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# Synthesis, Structural Characterization and Biological Activity of Peroxo Complexes of Zirconium (IV) Containing Organic Acid and Amine Bases

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**Abstract:** The study was extended to isolate the peroxo complexes of Zr (IV) containing organic acid and amine bases. The Zr (IV) complexes have been found to oxidize allyl alcohol and triphenylphosphine as well as triphenylarsine to their respective oxides. The analytical data are in good agreement with the proposed empirical formulae of the present complexes. The complexes display ν(C = O) bands at ~1630 $cm^{-1}$ and ν(C-O) bands at ~1412 $cm^{-1}$ significantly lower than the values of amino acid (~1650 and ~1450 $cm^{-1}$). These indicate the coordination of amino acid through their carboxylate anion. The broad band observed at about 3217-3350 $cm^{-1}$ for ν (N-H) modes indicate the coordination of amino group through nitrogen atom of amino acid. The metal peroxo grouping gives rise to three IR active vibrational modes. These are predominantly O-O stretching $\nu_1$, the symmetric M-O stretch $\nu_2$ and the antisymmetric M-O stretch $\nu_3$. The magnetic moment values indicated that these complexes were diamagnetic in nature suggesting no changes in their oxidation states of the metal ions upon complexation. These data also consistent with six fold coordination of Zr (IV). The electronic spectral data of the complexes showed bands in the region 230-372 nm due to the charge transfer band only. All the complexes of Zr (IV) did not show any remarkable antibacterial activity. It is interesting to note that these complexes were found to be fully inactive against the three pathogenic fungi *A. niger*, *A. fumigatus* and *A. flarus*. Moreover, all the complexes of Zr (IV) metals showed toxic effect against the brine shrimp.

**Key words:** Peroxo complexes, Zr (VI), organic acid, amine base, bioactivity, toxicity

## INTRODUCTION

Peroxo and superperoxo complexes are major importance because of the role they play as oxygen carrier systems in biology and preparative chemistry. For instance, peroxo complexes of vanadium show insulinomimetic properties (Horner *et al*., 2002a, Yudanov *et al*., 1999). Another example from this class of compounds is hemocyanin, which contains a dinuclear copper site capable of binding $O_2$ in a $\mu$-$\eta^2$: $\eta^2$ peroxo complexes (Biagioli *et al*., 2000). Finally peroxo complexes are potential intermediates or products during the oxidation of metals or metal clusters. Consequently, there is substantial interest in the exploration and isolation of new stable peroxo and superoxo complexes. The early transition elements in their highest oxidation states rapidly combine with hydrogen peroxide to form peroxo complexes with large formation constants (John *et al*., 2001; Winterhalter *et al*., 2001). The reactivities of these peroxo complexes toward a variety of reducing agents have been examined, both in organic solvents and in aqueous solution (Deubel *et al*., 2001, Horner *et al*. 2002b). In many cases impressive activation of the $\eta^2$-bound peroxo group relative to hydrogen peroxide is observed. Oxygen atom transfer from peroxide to the substrate has been demonstrated or assumed for many of the systems examined. The formulations of the peroxo complexes in solution are reasonably well established and vary depending on the $d^0$ metal ion, the concentration of excess hydrogen peroxide present and the pH (especially in aqueous solution).

The metal complexes of organic acids and amine bases have been studied both from pharmacological (Mastrolorenzo and Supuran, 2000) and industrial (Smicka *et al*., 2000) point of view as indicated by available literatures. The literatures are also rich in reports on the mixed ligand complexes prepared by using phthalic acid as primary and heterocyclic amine bases (Hassan, 2003), polyamines (Holmes *et al*., 2001) and thiocarbamides (Natile and Coluccia, 2001) as secondary ligands. Ternary complexes consisting of a metal ion and two different ligands other than the solvent have provided very useful and simple models for understanding the roles of metal ions in biological systems; which are rather complex in nature studied by Mukherjee *et al*. (1994).

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Around the same time as the start of development of prodrugs, transition metal complexes were found to have physiological properties (Paulsen *et al*., 1997). In all cases where transition metal complexes are used as drugs, the systems are designed so that upon ligand dissociation, cleavage or elimination, the metal is delivered as the cytotoxic species (Rodriguez Montelongo *et al*., 1993). The cytotoxicity of the metal raises the possibility of using transition metal complexes as potential prodrugs in conjunction with known anti cancer compounds. More specifically, by binding a known anti tumor agent as the dissociating ligand, we may have the capability of using a transition metal as a delivery system for anti tumor agents. Another incentive for the development of these types of systems is that upon cleavage of the pharmacologically active ligand, delivery of a cytotoxic metal species also occurs.

The present research describes here the synthesis and characterization of complexes of Zr(IV) containing organic acid and amine bases, the biological activities and cyto-toxicity of the metal complexes.

## MATERIALS AND METHODS

All the chemicals were of reagent grade and unless otherwise specified, were used as received. The solvents were purified using conventional methods.

