

## Synthesis and Characterization of Metal Chelates of Ti(III), Cr(III), Rh(III), V(IV), Zr(IV) and Pt(IV) with 2-Mercapto-3-butyl-quinazoline-4-one

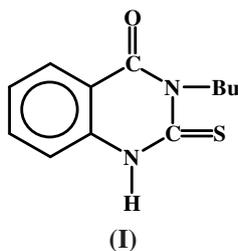
R.N. PANDEY\*, RAJNISH KR. SINGH, PRIYA and MANOJ RANJAN†  
Post Graduate Centre of Chemistry, College of Commerce, Patna-800 020, India  
E-mail: rameshwarnath.pandey@yahoo.com;  
rajnish\_sinha09@ymail.com; priya\_mmc09@yahoo.in

2-Mercapto-3-butyl-quinazoline-4-one forms *trans*-octahedral chelates having general formula  $[ML_2A_2]X$  (M = Ti, Cr, Rh; A = Py/H<sub>2</sub>O; X = Cl/NO<sub>3</sub>) and  $[M(LH)_4A_2]X_4$  (M = Pt, Zr; A = Py/H<sub>2</sub>O; X = NO<sub>3</sub>/Cl). Tentative structure of all the complexes have been assigned using micro-elemental analyses, magnetic moment, conductometric, IR, UV-vis and <sup>1</sup>H NMR spectra data.

**Key Words:** 2-Mercapto-3-butyl-quinazoline-4-one, Bis-metal chelates, IR, UV-vis and <sup>1</sup>H NMR spectra.

### INTRODUCTION

In continuation of our studies on the metal complexes of thioquinazoles<sup>1-3</sup>, we report here, IR, PMR and ligand field spectral characterization of metal chelates of 2-mercapto-3-butyl-quinazoline-4-one (I) with Ti(III), Cr(III), Rh(III), V(IV), Zr(IV) and Pt(IV) ions.



### EXPERIMENTAL

All the chemicals used were of AR grade or CP grade. The ligand 2-mercapto-3-butyl-quinazoline-4-one (BQTH) was prepared by the reported method<sup>4</sup>. Complexes were prepared using a general method. Ethanolic solution of the corresponding metal salt and ligand were mixed in appropriate molar ratios as desired and pH of

†Department of Chemistry, Patna University, Patna-800 005, India.

the resulting mixture was made 6/8 using acid of corresponding salt and pyridine. The mixture was further refluxed on a water bath for about 2 h and the precipitated complex was filtered after cooling, washed with distilled water, alcohol and ether. The complexes were dried in a desiccator over anhydrous  $\text{CaCl}_2$  and during drying they were kept in contact with pyridine vapours.

Elemental analyses, magnetic, conductometric, IR,  $^1\text{H}$  NMR. UV-vis spectral data were obtained as reported earlier<sup>5</sup>.

## RESULTS AND DISCUSSION

The analytical data (Table-1) show the following stoichiometry of complexes,  
 $[\text{M}(\text{BQT})_2\text{A}_2]\text{X}$  (M = Ti, Cr, Rh; A = Py/ $\text{H}_2\text{O}$ ; X = Cl/ $\text{NO}_3$ )  
 $[\text{M}(\text{BQTH})_4\text{A}_2]\text{X}_4$  (M = Pt, Zr; A = Py/ $\text{H}_2\text{O}$ , X =  $\text{NO}_3$ /Cl and  
 $[\text{VO}(\text{BQT})_2(\text{H}_2\text{O})]$

Molar conductance of complexes in DMF ( $10^{-3}$  M) were found to be less than  $10 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for non-electrolyte (S. No, 4, 5, 6), 85-98  $10 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for univalent electrolyte (S. No, 1, 2, 3) and 320.32-331.31  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  for 1:4 electrolyte (S. No. 7,8) suggesting the presence of ionic nitrate and coordinated sulphato group<sup>6</sup>. All complexes were non-hygroscopic solid and thermally stable up to 250 °C.

