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Physico-Chemical Studies on Some Metal Complexes of Ce(IV), V(V), Nb(V), Ta(V) and Mo(VI) with Substituted Thioquinazoles Having Thioamide Group

R.N. PANDEY*, A.N. SAHAY, (MRS.) P. SHARMA, SANJAY KUMAR
and A.K. PATHAK
P.G. Centre of Chemistry
College of Commerce, Patna-800 020, India

Complexes of 2-mercapto-3-substituted quinazoline-4-one have been prepared and investigated using Ce(IV), V(V), Nb(V), Ta(V) and Mo(VI). These have the stoichiometries $M(QTH)X_5$ ($M = Nb$ or Ta; $X = Cl$ or NCS), $[VO_2(PQTH)_3Cl]$, $[V_2O_4(QTH)_4(NCS)_2]$, $[Ce(PQTH)(H_2O)_5](NO_3)_4$ and $[MoO_2(PQTH)_2Cl_2]\cdot 4H_2O$ (QTH= 2--mercaptoquinazoline-4-one and PQTH = 2-mercapto-3-phenylquinazoline-4-one). Structures of these complexes have been tentatively assigned on the basis of micro-analytical, conductivity, UV, visible, infrared and far-infrared spectral data. All the complexes have octahedral configuration.

INTRODUCTION

Substituted thioquinazoles are an important class of organic compounds having great biological significance. They are reported to be potential antimalarials[1], hypnotics[2], active ataractic agents[3] and bacteriostatic agents[4, 5]. They are used as ligands by several workers[6–8]. However, no attention has been paid to study their complexes in higher oxidation state metal ions which are present in many biological systems[9, 10]. In view of this, some complexes of Ce(IV), V(V), Nb(V), Ta(V) and Mo(VI) have been prepared and investigated using 2-mercaptoquinazoline-4-one (QTH) and 2-mercapto-3-phenylquinazoline-4-one (PQTH). Tentative structure of complexes and metal-ligand vibrations in farinfrared spectra are also assigned.

EXPERIMENTAL

All the reagents used in the present work were of AR or CP quality. The ligands are prepared by the method of Dave *et al.*[1]

Preparation of Complexes

(i) *Penta-aquo-2-mercapto-3-phenylquinazoline-4-one cerium(IV) nitrate,* $[Ce(PQTH)(H_2O)_5](NO_3)_4$: 0.3 G $(NH_4)_2[Ce(NO_3)_6]$ was dissolved in minimum amount of water and few drops of conc. HNO_3 were added. The solution was filtered in the ligand solution in acetic acid (0.1 g in 10 cm^3 acetic acid) and refluxed for 1 h. Pale cream colour precipitate was obtained on cooling at room temperature. The precipitate was washed with dry ether several times and dried in a vacuum desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 23.01; H, 2.72; N, 11.56; S, 4.03; (Calc.) C, 22.95; H, 2.73; N, 11.47; S, 4.37.

(ii) *Monochloro - tris (2 - mercaptoquinazoline - 4 - one) dioxovanadium (V),* [$VO_2(QTH)_3Cl$]: 0.4 G $NaVO_3$ was dissolved in 10 ml dilute HCl (2 N) and solution was boiled for 1 h. Then it was diluted by distilled water (*ca.* 40 ml) and methanolic solution of ligand (1.6 g in 50 cm^3 MeOH) was mixed. The mixture was refluxed for 2 h and on cooling, ash-coloured precipitate was obtained which was further washed with ice-cold methanol and dried in a vacuum desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 44.01; H, 2.70; N, 13.01; Cl, 5.68; V, 7.62; (Calc.) C, 44.17; H, 2.76; N, 12.89; Cl, 5.44; V, 7.82.