**Physical measurements:** IR spectra were recorded on a Simadzu FTIR-8400 (Japan) spectrometer using KBr pellets. Carbon, hydrogen and nitrogen analysis were carried out at the Department of Chemistry, Rajshahi University, Bangladesh. Metals were determined by weighing as the oxide produced by direct ignition. 221, 222 The samples were digested in a mixture of concentrated nitric acid and hydrochloric acid. The molar conductance of 10-3 M solutions of the metal complexes in DMSO was measured at 30°C using a Jenway 4310 conductivity meter and a dip-cell with platinized electrode. The UV-Vis spectra were recorded on a LKB Ultrospec K4053 spectrophotometer. An electrothermal melting point apparatus was used for the determination of melting or decomposition point. Magnetic measurements have been carried out in a Sherwood scientific magnetic susceptibility balance at room temperature. All susceptibilities were corrected for diamagnetic contribution using Pascal's constant.

General method for the preparation of the complexes of the type $(Zr(O_2)$ (am H).L)$NO_3$ (where am H = deprotonated glycine, alanine, phenylalanine and leucine; L = quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline).

The aqueous solution of Zirconyl nitrate (0.6445 g, 0.002 mol) and amino acids like glycine (0.15014 g, 0.002 mol) or alanine (0.1782 g, 0.002 mol) or phenylalanine (0.330 g, 0.002 mol) or leucine (0.262 g, 0.002 mol) containing minimum amount of KOH (to make soluble) were mixed in a molar ratio of 1:1 and then allowed to stand for about ten minutes. A solution of L (0.01 mol) in ethanol was then added with continuous stirring to the above mixture followed by the addition of 30% $H_2O_2$ (2 mL). The precipitate appeared, which was filtered, washed several times successively with ethanol. It was then dried and stored in *Vacuo* over $P_4O_{10}$.

**Reaction of the complexes of 1, 3, 5 and 12 with allyl alcohol:** The complex 1 (1.05 g, 0.003 mol) was suspended in THF (30 mL) and a stoichiometric amount of allyl alcohol was added. The mixture was stirred under reflux at 60°C for 48 h, but it failed to produce any reaction product and complex 1 was recovered unchanged. The compounds 3, 5 and 12 also failed to give any reaction product.

**Reaction of the compounds 8 and 10 with allyl alchohol (Reaction A):** A suspension of compound 8 (1.67 g, 0.003 mol) in THF (30 mL) was added to a stoichiometric amount of allyl alcohol. The mixture was stirred under reflux at 65°C for 36 h. Microdistillation under a pressure of 19 mm Hg yielded glycidol (75% yield) at 145-150°C (IR 1055 $cm^{-1}$ (S, C-O-C)). The glycidol was definitely identified by means of its phenylurethan derivative, m.p. 58-59°C. The compound 10 also behaved in a similar fashion.

**Catalytic reaction of the compounds 8 and 10 with allyl alcohol (Reaction B):** A quantity of 20 mL allyl alcohol (17.08 g, 0.30 mol) was dissolved in dioxane (20 mL) and 1.0 g of compound 8 or 10 was added followed by $H_2O_2$ (30%, 20 mL). The mixture was refluxed at 90°C for 24 h. The reaction mixture was then filtered and the filtrate was distilled under reduced pressure (19 mm Hg). The fraction collected at 177-180°C was glycerol (IR 3190-3475 $cm^{-1}$ (br, O-H)). The glycerol was identified as its tribenzoyl ester derivative, m.p. 68-69°C.

**Reaction of the compounds 6 and 9 with triphenylphosphine (Reaction C):** A solution of triphenyl phosphine (0.786 g, 0.003 mol) in THF (20 mL) was added to a suspension of compound 6 (1.29 g, 0.003 mol) or 9 (1.94 g, 0.003 mol) in the same solvent (40 mL). The mixture was stirred under reflux at 60°C for 48 h. The TLC indicated that the reaction was completed. The reaction mixture was filtered and the residue was collected. A yellowish white powder was recovered from the filtrate which was identified as triphenyl phosphine oxide, m.p. 156-157°C.

**Reaction of the compounds 7 and 11 with triphenylarsine (Reaction D):** A solution of triphenylarsine (0.981 g, 0.003 mol) in THF (30 mL) was added to a suspension of compound 7 (1.52 g, 0.003 mol) or 11 (1.72 g, 0.003 mol) in the THF (40 mL). The mixture was refluxed for 48 h at 60°C. TLC indicated that triphenylarsine was completely converted into triphenylarsine oxide. The reaction mixture was filtered and the residue was collected. Evaporation of the filtrate yielded the product, m.p. 188-189°C.

**Antibacterial activity:** The test organisms (both bacteria and fungi) were collected from the Department of Pharmacy, Rajshahi University. All steps of the work were carried out at the Molecular Genetics Laboratory, Department of Pharmacy, Rajshahi University.

The complexes were screened for antibacterial activity against bacteria using disc diffusion technique at 200 μg $disc^{-1}$. Concentrations of each compound were mixed in nutrient agar media.

Tryptone, NaCl and yeast extract of calculated amount were taken in a conical flask and distilled water was added (volume should be less than 1 L). The contents were heated in a water bath to make a clear solution. The pH of the solution was then adjusted to 7.5 using NaOH or HCl as necessary. Distilled water was added sufficiently to make to final volume (1 L). The total volume was again heated in a water bath to obtain a clear solution. The conical flask was plugged with cotton and then autoclaved at 15 Ib pressure for 15 min at 121°C.