TABLE-1  
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

S. No.	Complex/colour (pH)	$\mu_{\text{eff}}$ (BM)	Molar cond. ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )	Analysis found/(calcd.) (%)			
				C	H	N	M
1	$[\text{Ti}(\text{BQT})_2(\text{Py})_2]\text{Cl}$ (Dull yellow, 8)	1.66	85.86	57.61 (57.50)	5.12 (5.07)	11.91 (11.83)	7.43 (7.04)
2	$[\text{Cr}(\text{BQT})_2(\text{H}_2\text{O})_2]\text{NO}_3$ (Greenish yellow, 8)	3.34	90.32	46.83 (46.75)	4.98 (4.87)	20.10 (20.45)	9.11 (8.44)
3	$[\text{Rh}(\text{BQT})_2(\text{Py})_2]\text{Cl}$ (yellowish brown, 8)	Diamag.	98.22	53.86 (53.50)	4.78 (4.72)	11.32 (11.01)	14.00 (13.51)
4	$[\text{VO}(\text{BQT})_2(\text{H}_2\text{O})]$ (Black, 6)	1.67	6.20	52.32 (52.26)	5.10 (5.08)	10.21 (10.16)	9.86 (9.25)
5	$[\text{Zr}(\text{OH})_2(\text{BQT})_2]$ (Light yellow, 8)	Diamag.	4.30	48.55 (48.71)	4.812 (4.73)	10.10 (9.47)	15.55 (15.43)
6	$[\text{Zr}(\text{BQTH})_4(\text{SO}_4)_2]$ (yellow, 6)	Diamag.	6.32	47.82 (47.24)	4.36 (4.26)	9.51 (9.19)	8.10 (7.48)
7	$[\text{Zr}(\text{BQTH})_4(\text{H}_2\text{O})_2](\text{NO}_3)_4$ (Yellow, 6)	Diamag.	330.32	48.55 (48.51)	4.98 (5.05)	14.32 (14.15)	7.70 (7.68)
8	$[\text{Pt}(\text{BQTH})_4(\text{Py})_2]\text{Cl}_4$ (Dull yellow, 6)	Diamag.	320.01	50.12 (48.63)	4.60 (4.61)	9.52 (9.78)	14.11 (13.62)

**Magnetic moment and electronic spectra:** All Zr(IV) complexes were found to be diamagnetic as expected for  $d^0$  configuration and display a strong broad band near 28950-28990  $\text{cm}^{-1}$  assigned to charge transfer band. However, no absorption was observed above 25000  $\text{cm}^{-1}$  indicating  $d^0$ -configuration of complexes<sup>7</sup>. The

effective magnetic moment of Cr(III) complex is found to be 3.34 BM in contrast to the spin value of 3.87 BM for a  $d^3$  system<sup>8</sup> indicating appreciable spin-orbit coupling and distortion of octahedral symmetry. Two bands in the reflectance spectrum at 17600 and 21800  $\text{cm}^{-1}$  are assigned due to  ${}^4A_{2g}(F) \rightarrow {}^4T_2(F)$  and  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$  transitions in agreement with octahedral structure<sup>9</sup>. A strong band at 28570  $\text{cm}^{-1}$  are assigned to charge transfer band. The ligand field parameters,  $Dq = 1760 \text{ cm}^{-1}$ ,  $B = 718 \text{ cm}^{-1}$ ,  $\beta = 0.37$  and the appearance of  $\nu_3$  at 27700  $\text{cm}^{-1}$  as compared to calculated value of 37300  $\text{cm}^{-1}$  indicates that environment in complex is not exactly octahedral.

The diamagnetic value of magnetic moment of Pt(IV) complex indicate  ${}^1A_{1g}$  ground term for  $d^6$  system in octahedral crystal field. The ligand field transition  $T_{2g}^6 \rightarrow T_{2g}^5 e_g^1$  gives  ${}^3T_{1g}$ ,  ${}^3T_{2g}$ ,  ${}^1T_{1g}$  and  ${}^1T_{2g}$  as excited state in increasing order of energy. The spectral bands at 16700 ( ${}^1A_{1g} \rightarrow {}^3T_{1g}$ ), 19920 ( ${}^1A_{1g} \rightarrow {}^3T_{2g}$ ), 21400 ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$ ) and 29400  $\text{cm}^{-1}$  ( ${}^1A_{1g} \rightarrow {}^1T_{2g}$ ) are due to  $d-d$  transition for octahedral structure<sup>10,11</sup>. The magnetic moment (1.67 BM) of oxovanadium(IV) complex is in agreement with lowest state  ${}^2B_2$  and excited states  ${}^2E$ ,  ${}^2B_1$  and  ${}^2A_1$  in order of increasing energy following Ballhausen and Grey molecular model<sup>12</sup>. The reflectance spectrum exhibits bands at 13000  $\text{cm}^{-1}$  ( $\nu_1$ ,  ${}^2B_2 \rightarrow {}^2E$ ), 16600  $\text{cm}^{-1}$  ( $\nu_2$ ,  ${}^2B_2 \rightarrow {}^2B_1$ ), 28500  $\text{cm}^{-1}$  ( ${}^2B_2 \rightarrow {}^2A_1$ ) corresponds to  $C_{4v}$  symmetry and characteristic feature of octahedral geometry<sup>13,14</sup>. The ligand field parameters are calculated and found to be  $\nu_2/\nu_1 = 1.28$ ,  $Dq = 1650 \text{ cm}^{-1}$ .