(iii) *Bis(2-mercaptoquinazoline-4-one) dioxovanadium(V)-4-di(isothiocyanato)-bis(2-mercaptoquinazoline-4-one)-dioxovanadium(V),* [$V_2O_4(QTH)_4(NCS)_2$]: 0.6 G $NaVO_3$ was added to 50 ml dilute HCl (2 N) and the mixture was boiled for 1 h and concentrated by evaporating the mixture on water bath about 20 ml. It was further diluted using 60 ml distilled water and mixed with methanolic solution of ligand (0.98 g). In the solution mixture 0.5 g of ammonium thiocyanate was added and again evaporated on water bath to *ca.* 30 ml and cooled. On cooling, dull white colour precipitate was obtained which was washed with ice cold methanol and dried in a vacuum desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 40.98; H, 2.41; N, 14.16; V, 10.69; (Calc.) C, 41.11; H, 2.42; N, 14.12; V, 10.28.

(iv) *Pentachloro-2-mercaptoquinazoline-4-one niobium(V),* [$Nb(QTH)Cl_5$]: 1.0 G $NbCl_5$ was dissolved in a mixture of carbon tetrachloride and dimethyl formamide (10 : 1) and mixed with ethanolic solution of ligand (2.1 g in 60 ml EtOH) and stirred on magnetic stirrer at 65°C till evolution of HCl(g) ceases. The mixture was kept for 2 h at room temperature and two drops NaOH (2 N) solution was added. Light yellow coloured precipitate was obtained which was further washed with ethanol and dried in a desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 21.50; H, 1.30; N, 6.32; Nb, 20.61; (Calc.) C, 21.40; H, 1.33; N, 6.24; Nb, 20.73.

(v) *Penta - isothiocyanato - 2 - mercaptoquinazoline - 4 - one niobium (V),* [$Nb(QTH)(NCS)_5$]: *This complex was isolated with filtrate of* [$Nb(QTH)Cl_5$].

In the filtrate of [$Nb(QTH)Cl_5$] 1.0 g NH_4SCN was added and the mixture was stirred for 2 h on magnetic stirrer and kept overnight at room temperature. Dull white colour precipitate was obtained. It was filtered, washed with dry benzene and dried in a desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 28.01; H, 1.01; N, 14.32; Nb, 16.87; (Calc.) C, 27.89; H, 1.06; N, 14.97; Nb, 16.83.

(vi) *Pentachloro-2-mercaptoquinazoline-4-one tantalum (V),* [$Ta(QTH)Cl_5$]: 0.7 G $TaCl_5$ in 30 ml absolute alcohol containing two drops of conc. HCl were mixed with ethanolic solution of ligand (0.75 g). The solution mixture was refluxed on water bath for about 2 h and evaporated further to 20 ml. Cooling the mixture, light grey coloured complex was obtained. The complex was washed carefully with ice-cold CCl_4 and dried in a vacuum desiccator over anhydrous $CaCl_2$. % Analysis: (Found) C, 18.01; H, 1.01; N, 7.32; Cl, 32.97; Ta, 33.33; (Calc.) C, 17.89; H, 1.11; N, 7.82; Cl, 33.08; Ta, 33.73.

(vii) *Dichloro-bis(2-mercapto-3-phenylquinazoline-4-one) dioxomolybdenum tetrahydrate,* $[MoO_2(PQTH)_2Cl_2]\cdot 4H_2O$: Ammonium molybdate (0.03 mole) was dissolved in 20 ml 2 N HCl by warming and filtered. The resulting solution was treated with ethanolic hot solution of ligand (0.1 mole in 100 ml EtOH). The mixture was evaporated on water bath to small volume (~ 30 ml) and kept overnight. A marine grey colour complex was obtained which was further dried in a vacuum desiccator over anhydrous $CaCl_2$ after filtration. % Analysis: (Found) C, 43.10; H, 3.50; N, 6.98; Mo, 12.01; (Calc.) C, 43.13; H, 3.59; N, 7.18; Mo, 12.32.

