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Synthesis and Characterization of Silver(I), Mercury(I), Ruthenium(III) and Bismuth(III) Complexes with 2-Mercapto-3-Substituted Quinazoline-4-Ones

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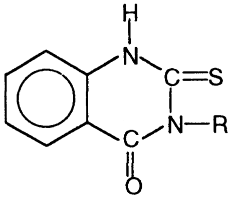
2-Mercapto quinazoline-4-one and its 3-substituted butyl, phenyl, and *meta-* tolyl derivatives form very stable complexes with Ag(I), Hg(I), Ru(III) and Bi(III) having the general formula $[Ag(LH)(H_2O)_2]NO_3$, $[Hg_2(LH)_2(H_2O)_4](NO_3)_2$, $[Ru(L_2)(H_2O)_2]Cl$ and $[Bi(LH)_3(H_2O)_2](NO_3)_3$, where LH = 2-mercapto-3-substituted quinazoline -4-ones. All complexes are characterized through elemental analysis, molar conductance, magnetic susceptibility, electronic and infrared spectral data. Ru(III) and Bi(III) complexes are six coordinated octahedral but Ag(I) and Hg(I) complexes are polymeric tetrahedral.

INTRODUCTION

2-Mercapto-3-substituted quinazoline-4-ones(I) are physiologically active compounds having several potential donor sites. Complexing behaviour of these compounds has been reported in literature with many class 'a' and 'b' types metal ions[1-4]. The present paper describes synthesis and characterization of Ag(I), Hg(I), Ru(III) and Bi(III) complexes with these bio-organic molecules[5-8].



(R = H, C_4H_9, C_6H_5 or $CH_3C_6H_4$)

(I)

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EXPERIMENTAL

All chemicals used in the present work were of CP grade. 2-Mercapto-3-substituted quinazoline-4-ones were prepared by the method of Dave et al.[5] All the complexes were prepared using a general method.

Ethanolic solutions of metal salts (0.01 mole) were mixed with ethanolic solution of ligand (0.02 mole) and refluxed on water bath for 1 h On cooling the mixture at room temperature, solid complexes were obtained. They were filtered, washed with ice-cold ethanol and dried over anhydrous $CaCl_2$ in a vacuum desiccator. The analytical data are given in Table 1.

TABLE 1
ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Compound	Elemental analysis		Found/(calcd.)		Molar conductance Λ^{-1} cm^2 mole^{-1}
	M	C	H	N	
1. $[Ag(QTH)(H_2O)_2]NO_3$ Light yellow	27.8 (27.9)	25.2 (25.1)	2.6 (2.6)	10.6 (10.7)	Insoluble
2. $[Ag(BQTH)(H_2O)_2]NO_3$ Grey	25.5 (24.4)	32.9 (32.8)	4.0 (4.1)	6.3 (6.4)	"
3. $[Ag(PQTH)(H_2O)_2]NO_3$ White	23.2 (23.3)	36.7 (36.6)	3.0 (3.1)	9.3 (9.2)	"
4. $[Ag(mtQTH)(H_2O)_2]NO_3$ Light yellow	22.5 (22.6)	38.1 (38.0)	3.4 (3.4)	8.6 (8.7)	"
5. $[Hg_2(QTH)(H_2O)_4](NO_3)_2$ Ash	41.2 (41.3)	19.6 (19.8)	2.0 (2.1)	8.4 (8.5)	"
6. $[Hg_2(BQTH)_2(H_2O)_4](NO_3)_2$ Yellow	37.1 (37.0)	26.6 (26.5)	3.2 (3.3)	7.6 (7.7)	"
7. $[Hg_2(PQTH)_2(H_2O)_4](NO_3)_2$ Ash	35.7 (35.6)	30.0 (29.9)	2.5 (2.5)	7.7 (7.5)	"
8. $[Hg_2(mtQTH)_2(H_2O)_4](NO_3)_2$ Ash	34.6 (34.7)	31.3 (31.2)	2.8 (2.8)	7.4 (7.3)	"
9. $[Bi(QTH)_3(H_2O)_2](NO_3)_3$ Light yellow	21.8 (21.6)	30.1 (29.8)	2.7 (2.8)	13.2 (13.0)	215.3
10. $[Bi(BQTH)_2(H_2O)_2](NO_3)_3$ Deep yellow	 (18.54)	 (38.3)	 (3.5)	11.4 (11.2)	202.3
11. $[Bi(mtQTH)_3(H_2O)_2](NO_3)_3$ Light yellow	16.8 (19.2)	43.2 (43.6)	3.4 (3.3)	10.4 (10.2)	201.2
12. $[Ru(QT)_2(H_2O)_2]Cl$ Dk. adm. grey	19.6 (19.2)	36.0 (36.4)	2.6 (2.5)	10.3 (10.6)	102.3
13. $[Ru(PQT)_2(H_2O)_2]Cl$ Grey	15.0 (14.9)	50.0 (49.8)	2.0 (2.0)	8.0 (8.2)	100.2
14. $[Ru(mtQT)_2(Py)_2]Cl$ Grey	12.5 (12.1)	57.3 (57.8)	3.9 (4.0)	6.8 (6.7)	98.2
15. $[Ru(mtQT)_2H_2O]Cl$ Grey	14.6 (14.2)	51.0 (50.8)	4.0 (3.9)	8.2 (7.9)	96.3