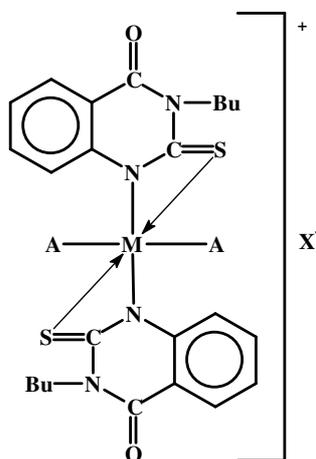
The diamagnetic nature of Rh(III) complexes indicate  ${}^1A_{1g}$  ground state for octahedral  $d^6$ -complex in octahedral crystal field. The electronic spectrum of complex exhibits two spin-forbidden transitions  ${}^1A_{1g} \rightarrow {}^3T_{1g}$  (16700  $\text{cm}^{-1}$ ) and  ${}^1A_{1g} \rightarrow {}^3T_{2g}$  (19140  $\text{cm}^{-1}$ ) and two spin-allowed transitions,  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  (32750  $\text{cm}^{-1}$ ) and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  (22300  $\text{cm}^{-1}$ ). In addition to  $d-d$  transition bands, two charge transfer bands ( $L \rightarrow M$ ) of high intensity at *ca.* 36200 and 40000  $\text{cm}^{-1}$  were also observed. The  $d-d$  transition splitting pattern and value of ligand field parameters,  $\nu_2/\nu_1 = 1.46$ ,  $B = 653 \text{ cm}^{-1}$ ,  $\beta = 0.90$  and  $10Dq = 23340 \text{ cm}^{-1}$  indicative of octahedral stereochemistry<sup>15</sup>. The reduced value of  $B$  obtained in comparison to free ion value (720  $\text{cm}^{-1}$ ) are associated to considerable orbital overlap with an increased covalency in the metal ligand  $\sigma$ -bond. The observed value of effective magnetic moment to be 1.66 BM of Ti(III) complex indicates trivalent oxidation state and  ${}^2T_{2g}$  ground term in octahedral structure. Electronic spectra in DMF exhibits one band at 20920  $\text{cm}^{-1}$  with a shoulder at 18520  $\text{cm}^{-1}$  obviously derived from the transition  ${}^2T_{2g} \rightarrow {}^2E_g$  for an octahedral geometry<sup>16</sup>.

**Infrared spectra:** The  $\nu(\text{N-H})$  band of the free ligand (BQTH) observed as medium band at 3225  $\text{cm}^{-1}$  is absent in the spectra of Ti(III), Cr(III) Rh(III), VO(IV), and hydroxo complexes of Zr(IV) indicating NH moiety is deprotonated due to complex formation and formation of metal-N bond. However, this band undergoes blue shift to higher frequency (85-110  $\text{cm}^{-1}$ ) in rest Zr(IV) and Pt(IV), complexes indicating presence of free NH group and absence of bonding through imino nitrogen.

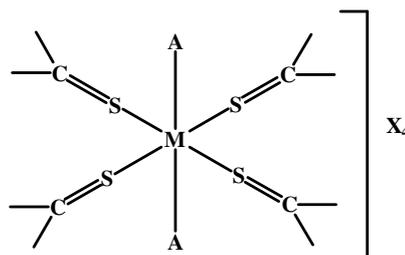
The  $\nu(\text{C}=\text{O})$  band at  $1680\text{ cm}^{-1}$  in free ligand remained unaltered in the complexes suggesting that carbonyl oxygen is not taken part in the complex formation.

Thioamide band IV is mainly due to  $\nu(\text{C}=\text{S})$  mode<sup>16-18</sup> and it is observed as medium band at  $803\text{ cm}^{-1}$  in the spectrum of free ligand red shift ( $40\text{-}60\text{ cm}^{-1}$ ) on coordination in all complexes indicating formation of metal-S bond<sup>19-21</sup>. The presence of pyridine is confirmed by its characteristic vibrations ( $1543, 1460, 1410, 1199, 1109, 1072$  and  $585\text{ cm}^{-1}$ ). On coordination pyridine ring vibrations in the higher frequency region are not shifted appreciably but in-plane deformation ( $604\text{ cm}^{-1}$ ) and out-of-plane ring deformation ( $405\text{ cm}^{-1}$ ) shifted to high frequency on complexation<sup>22</sup>.