Magnetic measurements were made by means of Gouy balance at room temperature. The conductometric measurements were done on Wiss-Werkstatter-weithein Obb type LBR conductivity meter in DMF. IR spectra of ligands and complexes were recorded in the range of 4000–200 cm^{-1} by Perkin-Elmer 577 spectrophotometer using KBr pellets. The UV and visible spectra were recorded by Backmann DU-6 spectrophotometer.

RESULT AND DISCUSSION

2-Mercaptoquinazoline-4-one and its 3-phenyl substituted derivative forms very stable complexes with Ce(IV), VO_2^+ Nb(V), Ta(V) and MoO_2^{2+} ions. The solubility tests of complexes were done with C_6H_6, $CHCl_3$, CCl_4, CH_3OH, and DMF. All were fairly soluble only in DMF and found to be non-conducting in this solvent except $[Ce(PQTH)(H_2O)_5](NO_3)_4$. Molar conductance of this complex was found to be 320 ohm^{-1} cm^2 $mole^{-1}$ indicating the presence of three ions. Thus, NCS^-, Cl^- groups are covalently bonded and NO_3^- groups are present in the ionic form outside the coordination sphere. The chemical analysis of Na_2CO_3-extract solution of complexes supported these observations. When complexes were shaken with aqueous concentrated solution of Na_2CO_3 and the resulting Na_2CO_3 extract was tested for the presence of Cl^- and NCS^- ions, then no positive results were obtained. This indicates that chloride and isothiocyanate ions are covalently bonded with metal ions. However, in case of Ce(IV) complex positive result was obtained for "nitrate test" and nitrate ion is probably present in the outer sphere of complex. The presence of ionic nitrate is further supported by infrared spectrum of $[Ce(PQTH)(H_2O)_5](NO_3)_4$. New strong bands at 1370 cm^{-1} and medium bands at 790 and 640 cm^{-1} are assigned due to presence of ionic nitrate following Addison *et al.*[11] and others[12, 13]. All complexes were found to be diamagnetic as expected for d^o-configuration and stabilisation of higher oxidation state of these metal ions are stabilised by complex formation. The UV and visible spectra of these complexes do not display any d-d transition bands. In VO_2^+ complexes, a single very strong band is observed at 355 ± 5 nm due to charge transfer. However, there is no band between 400–700 nm. This also supports d^o-configuration of complexes.

The νN–H bands of QTH (3400 and 3240 cm^{-1}) and PQTH (3420 and 3245

TABLE I

MAJOR IR BANDS OF THE LIGANDS AND COMPLEXES (in cm^{-1})

Compounds	νNH	νCO	Amide band-I	Thioamide Bands				ν(M–S)	ν(M–N)	ν(M–Cl)
				I	II	III	IV			
QTH	3400 mb 3240 m	1710 (s)	1668 vs	1520 s	1275 ms	990 m	800 m	—	—	—
[$V_2O_4(QTH)_4(NCS)_2$]	3600–3400 vbr 3260m	1730 s	1680 sb	1530 s	1260 m	960 w	785 w	280 w 265 w	450 w 410w	—
[$VO_2(QTH)_3Cl$]	3480–3400 mbr 3260 m	1720 sh	1670 vs	1530 s	1265 m	970 w	780 w	280 w 270 w	—	415 w
[$Nb(QTH)(NCS)_5$]	3440–3390 mbr 3235 mbr	1720 s	1668 sb	1530 sb	1260 m	950 wb	790 m	390 w	400 w 370 w	—
[$Nb(QTH)Cl_5$]	3400 wb 3240 mb	1710 sh	1670 s	1525 m	1265 m	975 w 950 w	780 w	390 m	—	460 w 440 w
[$Ta(QTH)Cl_5$]	3400 mb 3245 m	1715 sh	1680 s	1530 m	1260 m	970 w	785 w	370 w	—	510 w 480 w
PQTH	3420 mb 3245 m	1710 m	1665 m	1526 m	1270 s	995 w	810 m	—	—	—
[$Ce(PQTH)(H_2O)_5$]$(NO_3)_4$	3400–3300 sh	1720 sh	1660 m	1530 s	1250 w	935 m	785 w	280 w	—	—
[$MoO_2(PQTH)_2Cl_2$]$\cdot 4H_2O$	3400 m 3240 mb	1720 sh	1660 m	1530 m	1250 w 1220 w	970 w	780 w	340 w 300 w	—	420 w 350 w