TABLE 2
CHARACTERISTIC IR SPECTRAL BAND POSITIONS (IN cm^{-1}) OF LIGANDS AND COMPLEXES

Compd.	ν(NH)	ν(CO)	Thioamide bands†			
			I	II	III	IV
QTH	3240 m	1710 s	1530 s	1270 s	1030 s	800 w
$[Ag(QTH)(H_2O)_2]NO_3$	3180 w	1710 sb	1520 s 1510 s	1275 m	990 w	800 m
$[Hg_2(QTH)_2(H_2O)_4](NO_3)_2$	3360 m	1710 mb	1540 m	1290 m 1273 m	960 w	760 w
$[Bi(QTH)_3(H_2O)_2](NO_3)_3$	3350 m	1710 ms	1525 m	1290 m 1270 m	1000 m	780 w
$[Ru(QT)_2(H_2O)_2]Cl$	—	1720 s	1520 w 1490 w 1470 m 1440 m	1260 w	980 m	800 w
BQTH	3225 m	1715 s	1520 s	1270 s	1020 s	803 m
$[Ag(BQTH)(H_2O)_2]NO_3$	3200 mb	1720 s	1522 s 1510 s	1280 m	950 w	800 m
$[Hg_2(BQTH)_2(H_2O)_4](NO_3)_2$	3320 m	1725 s	1520 s	1290 m 1275 m	950 w	780 w
$[Bi(BQTH)_3(H_2O)_2](NO_3)_3$	3400 mb	1730 s	1530 s	1290 m	995 w	780 w
PQTH	3220 m	1705 s	1525 s	1270 s	1030 m	800 w
$[Ag(PQTH)(H_2O)_2]NO_3$	3190 m	1710 sb	1515 s 1510 s	1265 s	990 w	800 w
$[Hg_2(PQTH)_2(H_2O)_4](NO_3)_2$	3340 mb	1715 s	1520 m	1260 m 1250 m 1240 m	965 m	770 w
$[Ru(PQT)_2(H_2O)_2]Cl$	—	1720 s	1515 w 1490 m 1470 m 1460 m	1260 m	980 w 960 w	780 w
mtQTH	3210 m	1710 s	1525 s	1265 m	1020 m	800 w
$[Ag(mtQTH)(H_2O)_2]NO_3$	3190 ms	1720 s	1520 s 1510 s	1270 ms	920 w	795 m
$[Hg_2(mtQTH)(H_2O)_4](NO_3)_2$	3350 mb	1715 s	1525 s	1285 m 1270 m 1260 w	970 w	785 w
$[Ru(mtQT)_2(Py)_2]Cl$	—	1740 s	1530 m 1440 m	1270 m	985 w 960 w	750 m
$[Ru(mtQT)_2(H_2O)_2]Cl$	—	1730 s	1520 m 1450 m	1270 m	985 w	780 m
$[Bi(mtQTH)_3(H_2O)_2](NO_3)_3$	3360 mb	1720 s	1530 m	1290 m	985 m	780 m

†Band I δ(NH) + δ(CH) + ν(C=N); Band II ν(C=S) + ν(C–N) + δ(NH) + δ(CH); Band III $\nu(C\overset{\cdots}{-}S) + \nu(C\overset{\cdots}{-}N)$, ν(C=S).

