra

The characteristic absorptions of the N$_4$-macrocyclic ligands containing four amide groups have been presented previously.[5] The spectra of the corresponding complexes exhibit these absorptions at different frequencies indicating the coordination of the ligands. The ν(N–H) and amide-II stretching frequencies shift by 50–100 cm^{-1} and 20–30 cm^{-1} respectively towards low frequency confirming the coordination of amide N-atoms to the metal ions.[11] The amide-I, ν(C=O) stretching frequency in the spectra of all complexes shifted to high frequency by 15–30 cm^{-1} indicating that the amide oxygen is not coordinated.[12]

The analytical and thermal data revealed that there are water molecules associated with the metal complexes. In the IR spectra of the complexes a broad absorption is found between 3600 and 3300 cm^{-1} confirming the presence of water molecules. The Fe(III) complexes exhibit two absorptions in the IR spectra, one at 820 cm^{-1} and the other at 570 cm^{-1} assignable to (H$_2$O)$_{rock}$ and (H$_2$O)$_{wag}$ of the uncoordinated water molecule.[13] Similar absorptions are found in the spectra of Ru(III) and Rh(III) complexes. The non-coordination of water molecules is further confirmed by the absence of absorption around 400 cm^{-1} characteristic of ν(M–O).[14] In the far-IR region, all complexes exhibit absorptions around 350 cm^{-1} and 250 cm^{-1} attributed to ν(M–N)[15] and ν(M–Cl)[16] vibrations respectively.

^{1}H NMR spectra

The characteristic signals observed in the spectra of the ligands are described elsewhere.[5] The ^{1}H NMR spectra of diamagnetic Rh(III) complexes recorded in DMSO-*d*$_6$ exhibit aromatic proton resonance signals at the same field. The methylene protons' signal at 2.52 ppm (DBTAC15Tone) is also observed at the same field in the spectrum of the complex, **9**. The amide proton (OC-NH) signal exhibited a considerable down field

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* Correspondent. E-mail: sj_swamy@yahoo.com

Table 1 The analytical and physiochemical data of the complexes

Sample no.	Complex	Yield g/%)	Colour	M^+	Found (Calcd)					Λ^*_M	μ_{eff} B.M.
					%C	%H	%N	%Cl	%M		
1	[Fe(TBTAC14Tone)Cl_2]Cl.$2H_2O$	0.74	Dark Brown	597, 599	44.02	3.23	9.26	17.58	9.22	25.4	5.8
		(62)		601	(44.14	3.37	9.36	17.77	9.36)		
2	[Ru(TBTAC14Tone)Cl_2]Cl.$3H_2O$	0.79	Light Brown	572, 574	39.66	3.12	8.12	16.11	15.08	28.4	2.06
		(67)		576	(39.92	3.35	8.47	16.07	15.27)		
3	[Rh(TBTAC14Tone)Cl_2]Cl.$2H_2O$	0.81	Light Brown	574, 576	40.51	3.00	8.37	16.29	15.76	22.3	Dia
		(67)		578	(40.92	3.12	8.68	16.47	15.94)		
4	[Fe(DBTAC14Tone)Cl_2]Cl.$2H_2O$	0.62	Brown	479, 481	39.08	3.16	10.02	9.36	19.11	32.5	5.7
		(56)		483	(39.23	3.63	10.17	10.28	19.34)		
5	[Ru(DBTAC14Tone)Cl_2]Cl.$3H_2O$	0.74	Yellow	542, 544	35.11	3.36	9.12	16.20	15.27	35.3	1.85
		(62)		546	(35.20	3.58	9.34	17.35	16.46)		
6	[Rh(DBTAC14Tone)Cl_2]Cl.$2H_2O$	0.91	Light Brown	526, 528	35.96	3.12	8.68	17.52	15.95	29.2	Dia
		(74)		530	(36.15	3.34	9.37	17.82	17.24)		
7	[Fe(DBTAC15Tone)Cl_2]Cl.$2H_2O$	0.68	Dark Brown	493, 495	40.27	3.69	9.82	18.69	9.90	26.5	5.6
		(59)		498	(40.42	3.93	9.92	18.84	9.89)		
8	[Ru(DBTAC15Tone)Cl_2]Cl.$3H_2O$	0.82	Yellow	538, 540	36.13	3.68	8.78	16.77	15.98	35.0	1.91
		(66)		542	(36.35	3.85	8.92	16.94	16.10)		
9	[Rh(DBTAC15Tone)Cl_2]Cl.$2H_2O$	0.87	Yellow	540, 542	37.10	3.26	9.11	17.29	16.65	27.6	Dia
		(71)		544	(37.31	3.63	9.16	17.39	16.82)		