Fifty milliliter of broth medium was transferred in a conical flask. The test microorganisms of pure culture were streaked on the nutrient broth media with the help of sterile loop in an aseptic condition and incubated at 37°C for 24 h. The broth culture thus obtained was considered fresh culture. Fresh culture of this type was always used throughout the sensitivity testing.

**Preparation of plates:** The medium was poured into sterile petridishes in an aseptic condition on a level horizontal surface so as to give a uniform depth of approximately 4 mm. Then the medium had been allowed to cool at room temperature in order to solidify the medium.

**Preparation of discs:** Sterile filter paper discs were taken and the test material of known concentration was applied on the discs with the help of a micropipette. The solvents from the discs were evaporated by hot air blower. In the similar way control discs (containing only the solvents) were also prepared.

**Placement of the discs and incubation:** The solidified agar plates were seeded with 70 μL of fresh culture with the help of a micropipette and spread the microorganisms with the help of a sterile spreader in an aseptic condition. The prepared discs of samples were placed gently on the freshly seeded solidified agar plates with a sterile forceps. Standard discs and control discs were also placed on the test plates to compare the effect of the test samples and to nullify the effect of solvent, respectively. The plates were then kept in a refrigerator at 4°C for 4 h so that the materials had sufficient time to diffuse to a considerable area of the plates. After this, the plates were incubated at 37°C for 16 h.

**Calculation of the zone of inhibition:** After incubation, the diameter of the zone of inhibition were observed and measured in mm by a transparent scale.

**Antifungal activity testing:** The antifungal activity of the complexes was carried out against *Aspergillus niger*, *A. fumigatus* and *A. flarus* using disc diffusion technique.

**Culture media:** To prepare PDA medium potatoes were cut into pieces and weighed about 200 g and boiled in 1000 mL of distilled water for an hour, filtered and volume was made upto 1000 mL by adding more distilled water. Glucose and agar were then added and stirred. The pH of the medium was then adjusted to 5-6 (by using lactic acid) which is acidic in nature. The medium was then sterilized at 121°C under pressure for 15 min.

To prepare Sabouraud medium, the amount of each constituent was calculated from the above chart. Peptone, glucose of above mentioned amount were taken in a conical flask and distilled water was added (volume should be less than 1 L). The contents were heated in a water bath to make a clear solution. The pH of the solution was then adjusted at 6.5. Required amount of powder was added to the solution and distilled water was added sufficiently to make the final volume (1 L). The total volume was again heated in a water bath to obtain a clear solution. The medium was then sterilized at 121°C at 15 Ib pressure for 15 min.

Cyto-toxicity effect for brine shrimp *Artemia salina* leach
**Procedure:** Thirty eight grams sea salt was weighed and dissolved in one liter of distilled water and then filtered off. Sea water was taken in a small tank and shrimp eggs were added to one side of the divided tank. The shrimps were allowed for two days to hatch and mature as napulii (larvae). The hatched shrimps were attracted to the lamp on the other side of the divided tank through the perforations in the dam. These napulii were taken for bioassay. Ten milligram of sample was weighed accurately in a vial and dissolved in 1 mL of dimethyl sulfoxide. The concentration of this solution was 10 μg $\mu L^{-1}$. 10, 20, 40, 80 and 160 μL of the test solution were taken in vials and 5 mL of the sea water was added to each vial containing 10 brine shrimp napulii. The concentrations of the sample

in the vials were 10, 20, 40, 80 and 160 μg $mL^{-1}$, respectively. Three vials were used for each concentration and a control was used containing 100 μL of the solvent and 10 napulii in 5 mL of sea water. A magnifying glass was used for convenience counting of the napulii. After 16 and 36 h, the vials were observed and the number of survivors in each vial were counted and noted. The percentage of mortality of napulii was calculated at each concentration. The probit analysis was used to determine the lethality of 50 and 99% mortality levels.

## RESULTS AND DISCUSSION

**Synthesis and structural characterization of peroxo complexes of Zr (IV):** The complexes were prepared from the reaction of the Zirconyl nitrate with organic acids and amine bases. The reaction may be represented as follows:

$$Zr(NO_3)_4 + amH + 2L + H_2O_2 \rightarrow [ZrO(O_2)(amH)L]NO_3 + HNO_3$$

Where, amH = deprotonated glycine, alanine, phenylalanine and leucine; L = quinoline, isoquinoline, pyridine, 2-picoline or 4-picoline.

**Elemental analysis and conductivity measurement:** The analytical data and their physical properties of the complexes are shown in Table 2 and 3, respectively. All the complexes are insoluble in water but soluble in Dimethylsulphoxide (DMSO) and Dimethylformamide (DMF). The molar conductance of $10^{-3}$ M solutions of the complexes in DMSO were measured at 30°C. The molar conductance values (Table 3) indicate all the complexes are highly electrolyte in nature. The analytical data are in good agreement with the proposed emperical formulae of the present complexes. Their structures have been proposed on the basis of conductivity and magnetic measurements (Table 3) and electronic spectral data (Table 4).

