

SPECTRAL CHARACTERIZATION OF SOME OXO-METAL COMPLEXES OF 2-MERCAPTO-3-BUTYL-QUINAZOLINE-4-ONE

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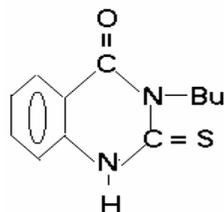
ABSTRACT

Oxo-metal (VI & IV) complexes of 2-mercapto-3-butyl-quinazoline-4-one having general formula $[MO_2(\text{ligand})_2A_2]$ ($M=V/Mo/W$; $A=H_2O/Py/Cl$) and $[MO(\text{ligand})_4X]$ ($M=V/Zr$; $X=H_2O/SO_4$) are prepared and characterized using elemental analyses, conductometric magnetic moment, IR, UV-vis, 1H NMR spectral data. Cis-dioxo structure of MO_2^{++} ($M=Mo/W$) and Trans-dioxo-structure of VO_2^+ species occurs in octahedral stereochemistry and ligand acts as monodentate (S-donor).

Key Words: dioxo-metal (V & VI)/ oxo-metal(IV) complexes, thioquinazoline, IR, UV-vis, 1H NMR Spectra.

INTRODUCTION

Substituted thioquinazolines are important class of organic compounds of great biological significances¹⁻⁵. These compounds are used as ligand by several workers⁶⁻⁸. However, no attention have been paid to study oxo-metal complexes of transition metals. The strongly bound oxygen (s) of oxo-cations provides additional means for studying the complexes⁹. Thus, some novel complexes of 2-mercapto-3-butyl-quinazoline-4-one(I) with VO^{++} , ZrO^{++} , MoO_2^{++} , WO_2^{++} and VO_2^+ species have been prepared and characterized by analytical, conductometric, magnetic moment, IR, UV-visible, 1HNMR spectral data.



(BQTH)
(I)

EXPERIMENTAL

All the chemicals used were of anal R grade or CP-quality. 2-Mercapto-3-butyl-quinazoline-4-one (BQTH) was prepared by the method of Dave et al.¹⁰ All complexes were prepared using a general method reported earlier¹¹. Carbon, hydrogen and nitrogen analyses, molar conductance, magnetic, IR, electronic and 1H NMR Spectral data were obtained as reported in our previous communications¹².

RESULTS AND DISCUSSION

The results of chemical analyses (table 1) are in agreement with the proposed formulation of the complexes as $[MO_2(\text{ligand})_2A_2]$ ($M=V/Mo/W$; $A=H_2O/Py/Cl$) and $[MO(\text{ligand})_4X]$ ($M=Zr/V$; $X=SO_4/H_2O$). The metal complexes are stable solid, non-hygroscopic and do not melt up to 250^0 C. Molar conductance measurements of the complexes in DMF (10^{-3} M) solution exhibited quite low value ($6-8\Omega^{-1}cm^2mol^{-1}$) and revealed their non electrolytic nature. However, molar conductance of

$[\text{ZrO}(\text{BQTH})_4(\text{H}_2\text{O})]\text{Cl}_2$ and $[\text{ZrO}(\text{BQTH})_4(\text{H}_2\text{O})](\text{NO}_3)_2$ was observed to be 86.2 and 75.6 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for 1:2 electrolyte¹³. The low value of molar conductance may be due to larger Zirconium(IV) ion or due to hydration. All complexes were found to be diamagnetic as expected for d^0 configuration for VO_2^+ , MoO_2^{++} , WO_2^{++} and ZrO^{++} species. But magnetic moment of oxovanadium(IV) complexes were found to be 1.66 BM indicating one unpaired electron in 3d orbitals and support existence of VO^{++} species.

Electronic spectra of complexes display very strong absorption band near 340-350 nm assigned to charge transfer band. However, no absorption was observed above 400 nm indicating d^0 – configuration for dioxometal (V & VI) ions. But oxo-vanadium(IV) complexes display d-d transition bands. The value of magnetic moment of vanadyl complexes indicate lowest state ${}^2\text{B}_2$ and excited states ${}^2\text{E}$, ${}^2\text{B}_1$ and ${}^2\text{A}_1$ in order of increasing energy considering Ballhausen and Gray¹⁴ molecular model. The reflectance spectra of complexes display very strong band at 350 nm and two medium broad band at 485 nm and 575 nm. The first band may be due to charge transfer origin but the two other bands are due to ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions characteristic for distorted octahedral structure¹⁵.

