

Complexes of Some Bivalent Metal Ions with Organic Ligands having Thioamide Group

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Complexes of Zn(II), Cd(II), Hg(II), Sn(II), Pd(II) and Cu(II) with butyl, phenyl, and *m*-tolyl derivative of 2-mercapto-3-substituted quinazoline-4-one have been prepared and investigated using various physico-chemical techniques. All are tetrahedral but Cu(II) complexes have distorted octahedral configuration. The nature of shifts and change in intensity of all four thioamide bands of the ligands are used as diagnostic for metal-ligand bonding. Metal ligand vibrations in the far infrared spectra of complexes have been thoroughly examined.

INTRODUCTION

In continuation of our earlier reports^{1,2} the present paper presents the complexes of some bivalent metal ions with 2-mercapto-3-substituted quinazoline-4-one.

EXPERIMENTAL

All the chemicals used were of AR/CP grade. The derivatives of 2-mercapto-3-substituted quinazoline-4-one were prepared following the method reported in literature³.

Preparation of Complexes

Ethanollic solutions of metal salts were mixed with ethanollic solutions of ligands in a desired molar ratio and refluxed for *ca* 2 hrs on water bath. The pH of the working mixture were fixed 6 or 7 using mineral acid of salt used and NaOH solution. Different coloured solid complexes were obtained immediately which were further washed with ice-cold ethanol and dried over anhydrous CaCl₂ in a vacuum desiccator. The analytical data of complexes have been given in Table 1.

RESULTS AND DISCUSSION

3-Substituted derivatives of 2-mercaptoquinazoline-4-one form very stable complexes with Cu(II), Zn(II), Cd(II), Hg(II), Sn(II) and Pb(II) ions. Micro-analytical, conductometric and magnetic moment data of the complexes suggest the following chemical formula:

- (i) $[\text{Cu}(\text{RQT})_2(\text{H}_2\text{O})_4]\text{Cl}$ (R=H; C₄H₉; C₆H₅)
- (ii) $[\text{M}(\text{RQTH})_2\text{X}_2]$ (M=Zn, Cd; R = H; X=Cl, NO₃, CH₃COO, Br, I).
- (iii) $[\text{Sn}(\text{RQTH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$ (R=H, C₄H₉, C₆H₅)
- (iv) $[\text{Pb}(\text{RQTH})_2\text{X}_2]$ (X=CH₃COO, H₂O; R=H, C₄H₉, C₆H₅)
- (v) $[\text{Pb}(\text{RQTH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (R=H, C₄H₉, C₆H₅)