cm^{-1}) are either blue shifted or almost identical in all complexes indicating the absence of bonding through nitrogen atom of imino group. The νS–H band of QTH (2360 cm^{-1}) and PQTH (2350 cm^{-1}) are not observed in the spectra of complexes suggesting the thione tautomeric form of the ligand and formation of metal-sulphur bond may be assumed[14]. The formation of metal-sulphur is also supported by the systematic change in position of thioamide bands[15–18] of the ligands (Table 1). The thioamide I band (δNH + δCH + νC=N) undergoes blue shift in the order of 5–10 cm^{-1}, thioamide II band (νC$\overset{\cdots}{-}$N+ δN–H + δCH + νC=S) undergoes red shift of 15–20 cm^{-1} and thioamide III band (νC$\overset{\cdots}{-}$N + νC$\overset{\cdots}{-}$S) undergoes red shift of 35–40 cm^{-1}. The thioamide band IV (νC$\overset{\cdots}{-}$S) also undergoes a red shift of the order of 10–15 cm^{-1} on coordination. These observations may be considered as bonding through thione sulphur resulting in increase in CN bond order and decrease in CS bond order.[19–21] The νCO band observed at 1710 cm^{-1} as strong band in the spectrum of both QTH and PQTH remains almost unchanged in position or blue shifted (few cases) on coordination which suggests that carbonyl oxygen is not involved in coordination.

New bands at 2080(s), 1920(w), and 1810(w) cm^{-1} in $[Nb(QTH)(NCS)_5]$ are assigned due to νCN of isothiocyanato group having bonding through N-atom. A weak band at 760 cm^{-1} (νCS) also supports coordination through N-atom considering the previous assignment of Turco *et al.*[22] and Nyholm *et al.*[23] However, νCN modes of isothiocyanato group in VO_2^+ complex are observed at 2160(s) and 1960(wb) cm^{-1} and CS modes at 860(m) cm^{-1}. Hence, νCN of VO_2^+ complex is higher than isothiocyanato complex of Nb(V). This is most probably due to V–N bond being stronger than Nb–N bond. In far infrared spectrum, the νV–N bands (450 and 410 cm^{-1}) are also observed at higher wave number than νNb–N band (400 and 370 cm^{-1}). Moreover, following Chatt *et al.*[24] the isothiocyanato group is present as bridge between two dioxovanadium atoms in $[V_2O_4(QTH)_4(NCS)_2]$. The new single medium band due to νV=O modes at 835 ± 5 cm^{-1} in both VO_2^+ complexes suggests *trans*-dioxo group[25]. However, in dioxomolybdenum(VI) complex two new bands at 960 and 850 cm^{-1} are assigned νMo=O stretching modes of *cis*-dioxo group[26, 27]. Akira Nakamura *et al.*[28], Stiefel[29], Wentworth and coworkers[30] have also assigned two νMo=O modes for several *cis*-dioxomolybdenum complexes.

Some new bands are present in the far-infrared spectra of complexes. Two bands of νNb–Cl (460 and 440 cm^{-1}), νTa–Cl (510 and 480 cm^{-1}) and one band of νNb–S (390 cm^{-1}) and νTa–S (370 cm^{-1}) are consistent with octahedral structure in C_{4v}-point group for $[Nb(QTH)Cl_5]$ and $[Ta(QTH)Cl_5]$.

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