**IR studies:** Infrared spectral data of the complexes are shown in Table 4. The complexes display ν(C = O) bands at ~1630 $cm^{-1}$ and ν(C-O) bands at ~1412 $cm^{-1}$ significantly lower than the values of amino acid (~1650 and ~1450 $cm^{-1}$). These indicate the coordination of amino acid through their carboxylate anion. The zirconium complexes display ν(M = O) modes in the region 917-945 $cm^{-1}$. Further, the presence of M-N bond in the complexes are evident from the appearance of ν(M-N) modes at 289-408 $cm^{-1}$ in the spectra of the complexes.

The broad band observed at about 3217-3350 $cm^{-1}$ for

Table 1: List of the test organisms

| Gram positive | Gram negative |
|---|---|
| *Streptococcus-β-haemolyticus* | *Escherichia coli* |
| *Bacillus subtilis* | *Salmonella typhi* |
| *Sarcina lutea* | *Shigella sonnei* |
| *Pseudomonas aeruginosa* | *S. flexneri* |
| *Bacillus megaterium* | *S. dysenteriae* |
| | *S. aurus* |
| | *S. shiga* |

Antibacterial Activity Testing

Table 2: Analytical data and physical properties of Zr(IV) complexes

| No. | Complexes | Y% | M% | C% | H% | N% |
|---|---|---|---|---|---|---|
| 1 | $K(ZrO(O_2)(gly)(py))$ | 77 | 27.37 | 25.21 | 2.59 | 8.29 |
| | | | (27.52) | (25.35) | (2.72) | (8.45) |
| 2 | $K(ZrO(O_2)(gly)(2\text{-pic}))$ | 65 | 26.23 | 27.57 | 3.01 | 8.00 |
| | | | (26.41) | (27.79) | (3.18) | (8.11) |
| 3 | $K(ZrO(O_2)(gly)(4\text{-pic}))$ | 60 | 26.18 | 27.58 | 3.02 | 8.02 |
| | | | (26.41) | (27.79) | (3.18) | (8.11) |
| 4 | $K(ZrO(O_2)(gly)(Q))$ | 74 | 23.77 | 34.42 | 2.71 | 7.18 |
| | | | (23.91) | (34.60) | (2.88) | (7.34) |
| 5 | $K(ZrO(O_2)(gly)(iso\text{-}Q))$ | 69 | 23.24 | 35.02 | 2.54 | 8.00 |
| | | | (23.35) | (35.12) | (2.67) | (8.02) |
| 6 | $K(ZrO(O_2)(ala)(py))$ | 62 | 26.02 | 27.56 | 3.03 | 8.02 |
| | | | (26.11) | (27.79) | (3.18) | (8.11) |
| 7 | $K(ZrO(O_2)(ala)(2\text{-pic}))$ | 70 | 25.17 | 30.00 | 3.41 | 7.56 |
| | | | (25.38) | (30.05) | (3.62) | (7.79) |
| 8 | $K(ZrO(O_2)(ala)(4\text{-pic}))$ | 60 | 26.51 | 31.29 | 3.72 | 7.47 |
| | | | (26.69) | (31.48) | (3.95) | (7.64) |
| 9 | $K(ZrO(O_2)(ala)(Q))$ | 64 | 23.00 | 36.28 | 3.10 | 7.00 |
| | | | (23.07) | (36.41) | (3.29) | (7.08) |
| 10 | $K(ZrO(O_2)(ala)(iso\text{-}Q)\}$ | 72 | 24.02 | 36.37 | 7.27 | 3.58 |
| | | | (24.15) | (3.79) | (7.45) | (36.58) |
| 11 | $K(ZrO(O_2)(pha)(py))$ | 63 | 21.47 | 39.68 | 3.41 | 6.51 |
| | | | (21.65) | (39.87) | (3.56) | (6.64) |
| 12 | $K(ZrO(O_2)(leu)(py))$ | 67 | 23.42 | 34.00 | 4.53 | 7.09 |
| | | | (23.55) | (34.07) | (4.65) | (7.23) |