•$ohm^{-1}cm^2mol^{-1}$

shift by 0.4 to 0.5 ppm [8.46 (**3**), 9.01 (**6**), 9.02 (**9**) ppm]. The resonance signal of methylene protons in the close proximity of the donor atoms are also affected by the coordination to the metal ion. They are slightly shifted up-field: 3.32 (**6**) and 3.38 (**9**) ppm. Thus the ^1H NMR spectra confirmed the coordination of the ligand to the metal ions. The signal intensity indicates that only one ligand molecule is coordinated. Further, a new signal at 4.21 (**3**), 3.98 (**6**) and 4.08 (**9**) is observed in the spectra of Rh(III) complexes which confirms the presence of water molecules out-side the coordination sphere.[8b]

These data confirm that the trivalent metal ions are coordinated to the quadridentate tetraaza macrocycle and to two chloride ions resulting in a cationic complex species. The geometry of these six coordinated complexes may be proposed as distorted octahedral. Recently, the crystal structure of an iron(III) complex, $[FeCl_2\{bispic(PA)_2en\}]^{3+}$, with a dipositive quadridentate ligand showed it to have distorted octahedral geometry.[17] For the six coordinated trivalent Ru(III) and Rh(III) complexes also the most common geometry is octahedral.[18]

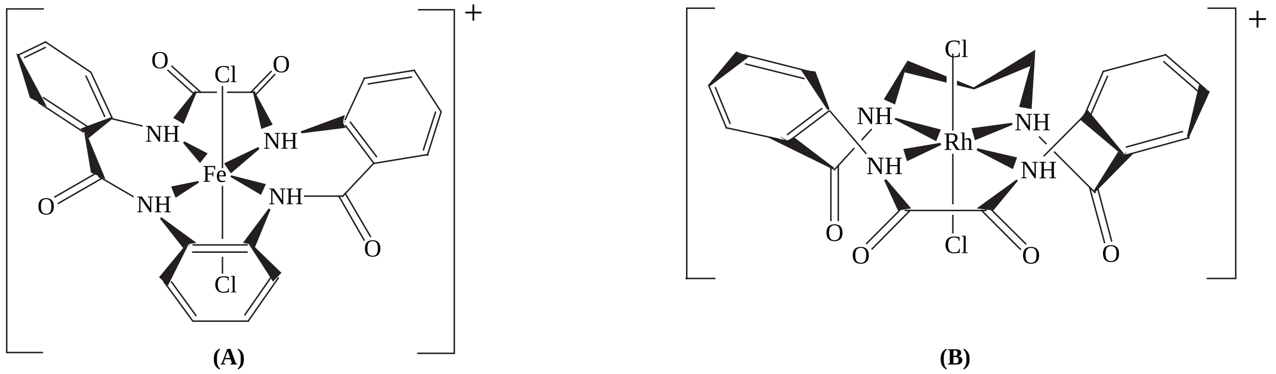
Magnetic moments and UV-Vis spectra

The magnetic moments of Fe(III) and Ru(III) complexes were found to be around 5.6 and 1.9 B.M. respectively, confirming that the d^5 Fe(III) complexes are high spin, while the Ru(III) complexes are low spin. The Rh(III) complexes were found to be diamagnetic. The ground state term $^6A_{1g}$ of Fe(III), derived from the $t_{2g}{}^3e_g{}^2$ configuration, results in three spin forbidden transitions of low intensity to $^4T_{1g}$, $^4T_{2g}$, and $^4A_{1g}$ (^4E_g) excited states. In the present cases, an absorption of very high intensity assignable to ligand → metal charge transfer transition and two absorptions of low intensity attributable to *d–d* transitions are observed as given in Table 2. The low spin Ru(III) complexes exhibit three absorptions from the ground term $^2T_{2g}$ ($t_{2g}{}^5$) to the excited state configurations. Rh(III), a d^6 ion, that forms a vast majority of octahedral complexes as in the present study, with an $^1A_{1g}$ ground state term exhibits two low intensity absorptions corresponding to the transitions $^1T_{1g} \leftarrow {}^1A_{1g}$,($\nu_1$) and $^1T_{2g} \leftarrow {}^1A_{1g}$ (ν_2). The low intensity absorptions of Rh(III) complexes indicate that they are *trans*-complexes. The *cis*-complexes generally exhibit high intensity absorptions due to the absence of center of symmetry. In analogy with the Rh(III) complexes, the Fe(III) and Ru(III) complexes may also be expected to have *trans*-octahedral geometry.