TABLE 1

Compounds	M. pt. (°C)	Analysis % Found/(Calcd)			
		Metal	N	S	Halogen
[Sn(QTH) ₂ (H ₂ O) ₂]Cl ₂ Dull white	250	20.50 (20.44)	9.39 (9.62)	10.98 (10.99)	12.12 (12.19)
[Sn(BuQTH) ₂ Cl ₂] Dull white	220	18.00 (18.04)	8.56 (8.51)	10.01 (9.73)	10.56 (10.79)
[Sn(QTH) ₂ Cl ₂] White	250	21.70 (21.79)	10.20 (10.25)	11.82 (11.72)	13.21 (13.00)
[Sn(BuQTH) ₂ (H ₂ O) ₂]Cl ₂ Dull white	200	17.23 (17.10)	8.23 (8.06)	9.32 (9.22)	10.56 (10.23)
[Pb(QTH) ₂ (H ₂ O) ₂](NO ₃) ₂ White	190 d	28.56 (28.63)	11.72 (11.61)	8.87 (8.85)	—
[Pb(QTH) ₂ (ac) ₂] Ash	250	30.20 (30.39)	8.21 (8.22)	9.49 (9.39)	—
[Pb(BuQTH) ₂ (ac) ₂] Grey	185 d	26.12 (26.10)	7.00 (7.06)	8.11 (8.07)	—
[Pb(BuQTH) ₂ (H ₂ O) ₂](NO ₃) ₂ Light yellow	241	26.70 (26.77)	10.83 (10.86)	8.00 (8.27)	—
[Pb(PQTH) ₂ (ac) ₂] Dull white	250	24.81 (24.84)	6.81 (6.72)	7.67 (7.68)	—
[Pb(PQTH)(H ₂ O) ₂](NO ₃) ₂ White	250	23.62 (23.65)	9.61 (9.60)	7.34 (7.31)	—
[Zn(PQTH) ₂ (H ₂ O) ₂ SO ₄] Dull white	250	14.56 (14.46)	6.30 (6.21)	6.97 (7.09)	—
[Zn(PQTH) ₂ (ac) ₂] Cream	250	9.52 (9.41)	7.67 (7.87)	8.96 (9.00)	—
[Zn(PQTH) ₂ Cl ₂] Dull white	250	10.72 (10.62)	9.10 (9.12)	10.45 (10.46)	11.60 (11.60)
[Cd(PQTH) ₂ Cl ₂] Greenish-yellow	250	16.98 (17.00)	8.40 (8.50)	9.68 (9.71)	10.70 (10.77)
[Cd(PQTH) ₂ Br ₂] White	250	15.01 (14.97)	7.32 (7.49)	8.50 (8.56)	21.49 (21.39)
[Cd(PQTH) ₂ I ₂] Greenish-yellow	250	13.23 (13.30)	6.52 (6.65)	7.50 (7.60)	30.01 (30.17)
[Cd(PQTH) ₂ (ac) ₂] Cream	250	15.78 (15.86)	8.00 (7.93)	9.01 (9.07)	—
[Hg(QTH) ₂ (ac) ₂] Grey	250	31.56 (31.26)	8.72 (8.71)	9.90 (9.95)	—
[Hg ₂ (PQTH) ₂ Cl ₄] White	250	39.40 (39.42)	5.45 (5.49)	6.32 (6.27)	13.89 (13.92)

Compounds	M. pt. (°C)	Analysis % Found/(Calcd)			
		Metal	N	S	Halogen
[Hg ₂ (PQTH) ₂ Br ₄] Yellow	250	33.54 (33.56)	4.32 (4.67)	5.32 (5.34)	26.70 (26.71)
[Hg ₂ (PQTH) ₂ I ₄] Light yellow	250	35.50 (35.51)	4.92 (4.95)	5.48 (5.65)	22.32 (22.44)
[Hg(PQTH)(ac) ₂] White	250	36.11 (36.09)	5.02 (5.03)	5.62 (5.75)	—
[Cu(QT)(H ₂ O) ₄]Cl Yellow	250	19.01 (19.13)	8.34 (8.43)	9.52 (9.62)	10.82 (10.69)
[Cu(BQT)(H ₂ O) ₄]Cl Light yellow	250	16.47 (16.37)	7.43 (7.22)	8.21 (8.25)	9.01 (9.12)
[Cu(PQT)(H ₂ O) ₄]Cl Black	250	15.46 (15.56)	6.38 (6.86)	7.81 (7.84)	8.68 (8.70)

The magnetic moments of Cu(II) complexes were found between 1.76–1.81 B.M., indicating d^9 -configuration having sp^3d^2 hybridisation for distorted octahedral structure. The visible spectra of complexes display the bands at 970, 765 ± 5 and 585 ± 5 nm assigned to $2B_{1g} \rightarrow 2A_{1g}$, $2B_{1g} \rightarrow 2B_{2g}$ and $2B_{1g} \rightarrow 2E_g$ transitions respectively and distorted octahedral configuration was assumed following previous literature⁴⁻⁶.