Figure in parenthesis indicates the calculated values

Table 3: Physical properties of Zr(IV) complexes

| No. | Complexes | Colour | Melting point (±0.5°C) | Molar conductance $\Omega^{-1}cm^{-2}Mole^{-1}$ | Magnetic moment $\mu_{eff}$(BM) |
|---|---|---|---|---|---|
| 1 | K(ZrO($O_2$)(gly)(py)) | Colourless | 140 | 72.40 | -0.329 |
| 2 | K(ZrO($O_2$)(gly)(2-pic)) | Colourless | 132 | 74.40 | -0.299 |
| 3 | K(ZrO($O_2$)(gly)(4-pic)) | Colourless | 145 | 76.30 | diamagnetic |
| 4 | K(ZrO($O_2$)(gly)(Q)) | Colourless | 134 | 68.30 | diamagnetic |
| 5 | K(ZrO($O_2$)(gly)(iso-Q)) | Colourless | 138 | 77.20 | diamagnetic |
| 6 | K(ZrO($O_2$)(ala)(py)) | Colourless | 139 | 79.80 | diamagnetic |
| 7 | K(ZrO($O_2$)(ala)(2-pic)) | Colourless | 122 | 73.70 | -0.483 |
| 8 | K(ZrO($O_2$)(ala)(4-pic)) | Colourless | 146 | 77.30 | -0.432 |
| 9 | K(ZrO($O_2$)(ala)(Q)) | Colourless | 126 | 84.30 | -0.499 |
| 10 | K(ZrO($O_2$)(ala)(iso-Q)) | Colourless | 135 | 79.40 | -0.519 |
| 11 | K(ZrO($O_2$)(pha)(py)) | Colourless | 139 | 71.30 | diamagnetic |
| 12 | K(ZrO($O_2$)(leu)(py)) | Colourless | 138 | 75.40 | diamagnetic |

Table 4: IR spectral data of Zr(IV) complexes

| No. | υ (N-H) $cm^{-1}$ | υ (C = O) $cm^{-1}$ | υ (C-O) $cm^{-1}$ | υ (M = O) $cm^{-1}$ | υ (M-N) $cm^{-1}$ | $\upsilon_1$ (O-O) $cm^{-1}$ | $\upsilon_3$ $cm^{-1}$ | $\upsilon_2$ $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 3286br | 1612m | 1350w | 933m | 314m | 842s | 658m | 604w |
| 2 | 3304br | 1620s | 1380s | 935w | 312m | 820s | 652m | 630w |
| 3 | 3299br | 1615s | 1382s | 927w | 289w | 830s | 663m | 605w |
| 4 | 3272br | 1622s | 1403s | 945m | 406w | 837m | 653m | 614w |
| 5 | 3217br | 1603s | 1382s | 917m | 308w | 825s | 662m | 623w |
| 6 | 3350br | 1608s | 1410s | 928w | 305m | 832s | 677m | 638w |
| 7 | 3229br | 1617s | 1408s | 918w | 300w | 836m | 672m | 624w |
| 8 | 3243br | 1615s | 1412s | 938w | 310w | 840m | 654m | 620w |
| 9 | 3247br | 1616s | 1380s | 936w | 307w | 838m | 650m | 629w |
| 10 | 3250br | 1630s | 1385s | 917w | 319w | 844m | 658m | 620w |
| 11 | 3288br | 1615s | 1382s | 930m | 308m | 833s | 653m | 590w |
| 12 | 3280br | 1610s | 1388s | 936m | 322w | 820m | 682m | 633w |

Related band intensities are denoted by vs, s, m, w and br representing very strong, strong, medium, weak and broad band, respectively

Table 5: Electronic spectral data of Zr(IV) complexes

| Complex No. | Complexes | λmax (nm) |
|---|---|---|
| 1 | K(ZrO($O_2$)(gly)(py)) | 232, 335 |
| 2 | K(ZrO($O_2$)(gly)(2-pic)) | 230, 315 |
| 3 | K(ZrO($O_2$)(gly)(4-pic)) | 260, 295 |
| 4 | K(ZrO($O_2$)(gly)(Q)) | 268, 355 |
| 5 | K(ZrO($O_2$)(gly)(iso-Q)) | 331, 340 |
| 6 | K(ZrO($O_2$)(ala)(py)) | 295, 325 |
| 7 | K(ZrO($O_2$)(ala)(2-pic)) | 300 |
| 8 | K(ZrO($O_2$)(ala)(4-pic)) | 360 |
| 9 | K(ZrO($O_2$)(ala)(Q)) | 315, 350 |
| 10 | K(ZrO($O_2$)(ala)(iso-Q)) | 372 |
| 11 | K(ZrO($O_2$)(pha)(py)) | 365 |
| 12 | K(ZrO($O_2$)(leu)(py)) | 239, 311 |

ν(N-H) modes indicate the coordination of amino group through nitrogen atom of amino acid.

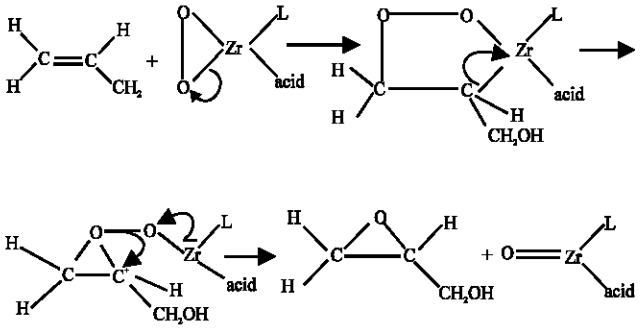
The metal peroxo grouping gives rise to three IR active vibrational modes. These are predominantly O-O stretching $\nu_1$, the symmetric M-O stretch $\nu_2$ and the antisymmetric M-O stretch $\nu_3$. The characteristics $\nu_1$(O-O) modes of the complexes appear at 820-844 $cm^{-1}$. It is observed that the $\nu_1$ mode decreases with the increase of atomic number of the metal in a particular group. In the present complexes the $\nu_3$ and $\nu_2$ modes appear at 650-6821 and 590-538 $cm^{-1}$, respectively.