IR spectra

Infrared spectral bands of ligand (BQTH) observed at 3225 cm^{-1} (ν NH) and at 1680 cm^{-1} (ν C=O) remained almost unchanged in position on complexation indicating absence of bonding through imino nitrogen and carbonyl oxygen atom. However, thiomide band IV (ν C=S) of the ligand undergoes red shift of 35- 40 cm^{-1} on complexation indicating bonding through thiocarbonyl sulphur in all complexes¹⁶⁻¹⁸. The systematic shift in thioamide bands of ligands clearly indicate formation of metal sulphur bond. Thiomide band I (δ NH + δ CH + ν C=N), band II (ν C-N + δ NH + ν C=S), band III (ν C-N + ν C-S) of the ligand observed at 1520 (s), 1270 (m) and 1020 (m) cm^{-1} respectively undergo blue shift (10-15 cm^{-1}) of band I, red shift of band II (20-25 cm^{-1}) and band III (30-40 cm^{-1}) confirms coordination of BQTH through thiocarbonyl sulphur which results increase in CN bond order and decrease in CS bond order¹⁹⁻²¹. New bands at 3420, 1605 and 810 cm^{-1} in aquo-complexes (1,7,8 & 10) assigned to ν H₂O, δ H₂O and π H₂O of coordinated water molecules in these complexes²². All hydroxo-complexes lack of HOH bending mode at 1605 cm^{-1} and exhibits MOH bending mode at 1150 cm^{-1} indicating coordinated hydroxyl group²³. The characteristic vibrations of free pyridine in the high-frequency region are not shifted appreciably on complexation. But in-plane ring deformation (604 cm^{-1}) and out-of-plane-ring deformation (405 cm^{-1}) are shifts to higher frequencies on complexation²⁴ in all pyridine complexes.

All the MoO_2^{++} and WO_2^{++} complexes show two bands (880,860) and (890 & 870) cm^{-1} assignable to the two Mo=O and W=O stretching modes respectively. The presence of the two bands is consistent with the cis-dioxo structure of the MoO_2^{++} and WO_2^{++} groups²⁵⁻²⁶. However, in dioxovanadium(V) complexes, the presence of a single medium band at 830-820 cm^{-1} indicate the trans-dioxo configuration of the VO_2^+ species²⁷. The presence of mono oxo-cations VO^{++} and ZrO^{++} in the complexes are indicated by medium band at 960 cm^{-1} and weak band at 880 cm^{-1} respectively in the spectra of complexes. Kharitonov and Zaitsev²⁸ suggested the range 800-1100 cm^{-1} for ν Zr=O but also noted that δ ZrOH deformation mode can give rise to strong bands in the same region. The low intensity of ν Zr=O band argues against such assignment²⁹.

The absorption associated with anions in these complexes are identified at 1360 and 830 cm^{-1} for ionic nitrate³⁰, at 1050, 1000 and 640 cm^{-1} for unidentate sulphate³¹ and 530 cm^{-1} for coordinated chloride³². Far IR spectra of the complexes contain several bands which are present in the spectrum of the ligand also. Hence, it is very difficult to assign metal-ligand vibrations in 600-200 cm^{-1} region. However, new bands at 540 cm^{-1} (ν Zr-O), 450- 400 cm^{-1} (ν Zr-S), 420-415 cm^{-1} (ν Mo-S) and at 340 cm^{-1} (ν W-S) are tentatively assigned following our previous observations¹¹.

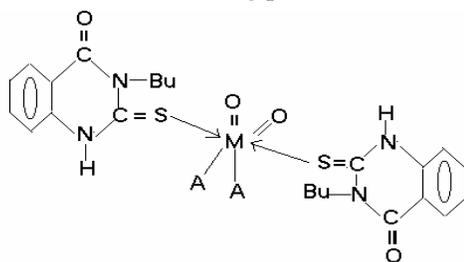
¹H NMR spectra

The ¹H NMR spectra of complexes display triplet at δ 1.70 ppm for methyl proton of butyl group. The two middle CH₂ signals are complex and are centered at δ 2.0 ppm and 2.3 ppm. The CH₂ group attached to the nitrogen atom of the quinazoline ring is deshielded giving triplet at δ 4.8 ppm. The signals due to