Infrared Spectra

The major infrared spectral bands of the ligands and their metal complexes are given in Table 2. A medium band around $3230\text{--}3215\text{ cm}^{-1}$ in the spectrum of 2-mercapto-3-substituted quinazoline-4-one is assigned due to $\nu(\text{NH})$ mode^{7,8}. However, Chaurasia *et al.*⁹ have assigned $\nu(\text{NH})$ for substituted quinazolines at 3350 cm^{-1} . Roberts and coworkers¹⁰ have assigned $\nu(\text{NH})$ in amide and thioamides near 3440 cm^{-1} which show shifts of $100\text{--}200\text{ cm}^{-1}$ to lower frequency due to various degree of hydrogen bonding. In the present case, this band is not observed in Cu(II) complexes and deprotonation of imino nitrogen is assumed resulting in formation of copper-nitrogen bond. In other complexes, this band is blue shifted to higher frequency suggesting absence of bonding through imino nitrogen. Although, some contribution from $\nu\text{H}_2\text{O}$ may not be ruled out in all aquo complexes. The four thioamide bands of the ligand due to mixed vibrations of $\nu(\text{C}=\text{S})$, $\nu(\text{C}-\text{N})$, $\delta(\text{C}-\text{H})$ and $\delta(\text{N}-\text{H})$ ⁽¹¹⁾ undergo considerable change in position and intensity on coordination to these divalent metal ions. Band II experiences a blue shift of the order of 10 cm^{-1} . Band III is either considerably lowered in intensity and/or experiences red shift and the thioamide band I is red shifted to the extent of $20\text{--}30\text{ cm}^{-1}$. Since band I is a mixed band having contribution from $\delta(\text{CH}) + \delta(\text{NH}) + \nu(\text{C}=\text{N})$, coordination through imino nitrogen should result in a red shift of band I and coordination through thiocarbonyl sulphur should result in a red shift of thioamide band IV which is essentially due to $\nu(\text{C}=\text{S})$. Band II has been assigned to mixed vibrations $\nu(\text{C}-\text{N}) + \nu(\text{C}-\text{S}) + \delta(\text{NH}) + \delta(\text{CH})$ by Lieber *et al.*¹² and band III to mainly

TABLE 2
KEY IR BANDS (cm^{-1}) OF LIGANDS AND THEIR METAL-COMPLEXES

Compounds	$\nu(\text{NH})$	$\nu(\text{SH})$	$\nu(\text{CO})$	Thioamide bands				$\text{SO}_4^{2-}/\text{NO}_3^-/\text{CH}_3\text{COO}^-$	Nature of bonding
				I	II	III	IV		
QTH	3215 mb	2365 wb	1670 s	1530 s	1270 s	1030 m	800 w	—	—
$[\text{Sn}(\text{QTH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3230 mb	—	1668 sb	1530 m	1260 m	990 w	780 vw	—	(M-S)
$[\text{Sn}(\text{QTH})_2\text{Cl}_2]$	3360 mb	—	1665 sb	1520 m	1230 m	970 w	780 w	—	(M-S)
$[\text{Pb}(\text{QTH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3240 mb	—	1665 sb	1525 m	1260 m	1010 w	770 w	1405 vs 850 m	(M-S)
$[\text{Pb}(\text{QTH})_2(\text{ac})_2]$	3235 mb	—	1665 sb	1520 m	1260 m	980 w	770 w	1550 s 1340 m	(M-S)
$[\text{Hg}(\text{QTH})_2(\text{ac})_2]$	3360 mb	—	1680 s	1520 m	1240 m	970 w	770 vw	1515 s 1305 ms	(M-S)
$[\text{Cu}(\text{QTH})_2(\text{H}_2\text{O})_4]\text{Cl}$	—	—	—	1500 m 1490 m	1260 m	980 w	810 w	—	(M-N) & (M-S)
BuQTH	3225 m	2340 wb	1645 s	1520 s	1265 s	1010 w	795 m	—	—
$[\text{Sn}(\text{BuQTH})_2(\text{H}_2\text{O})_2]\text{Cl}_2$	3250 mb	—	1630 s	1520 m	1260 s	950 w	785 w	—	(M-S)
$[\text{Sn}(\text{BuQTH})(\text{H}_2\text{O})\text{Cl}_2]$	3250 mb	—	1640 s	1520 m	1260 s	950 w	780 w	—	(M-S)
$[\text{Pb}(\text{BuQTH})_2(\text{ac})_2]$	3240 mb	—	1640 s	1510 m	1255 s	990 w	780 w	1565 s 1350 ms	(M-S)