**Magnetic moment and electronic spectra:** The observed values of effective magnetic moment ($\mu_{eff}$) at room temperature are given in Table 3 The magnetic moment values of dioxozirconium (VI) complexes are -0.299 to –0.519 BM indicated that these complexes were diamagnetic in nature suggesting no changes in the oxidation states of the metal ions upon complexation.

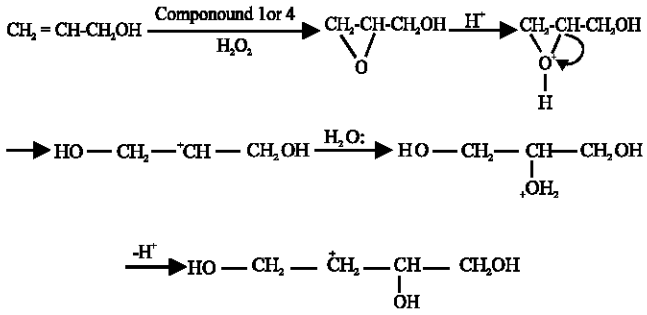
The electronic spectral data (Table 5) of the complexes 1-12 showed bands between 230-372 nm region due to the charge transfer band only.

**Reactivity:** The present peroxo complexes were found to liberate iodine within 1-2 min on treatment with aqueous potassium iodide. A stoichiometric mixture of compounds 1, 3, 5 and 12 with allyl alcohol did not show any reaction. However, compound 8 and 10 react stoichiometrically with allyl alcohol (Reaction A) producing glycidol as indicated by IR band at 1060 $cm^{-1}$ due to the C-O-C stretching mode. A possible reaction path is shown in Scheme 1.

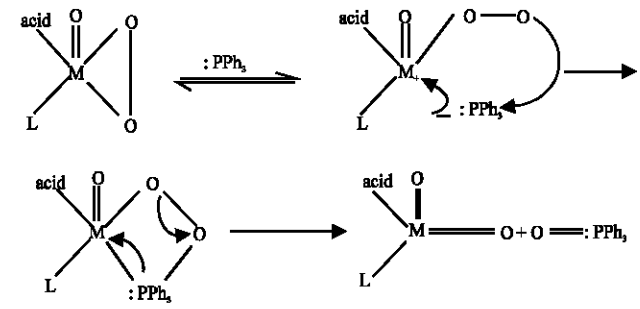
In reaction B, compound 8 or 10 was used to catalyze the oxidation of allyl alcohol by $H_2O_2$ and in this case the product isolated was glycerol. The IR spectrum of this product was identical with that of an authentic sample. A possible reaction path is shown in Scheme 2. The reaction C and D produced triphenylphosphine oxide and triphenylarsine oxide, respectively. The products display IR bands at 1190 and 880 $cm^{-1}$ due to ν(P = O) and ν(As = O) modes, respectively [339-341]. The IR spectra of the residue of reaction C and D showed the disappearance of $\nu_1$(O-O) bands which indicate the transfer of peroxo oxygen to the substrate. A possible reaction path is shown in Scheme 3.



Scheme 1



Scheme 2



M = Zr (IV)

Scheme 3

On the basis of spectroscopic interpretation and physical measurements the molecular structure of the compound (7) could be illustrated as shown in Fig. 1.

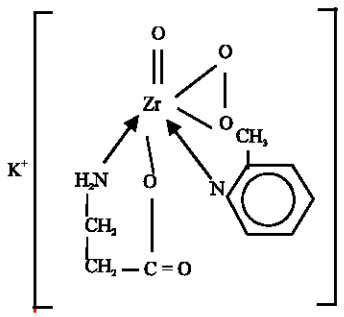


Fig. 1: Proposed structure of complex (7). K(ZrO ($O_2$) (ala) (2-pic))

**Antimicrobial activity studies:** Antimicrobial activities of the test samples are expressed by measuring the zone of inhibition observed around the area.

The results revealed that the complexes are more microbial toxic than the free metal ions or ligands. All he complexes under investigations showed more or less activities against the thirteen pathogenic bacteria tested. The Zr(IV) complexes did not show any remarkable antibacterial activity (Table 6-8). Results also illustrate

Table 6: Antibacterial activity of the complexes of Zr(IV) against *Shigella dysenteriae*, *Escherichia coli* and *Streptococcus-β-haemolyticus*

| | | Diameter of zone inhibition (mm) 600 μg/disc | | | |
|---|---|---|---|---|---|
| No. | Complexes | *S. dysenteriae* | *E. coli* | *S. bodyii* | *S.-β-haemolyticus* |
| 1 | $K(ZrO(O_2)(gly)(py))$ | - | - | - | - |
| 2 | $K(ZrO(O_2)(gly)(2\text{-}pic))$ | - | - | - | - |
| 3 | $K(ZrO(O_2)(gly)(4\text{-}pic))$ | - | - | - | - |
| 4 | $K(ZrO(O_2)(ala)(2\text{-}pic))$ | - | - | - | - |
| 5 | $K(ZrO(O_2)(ala)(4\text{-}pic))$ | - | - | - | - |
| 6 | $K(ZrO(O_2)(ala)(Q))$ | - | - | - | - |
| 7 | $K(ZrO(O_2)(pha)(py))$ | - | - | - | - |
| 8 | $K(ZrO(O_2)(leu)(py))$ | - | - | - | - |