The absorption associated with anions in the complexes are identified at  $1365$  and  $810\text{ cm}^{-1}$  for ionic nitrate<sup>23</sup> and at  $1020, 980, 640$  and  $480\text{ cm}^{-1}$  for unidentate sulphato group<sup>24</sup>. The non-ligand bands at  $3440, 1605$  and  $785\text{ cm}^{-1}$  in complexes assigned to  $\nu(\text{H}_2\text{O}), \delta(\text{H}_2\text{O})$  and  $\pi(\text{H}_2\text{O})$  of coordinated water molecules<sup>25</sup>. The only one band in far ir of complexes at  $490\text{-}510\text{ cm}^{-1}$  assigned to  $\nu(\text{M}-\text{O})$  mode indicates two water molecules are at *trans*-position in octahedral structure. The hydroxo complex (S. No. 5) exhibits  $\nu(\text{OH})$  at  $3110\text{ cm}^{-1}$  which indicates intense hydrogen bonding and the presence of only one  $\nu(\text{Zr}-\text{OH})$  indicates identical environment of two OH groups in the crystal lattice of solid complex and probably they are at *trans*-position in octahedral structure. All complexes display only one metal-S stretching mode indicating two ligands are at *trans*-position in all six-coordinated complexes. Thus, the following structure may be tentatively assigned.



*trans*-O<sub>h</sub>-structure of  $[\text{M}(\text{BQT})_2\text{A}_2]\text{X}$   
(M = Ti, Cr, Rh; A = Py/H<sub>2</sub>O; X = NO<sub>3</sub>/Cl)



*trans*-O<sub>h</sub>-structure of  $[\text{M}(\text{BQTH})_4\text{A}_2]\text{X}_4$   
(M = Pt, Zr; A = Py/H<sub>2</sub>O; X = NO<sub>3</sub>/Cl)

**<sup>1</sup>H NMR spectra:** <sup>1</sup>H NMR spectra of ligand (BQTH) and complexes were recorded in CDCl<sub>3</sub>/TMS to substantiate further metal-ligand bonding and proton chemical shift ( $\delta$  ppm) of some important groups of complexes are given Table-2.

TABLE-2  
LIGAND FIELD PARAMETERS AND PROTON CHEMICAL SHIFT  
( $\delta$  ppm) OF SOME IMPORTANT GROUPS OF COMPLEXES

Complex/(S. No.)	Electronic spectra crystal field parameters			$^1\text{H}$ NMR ( $\delta$ PPM) spectra				
	B	$\beta$	10Dq ( $\text{cm}^{-1}$ )	Phenyl protons	$\text{CH}_3$ protons	$\text{CH}_2$ protons	Pyridine protons ( $\alpha, \beta, \gamma$ )	$\text{H}_2\text{O}$ protons
Ti(III) (1)	–	–	20920	7.6 (bs)	1.73 (t)	2, 2.3	7.62, 8.18, 8.80	–
Cr (III) (2)	718	0.37	23340	7.7 (bs)	1.74 (t)	2, 2.3	7.72, 8.07, 8.81	1.2 and (2.1)
Rh (III) (3)	653	0.90	16500	7.46 (bs)	1.73 (t)	2.0, 2.31	7.76, 8.10, 8.82	–
VO(IV) (4)	–	–	–	7.68 (bs)	1.74 (t)	2.0, 2.21	7.78, 8.30, 8.86	1.21 and 2.2
Zr (IV) (5)	–	–	–	7.6 (bs)	1.74 (t)	2.0 2.4	–	1.20 and 2.3
Pt (IV) (6)	560	–	23000	7.72 (bs)	1.73 (t)	2.1 2.4	7.76, 8.12, 8.78	–

bs = broad signal, t = triplet; S. No. = complexes in Table-1.

The signals due to the phenyl protons are observed at  $\delta$  7.6-8.3 ppm. The aromatic proton at position-5 is deshielded by the carbonyl oxygen and the extreme signals at  $\delta$  8.4 is considered to be due to this proton. The triplet at  $\nu$  1.71 ppm for methyl group and the two middle  $\text{CH}_2$  signals are complex and are centred at  $\delta$  2.0 and 2.3 ppm. The  $\text{CH}_2$  group attached to the nitrogen atom of the quinazoline ring is deshielded giving a triplet at  $\delta$  4.8 ppm. The signal due to imino proton is always difficult to identify because of the quadrupole moment of nitrogen and exchange of this proton. However, a peak observed at  $\delta$  3.2 ppm in the ligand (BQTH) remains almost at the same positions in Zr(IV), Pt(IV) and Ce(IV) complexes but found to absent in Ti(III), Cr(III) and VO(IV) complexes.

The resonances in the region  $\delta$  7.61, 8.17 and 8.97 ppm assignable to the protons of pyridine ligand along with the resonances due to aromatic protons in pyridino complexes. The pyridine proton resonances exhibited down field as compared to that in free ligand indicate the complexation of pyridine nitrogen atom with metal centre<sup>26</sup>. All aquo complexes exhibit singlet signal at  $\delta$  1.31 ppm which corresponds to two protons and another multiplet at  $\delta$  2.1 ppm corresponding to two protons. This is due to four protons of the two coordinated water molecules<sup>27</sup>. These observations are consistent with the conclusions drawn from IR spectra studies.

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