Compounds	$\nu(\text{NH})$	$\nu(\text{SH})$	$\nu(\text{CO})$	Thioamide bands				$\text{SO}_4^{2-}/\text{NO}_3^-/\text{CH}_3\text{COO}^-$	Nature of bonding
				I	II	III	IV		
$[\text{Pb}(\text{BuOTH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3250 mb	—	1650 s	1510 m 1500 m	1240 w	970 w 950 w	730 w	1380 s 804 m	(M-S)
$[\text{Cu}(\text{BuQT})(\text{H}_2\text{O})_4]\text{Cl}$	—	—	1650 sb	1495 m	1250 m	990 w	800 w	—	(M-N) & (M-S)
PQTH	3440 mb	2350 wb	1648 sb	1525 vs	1270 vs	1030 m	800 w	—	—
$[\text{Pb}(\text{POTH})_2(\text{ac})_2]$	3240 mb	—	1650 s	1520 s	1260 s	980 w	790 w	1565 s 1340 m	(M-S)
$[\text{Pb}(\text{PQTH})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$	3255 mb	—	1660 sb	1520 mb	1260 m	1005 w 990 m	800 w	1405 s 850 m	(M-S)
$[\text{Zn}(\text{PQTH})(\text{H}_2\text{O})(\text{SO}_4)]$	3450 sb	—	1640 sb	1530 s 1220 m	1290 s 1260 m	1020 m	800 m	1030 m 955 w 640 m	(M-O)
$[\text{Zn}(\text{PQTH})_2(\text{ac})_2]$	3470 mb	—	1620 m	1540 s 1530 m	1290 w 1260 m	1020 w	800 m	1690 s 1400 m	(M-O)
$[\text{Zn}(\text{PQTH})_2\text{Cl}_2]$	3230 sb	—	1610 m	1520 s	1270 ms	1020 m	795 m	—	(M-O)
$[\text{Cd}(\text{PQTH})_2\text{Cl}_2]$	3360 mb	—	1670 sb	1520 m	1250 m	970 m	740 m	—	(M-O)
$[\text{Cd}(\text{PQTH})_2\text{Br}_2]$	3240 mb	—	1670 sb	1525 m	1230 m	970 w	780 w	—	(M-S)
$[\text{Cd}(\text{PQTH})_2]$	3230 m	—	1670 m	1480 m	1250 m	980 m	780 w	—	(M-S)
$[\text{Cd}(\text{PQTH})_2(\text{ac})_2]$	3240 ms	—	1670 sb	1530 m	1250 m	970 m	785 w	1515 s 1305 m	(M-S)

Compounds	$\nu(\text{NH})$	$\nu(\text{SH})$	$\nu(\text{CO})$	Thioamide bands				$\text{SO}_4^{2-}/\text{NO}_3^-/$ CH_3COO^-	Nature of bonding
				I	II	III	IV		
$[\text{Hg}_2(\text{PQTH})_2\text{Cl}_4]$	3260 mb	—	1665 sb	1525 m	1270 m	960 w	770 m	—	(M-S)
$[\text{Hg}_2(\text{PQTH})_2\text{Br}_4]$	3240 mb	—	1660 sb	1520 s	1270 m	960 m	780 w	—	(M-S)
$[\text{Hg}_2(\text{PQTH})_2\text{I}_4]$	3250 mb	—	1670 sb	1530 s	1260 m	960 w	790 w	—	(M-S)
$[\text{Hg}(\text{PQTH})_2(\text{ac})_2]$	3240 mb	—	1675 sb	1525 s	1270 m	980 w	785 w	1415 s 1310 m	(M-S)
$[\text{Cu}(\text{PQT})(\text{H}_2\text{O})_4]\text{Cl}$	—	—	1690 sb	1510 m	1270 m	990 w	810 w	—	(M-N) & (M-S)

QTH = 2-mercaptoquina. oline-4-one; PQTH = 2-mercapto-3-phenylquinazoline-4-one; BuQTH = 2-mercapto-3-butylquinazoline-4-one.