Table 7: Antibacterial activity of the complexes of Zr(IV) against *Shigella sonnei*, *Pseudomonas aeruginosa*, *Shigella aurus* and *Bacillus subtilis*

| | | Diameter of zone inhibition (mm) 600 μg/disc | | | |
|---|---|---|---|---|---|
| No. | Complexes | *S. sonnei* | *P. auriginosa* | *S. aureus* | *B. subtilis* |
| 1 | $K(ZrO(O_2)(gly)(py))$ | - | - | - | - |
| 2 | $K(ZrO(O_2)(gly)(2\text{-}pic))$ | - | - | - | - |
| 3 | $K(ZrO(O_2)(gly)(4\text{-}pic))$ | - | - | - | - |
| 4 | $K(ZrO(O_2)(ala)(2\text{-}pic))$ | - | - | - | - |
| 5 | $K(ZrO(O_2)(ala)(4\text{-}pic))$ | - | - | - | - |
| 6 | $K(ZrO(O_2)(ala)(Q))$ | - | - | - | - |
| 7 | $K(ZrO(O_2)(pha)(py))$ | - | - | - | - |
| 8 | $K(ZrO(O_2)(leu)(py))$ | - | - | - | - |

Table 8: Antibacterial activity of the complexes of Zr(IV) against *Salmonella typhi*, *Shigella flexneri*, *Bacillus megaterium*, *Sarcina lutea*and *Shigella shiga*

| | | Diameter of zone inhibition (mm) 600 μg/disc | | | | |
|---|---|---|---|---|---|---|
| No. | Complexes | *S. typhi* | *S. flexneri* | *B. megatrium* | *S. lutea* | *S. shiga* |
| 1 | $K(ZrO(O_2)(gly)(py))$ | - | - | - | - | - |
| 2 | $K(ZrO(O_2)(gly)(2\text{-}pic))$ | - | - | - | - | - |
| 3 | $K(ZrO(O_2)(gly)(4\text{-}pic))$ | - | - | - | - | - |
| 4 | $K(ZrO(O_2)(ala)(2\text{-}pic))$ | - | - | - | - | - |
| 5 | $K(ZrO(O_2)(ala)(4\text{-}pic))$ | - | - | - | - | - |
| 6 | $K(ZrO(O_2)(ala)(Q))$ | - | - | - | - | - |
| 7 | $K(ZrO(O_2)(pha)(py))$ | - | - | - | - | - |
| 8 | $K(ZrO(O_2)(leu)(py))$ | - | - | - | - | - |

Table 9: Antifungal activity of the complexes of Zr(IV) against *Aspergillus niger*, *Aspergillus fumigatus*, *Aspergillus flarus*

| | | Diameter of zone inhibition (mm) 200 μg/disc | | |
|---|---|---|---|---|
| No. | Complexes | *A. niger* | *A. fumigatus* | *A. flarus* |
| 1 | $K(ZrO(O_2)(gly)(py))$ | - | - | - |
| 2 | $K(ZrO(O_2)(gly)(2\text{-}pic))$ | - | - | - |
| 3 | $K(ZrO(O_2)(gly)(4\text{-}pic))$ | - | - | - |
| 4 | $K(ZrO(O_2)(ala)(2\text{-}pic))$ | - | - | - |
| 5 | $K(ZrO(O_2)(ala)(4\text{-}pic))$ | - | - | - |
| 6 | $K(ZrO(O_2)(ala)(Q))$ | - | - | - |
| 7 | $K(ZrO(O_2)(pha)(py))$ | - | - | - |
| 8 | $K(ZrO(O_2)(leu)(py))$ | - | - | - |

Table 10: Brine shrimp lethality bioassay for Zr(IV) complexes

| | | Exposure 16 h | | Exposure 36 h | |
|---|---|---|---|---|---|
| Sample No. | Complexes | $LC_{50}$ μg $mL^{-1}$ | $LC_{99}$ μg $mL^{-1}$ | $LC_{50}$ μg $mL^{-1}$ | $LC_{99}$ μg $mL^{-1}$ |
| 1 | $K(ZrO(O_2)(gly)(py))$ | 909.28 | 30983.7 | 188.41 | 4522.51 |
| 2 | $K(ZrO(O_2)(gly)(2\text{-}pic))$ | 233.89 | 2068.0 | 284.86 | 6401.01 |
| 3 | $K(ZrO(O_2)(gly)(4\text{-}pic))$ | 340.91 | 19923.0 | 177.07 | 22481.8 |
| 4 | $K(ZrO(O_2)(ala)(2\text{-}pic))$ | 227.92 | 1253.1 | 218.65 | 5537.16 |
| 5 | $K(ZrO(O_2)(ala)(4\text{-}pic))$ | 666.50 | 39796.0 | 129.95 | 63995.3 |
| 6 | $K(ZrO(O_2)(ala)(Q))$ | 372.66 | 6950.7 | 118.74 | 15225.8 |
| 7 | $K(ZrO(O_2)(pha)(py))$ | 512.44 | 29687.6 | 84.37 | 2404.48 |
| 8 | $K(ZrO(O_2)(leu)(py))$ | 334.97 | 3098.1 | 181.39 | 2408.02 |

that the complexes of Zr (IV) were not able to inhibit the bacterial growth. It is also interesting to note that the complexes of Zr (IV) were found to be fully inactive against the three pathogenic fungi *A. niger*, *A. fumigatus* and *A. flarus* (Table 9).