RESULTS AND DISCUSSION

2-Mercapto quinazoline-4-one (QTH) and its 3-substituted butyl (BQTH), phenyl (PQTH) and *meta*- tolyl (*m*QTH) derivatives form very stable complexes with Ag(I), Hg(I), Ru(III) and Bi(III) ions. The analytical data (Table 1) reveal that the complexes have stoichiometry 1:1 for Ag(I) & Hg(I), 1 : 2 for Ru(III) and 1 : 3 for Bi(III) having general formula $[Ag(LH)(H_2O)_2]NO_3$, $[Hg_2(LH)_2(H_2O)_4](NO_3)_3$ where LH = QTH, BQTH, PQTH and *m*QTH. All Ag(I) and Hg(I) complexes were insoluble in common organic solvents having m.pt. beyond 300°C indicating their polymeric nature. However, Ru(III) and Bi(III) complexes were fairly soluble in DMF and their molar conductance data supports their general stoichiometry (Table 1). The magnetic moments of Ru(III) complexes were observed between 1.69–1.88 BM indicating the presence of one unpaired electron in most probable preferential octahedral structure.[9] The diamagnetic nature of Hg(I) complexes suggest the presence of Hg_2^{++} moiety. The two electrons each from Hg^+ ($5d^{10}6s^1$) in σ-bonding molecular orbital are paired forming Hg_2^{++} and formation of metal-metal bond may be assumed by 6s-6s overlapping.[10]

The electronic spectra of Ru(III) complexes display absorption bands at 20700, 16500 and 22700 cm^{-1} (with QTH); 18780, 14200 and 21210 cm^{-1} (with PQTH) and 18700, 16600 and 22500 cm^{-1} (with *m*QTH). The first band is assigned to $2T_{1g} \rightarrow 2A_{2g}$ transition[11] corresponding to octahedral geometry. However, the other two bands are probably due to spin forbidden transitions[12, 13] in octahedral configuration around Ru(III) ion.

Infrared Spectra

If the IR spectra of the ligands and the present complexes are compared, changes in positions and intensities of the thioamide bands are observed which are given in Table 2. It is expected that the coordination of the ligand to the metal ion should take place through sulphur. This seems to be supported by the fact that the thioamide bands II, III and IV which have contributions from ν(C=S) have undergone either red shift or have decreased intensity considerably or both have happpened because of coordination of the ligand through sulphur.[14–16] However, the thioamide band I has undergone blue shift or remains almost unchanged in position and intensity. The thioamide band IV (mainly due to ν(C=S)) of the ligand more or less remains unchanged in position on coordination to Ag(I) and Ru(III) ions. It appears that blue shift of this band due to formation of metal-nitrogen bond is compensated by the red shift of this band due to formation of metal-sulphur bond. Moreover, the increase in intensity of this band in Ag(I) complexes is probably due to their polymeric nature.

The ν(NH) band of the free ligands QTH (*ca.* 3240 cm^{-1}), BQTH (*ca.* 3225 cm^{-1}) PQTH (*ca.* 3220 cm^{-1}) and *m*QTH (*ca.* 3210 cm^{-1}) red shift to lower frequency on coordination to Ag(I) but blue shift to higher frequency (145–95 cm^{-1}) to Hg(I) and Bi(III). This suggests bonding of the ligand through imino nitrogen in Ag(I) and presence of free imino group in Hg(I) and Bi(III) complexes. However, ν(NH) band is not observed in Ru(III) complexes due to deprotonation of imino hydrogen and formation of Ru–N bond.

The new bands arising in the spectra of aquo complexes at 3460–3440, 1610–1600 and 820 ± 5 cm^{-1} may respectively be assigned to $\nu(H_2O)$, $\delta(H_2O)$ and $\pi(H_2O)$ of coordinated water.[17] The non-ligand very strong band at 1414–1390 cm^{-1} and medium band at 840 ± 5 cm^{-1} in complexes indicate the presence of ionic nitrate.[18]

In the far IR spectra of complexes medium to weak non-ligand bands are observed. The new bands in the region of 500–300 cm^{-1}, 520–450 cm^{-1} in Ag(I) and Ru(III) complexes are assigned to inter and/or intramolecular interaction of metal-nitrogen and metal-sulphur stretching modes respectively. In the case of Bi(III) and Ru(III) complexes, ν(M–S) band is not clearly visible upto 200 cm^{-1}. They probably fall below 200 cm^{-1}.

Thus, on the basis of aforesaid results, all Bi(III) and Ru(III) complexes are six-coordinated octahedral. One of the coordination sites is occupied by the inert pair electrons in octahedral structure of Bi(III)-complexes. Polymeric tetrahedral configuration for Ag(I) and Hg(I) complexes are also tentatively assigned.

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