Table 2 Electronic spectral data of complexes

Complex n.	Absorption, nm (ε_{max})
1	420.5(2684), 525 (4.58), 605 (1.98)
2	410.0 (1045), 538.7 (3.56), 610.6(1.28)
3	423.0 (5675), 510.0(15.25), 580.0(1.38)
4	416.0(4028), 486.5(15.20),579.5(5.66)
5	420.0(4028),486.5(15.20),579.5(5.66)
6	422.5(4380),538.5.(12.30),597.0(1.72)
7	423.0(5675),510.0(15.20), 580.0 (1.38)
8	420.5(3850), 487.0(9.87),615.0(3.68)
9	420.9(4375), 525.0 (12.18), 597.0(1.68)

Based on the analytical and spectral studies, the tentative structures of the complexes are proposed as shown in Fig. 1.



(A) **(B)**

Fig. 1 Tentative structures of the complexes, (A) $[Fe(TBTAC14Tone)Cl_2]^+$ and (B) $[Ru(DBTAC15Tone)Cl_2]^+$.

Experimental

All the chemicals used were of AR grade. The ligands TBTAC14Tone, DBTAC14Tone and DBTAC15Tone were prepared by the methods reported in literature.[5] The purity of the compounds was checked by TLC and melting point determination. The metal chlorides were purchased from the Aldrich Chemical Company. The solvents were dried and distilled before use.

The analytical and spectral data were measured using the following instruments Elemental analysis (Perkin-Elmer CHN analyser-2400), IR spectra – KBr pellets (Perkin-Elmer BX1 series), UV–Vis spectra (Shimadzu UV-2401 PC) in methanol, ^{1}H NMR spectra (JEOL 200 MHz) in DMSO-d_6, magnetic susceptibility (EC&G PARC VSM 155 Vibrating Sample Magnetometer) and conductance (Digisun Digital Conductivity Meter DI-909) at 10^{-3} M concentration in DMSO. The percentages of metal ions in the complexes are estimated using standard procedures. The chloride ions are estimated using spectrophotometric method.[19]

Preparation of complexes

2.0 mmol of the appropriate ligand (0.8 g TBTAC14Tone/0.74 g DBTAC14Tone/0.74 g DBTAC15Tone) was dissolved in 30 ml of methanol. To this a 20 ml solution containing 2.0 mmol of respective metal chloride ($FeCl_3$: 0.25 g/$RuCl_3.6\ H_2O$: 0.41 g/$RhCl_3.6\ H_2O$: 0.42 g) was added slowly. The reaction mixture was refluxed for about 2 h while stirring continuously. The solution became turbid and slowly the complexes started to separate. Then 30 ml of the solvent was removed under reduced pressure and the residue was cooled overnight at 0 °C. The solids were filtered and washed with cold methanol and acetone. The complexes were purified by extracting into an excess of hot methanol, concentrating and cooling. The analytical and physical characteristics are presented in Table 1.

Conclusions and perspectives

Williams *et al.*[13b] have recently investigated the complexes of a macrocyclic ligand containing amide and amine nitrogen atoms, 1,4,8,11-tetraazacyclotetradecane-5,12-dione. They have reported that metal binding is highly pH sensitive and *reversible* (a very useful property for metal sensing applications). The Cu(II) complexes prepared at neutral and basic pH were found to have different structures, depending on the number of amide groups deprotonated. The three ligands used in the present study have four amide groups. In the complexes prepared in neutral conditions the ligands were found to be non-ionic. Attempts are being made to prepare and characterise the complexes of bi- tri- and tetravalent transition metal ions with these ligands in different pH conditions. Further, the influence of the macrocyclic ligands on the redox potentials of the metal ions will also be investigated as all the three trivalent metal ions have other accessible oxidation states.

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