$\nu(\text{C}-\text{N}) + \nu(\text{C}=\text{S})$ modes by Rao and coworkers.^{13, 14} Simultaneous metal-sulphur and metal-nitrogen bonding in Cu(II) complexes results in red shifting of band II due to increase in CN bond order and decrease in CS bond order. Moreover, thioamide band IV (mainly $\text{C}=\text{S}$) is blue shifted by 10 cm^{-1} in Cu(II) complexes as probably due to stronger (Cu-N) bond than (Cu-S) bond. Here, the red shifting of this band due to formation of (Cu-S) bond is compensated by its blue shifting due to formation of (Cu-N) bond. The $\nu(\text{CO})$ of ligands observed at $1650 \pm 10 \text{ cm}^{-1}$ is red shifted *ca* 40 cm^{-1} in all Zn(II) complexes indicating the bonding through carbonyl oxygen. However, the band remains almost unchanged when coordinated to Hg(II), Cd(II), Pb(II), Sn(II) and Cu(II) ions. Two bands near 1625(s), 1310(m); 1630(s), 1340(m); and 1620(s), 1370(m) cm^{-1} acetato complexes of Hg(II), Cd(II) and Zn(II) are assigned to $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ modes of coordinated acetato group. The magnitude of separation (Δ) between the frequencies due to $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ clearly indicate the presence of monodentate acetato group¹⁵⁻¹⁷. Moreover, the Δ values of Hg(II) complexes are greater than Δ value of acetato complexes of Zn(II) and Cd(II). So, it appears that Hg-O bond is more covalent than (Zn-O) and (Cd-O) bond¹⁸.

The far infrared spectra of all the complexes display some new bands. New bands in monomeric mercury(II) complexes at 460 and 315 cm^{-1} are assigned to $\nu(\text{Hg}-\text{O})$ and $\nu(\text{Hg}-\text{S})$ modes respectively. However, in other dimeric halogen bridge complexes of mercury(II) new bands near 320(w) and 280(w) cm^{-1} are assigned to $\nu(\text{Hg}-\text{X})$ and $\nu(\text{Hg}-\text{X}-\text{Hg})$ modes ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) of vibrations. Terminal $\nu(\text{Hg}-\text{X})$ mode have been observed in the same region by Lever *et al.*¹⁹ for tetrahedral complexes having metal-ligand ratio 1 : 2. However, polymeric distorted octahedral²⁰ complexes of Hg(II) exhibit $\nu(\text{Hg}-\text{Cl})$ (terminal) band in the range of 220-230 cm^{-1} . In Cd(II) complexes $\nu(\text{Cd}-\text{O})$, (350 cm^{-1}), $\nu(\text{Cd}-\text{Cl})$ (440 cm^{-1}), $\nu(\text{Cd}-\text{Br})$ (445 cm^{-1}), $\nu(\text{Cd}-\text{I})$ (340 cm^{-1}) and $\nu(\text{Cd}-\text{S})$ (300 cm^{-1}) are in good agreement with previous literature²¹⁻²³. New bands at 360 cm^{-1} in Zn(II) complexes are assigned to $\nu(\text{Zn}-\text{O})$ modes.

In the far infrared spectra of all Cu(II) complexes there are some new bands at 470, 420 and 320 cm^{-1} are assigned as $\nu(\text{Cu}-\text{O})$, $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cu}-\text{S})$ modes respectively.²⁴⁻²⁶ Udupa *et al.*²⁷ have assigned Cu-N for distorted octahedral diaminodiglycolato Cu(II) at 420 cm^{-1} . Mohapatra and coworkers²⁸ have observed $\nu(\text{Cu}-\text{O})$ and $\nu(\text{Cu}-\text{N})$ in the region of 460-480 cm^{-1} and 320-335 cm^{-1} for distorted octahedral $[\text{Cu}(\text{benzilmino oxime})_2(\text{NCS})_2]$.

Metal-sulphur stretching modes in Sn(II) and Pb(II) complexes are observed at 315 and 295 cm^{-1} respectively. Moreover, some contribution from ring vibration cannot be overruled.

Thus, distorted tetrahedral structure for all Sn(II), Pb(II), Zn(II), Cd(II), Hg(II) and distorted octahedral configuration for Cu(II) complexes may be tentatively assigned.

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