**Result of brine shrimp lethality bioassay:** The mortality rate of brine shrimp nauplii was found to be increased with the increase of concentration for all the complexes. The complexes for the Zr (IV) caused up to 50% mortality in brine shrimp. On the other hand, the complex 4 for Zr

(IV) showed the more toxic effect to the brine shrimp (Table 10). Moreover, it could be concluded that all the complexes of metals showed toxic effect against the brine shrimp.

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## REFERENCES

Biagioli, M., L. Strinna-Erre, G. Micera, A. Panzanelli and A. Zema, 2000. Molecular structure, characterization and reactivity of dioxo complexes formed by vanadium (V) with α-hydroxycarboxylate ligands. Inorganica Chimica Acta, 310: 1.

Deubel, D.V., J. Sundermeyer and G. Frenking, 2001. Olefin epoxidation with transition metal $\eta^2$-peroxo complexes: The control of reactivity. Eur. J. Inorg. Chem., 7: 1819.

Hassan, M., Z.H. Chohan and C.T. Supuran, 2003. Antibacterial Co (II) and Ni (II) complexes of benzothiazole-derived schiff bases. Syn. React. Inorg. Met. Org. Chem., 32: 29.

Holmes, R.J., M.J. McKeage, V. Murray, W.A. Denny and W.D. McFadyen, 2001. cis-Dichloroplatinum (II) complexes tethered to 9-aminoacridine-4-carboxamides: Synthesis and action in resistant cell lines *in vitro*. J. Inorg. Biochem., 85: 209.

Horner, O., C. Jeandey, J. Oddou, P. Bonville and J.A. Latour, 2002a. Mössbauer study of (Fe (edta) ($O_2$)) 3-agrees with a high-spin FeIII peroxo complex. Eur. J. Inorg. Chem., 5: 1186.

Horner, O., C. Jeandey, J. Oddou and P. Bonville, 2002b. Hydrogenperoxo-((bztpen) Fe (OOH))2+and its deprotonation product peroxo-((bztpen) Fe ($O_2$))+, studied by EPR and mössbauer spectroscopy - implications for the electronic structures of peroxo model complexes. Eur. J. Inorg. Chem., 12: 3278.

John, J., E. Xin Ma, K.I. Han, J.N. Gitua and C. Krüger, 2001. Mechanistic Comparison of the Nickel (0)-Catalyzed Homo-Oligomerization and Co-Oligomerization of Alkynes and Nitriles. Eur. J. Inorg. Chem., 1: 77.

Mastrolorenzo, A. and C.T. Supuran, 2000. Antifungal activity of Ag (I) and Zn (II) complexes of sulfacetamide derivatives. Metal-Based Drugs, 7: 49.

Mukharjee, G.N., S.K. Chattopadhyay and S. Sarkar, 1994. Metal complexes of some model peptide derivatives. Part-XI. Mixed Ligand complex formation of copper (II) with salicyloyl-glaycine and typical ligand. J. Indian Chem. Soc., 71: 45.

Natile, G. and M. Coluccia, 2001. Current status of trans-platinum compounds in cancer therapy. Coord. Chem. Rev., 216: 383.

Paulsen, I.T.J., H. Park, P.S. Choi and M.H.J. Saier, 1997. A family of Gram-negative bacterial outer membrane factors that function in the export of proteins, carbohydrates, drugs and heavy metals form Gram-negative bacteria. FEMS Micr. Lett., 156: 1.

Rodriguez, M.L., L.C. Dela Cruz Rodriguez, R.N. Farias and E.M. Massa, 1993. Membrane-associated redox cycling of copper mediates hydroperoxide toxicity in *Escherichia coli*. Biochim. Biophys. Acta, 1144: 77.

Smicka, A., V. Buchta and K. Handlir, 2000. Synthesis, characterization and *in vitro* antifungal effect of some Butyltin(IV) N-Substituted 2-Aminoethanethiolates. Metal-Based Drugs, 7: 165.

Winterhalter, U., L. Zsolnai, P. Kircher, K. Heinze and G. Huttner, 2001. Reductive activation of tripod cobalt compounds: Oxidative Addition of H-H, P-Hand Sn-H Functions. Eur. J. Inorg. Chem., 1: 89.

Yudanov, I.V., P. Gisdakis, C.D. Valentin and N. Rösch, 1999. Activity of peroxo and hydroperoxo complexes of TiIV in olefin epoxidation: A density functional model study of energetics and mechanism. Eur. J. Inorg. Chem., 12: 2135.