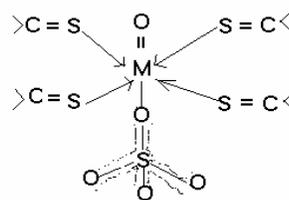
aromatic protons are observed at δ 7.6-8.3 ppm. The aromatic proton at position-5 is deshielded by the carbonyl oxygen and the extreme signal at δ 8.5 ppm is considered to be due to this proton. The signal due to N-H group is always difficult to identify because of the quadrupole moment of nitrogen and the exchange of this proton. However, a peak observed at δ 3.28 ppm in the ligand remains almost at the same position (δ 3.21 ppm) in the complexes assigned to N-H proton of coordinated ligand which is intact after complexation.

The resonance in the region δ 7.2, 8.18 and 8.98 ppm assignable to the protons of the pyridine ligand along with the resonances due to aromatic protons in $[\text{VO}_2(\text{BQTH})_2(\text{Py})_2]\text{Cl}$. The pyridine proton resonances exhibited down field as compared to that in free ligand, indicate the complexation of pyridine nitrogen atom with metal center³³. The aquo-complexes (Sl.No. 1,7,8 & 10) exhibits singlet signal δ 1.30 ppm which corresponds to two protons and another multiplet at δ 2.1 ppm corresponding to two protons. This is due to 4 protons of the two coordinated water molecules³⁴, which are in different magnetic environments. The singlet signal centred at 1.80 ppm in hydroxy- complexes (Sl.No. 5&6) assigned to protons of -OH group³⁵ coordinated to MO_2^{++} (M=Mo/W).

Thus, on the basis of aforesaid observations on elemental analyses, conductometric, magnetic, IR, ^1H NMR spectral data, the following probable structure of complexes may be assigned.



Oh-str. Of $[\text{MO}_2(\text{ligand})_2\text{A}_2]$
(M=V/Mo/W; A=H₂O/Py/Cl)



Oh str. Of $[\text{MO}(\text{ligand})_4\text{SO}_4]$
(M=Zr/V)

Table-1 : Analytical and Physical Data of Complexes:

Sl. No	Complexes	Mol. Conductivity ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	%Analyses:Found/ (calcd)			
			C	H	N	Metal
1	$[\text{VO}_2(\text{BQTH})_2\text{H}_2\text{O}]\text{Cl}$ (Grey, 6)	65.7	46.3 (46.2)	5.1 (5.2)	9.1 (8.9)	8.5 (8.2)
2	$[\text{VO}_2(\text{BQTH})_2(\text{Py})_2]\text{Cl}$ (Grey, 8)	60.8	54.4 (54.8)	5.1 (5.1)	7.6 (7.5)	6.9 (6.8)
3	$[\text{MO}_2(\text{BQTH})_2\text{Cl}_2]$ (Voilet, 6)	8.2	43.2 (43.1)	4.3 (4.1)	8.1 (8.4)	14.5 (14.4)
4	$[\text{WO}_2(\text{BQTH})_2\text{Cl}_2]$ (Yellow, 4)	7.6	38.4 (38.1)	3.9 (3.7)	7.1 (7.4)	25.0 (24.4)
5	$[\text{MO}_2(\text{BQTH})_2(\text{OH})_2]$ (Yellowish green, 8)	6.6	45.8 (45.7)	4.8 (4.7)	9.1 (8.9)	15.6 (15.2)
6	$[\text{WO}_2(\text{BQTH})_2(\text{OH})_2]$ (Light yellow, 8)	8.8	40.4 (40.1)	4.2 (4.1)	7.9 (7.8)	26.1 (25.6)
7	$[\text{VO}(\text{BQTH})_4(\text{SO}_4)]$ (Black, 6)	8.2	52.5 (52.4)	5.2 (5.0)	10.5 (10.1)	5.1 (4.7)

8	[ZrO (BQTH) ₄ H ₂ O] (Light yellow, 6)	86.2	48.6 (48.5)	4.9 (4.8)	9.6 (9.4)	7.7 (7.7)
9	[ZrO (BQTH) ₄ H ₂ O](NO ₃) ₂ (Yellow, 4)	75.6	48.7 (48.6)	4.9 (4.9)	11.9 (11.8)	7.7 (6.9)

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