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REVIEW

Platinum Group Metals Bonded Thiolato Sulfur Oxygenation: Photoactivity and Bioactivity

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Platinum group metals mediated thiolato compounds are highly susceptible for S-centered reactivity owing to high nucleophilicity and which is enormously significant in the point of its bioactivity and photoactivity. A series of oxygenation reactions of thiolate sulfur attached with platinum metals occurred with molecular O_2 in varying conditions. A variety of sulfenates and sulfinates are produced depending on nature of starting substrate thiolato and the oxygenations are facile under harshly oxygen environment. There are numerous mechanistic paths for the oxygenation of platinum metals bonded thiolate S-center unlike the oxygenation reaction of organic sulphides. It is assumed that S-oxygenation occurs *via* the intramolecular and intermolecular dioxygen addition pathways. A number of mysterious photo-induced sulphur oxygenation and self-sensitization reactions of metal-thiolato to analogous oxygenate are also mentioned. These compounds show enzymatic catalytic activity and remarkable bioactivity also interaction with the biomolecules like DNA, which opens a new area for the researchers for designing novel heavier metals-sulfur-oxygenates compounds as metallodrugs.

Keywords: Oxygenates, Self sensitization, Sulfinate, Photooxidation, Metallodrugs, Dioxirane.

INTRODUCTION

The metallo-thiolate ligands are vulnerable to sulfur-centered reactivity and such compounds have been extensively studied. It has been discovered that sulfur-oxygenation is mechanistically more complex and significantly different than organic sulphides [1-3] and is discussed in brief in this review. The superior nucleophilicity [4-10] of the metal-bound sulfur atom is the most incredible properties, which leads to a variety of derivatives modified at thiolato sulfur center. This sulfur-based reactivity is well documented for first row 3*d* transition-metal thiolates producing sulfur oxygenates, with initial efforts focused mostly on Fe^{III}, Co^{III} and Ni^{II} [11-13]. Beside alkylation, allylation and metalation reactions of transition metal thiolates, they are widely known for the S-oxygenation processes [14,15]. The bonding nature of transition metal thiolates basically the *p*-back-donation from M^{n+}-t_2 to 3*p*-orbital of thiolate sulfur *vis-a-vis* drifting of larger electron density to the coordinated thiolato sulfur in [R/Ar–S–M] plays key role for the escalation of S-centered reactivity as a nucleophile compared to thiols [R/Ar–S–H] [16]. This nucleophilic sulfur centers are the potential target for the external electrophiles for instance molecular oxygen in these oxygenation processes.

Heavier transition-metal sulfur complexes have rich redox chemistry, due to involvement of their reactive sulfur center resulted in ligand-based oxidation and the second contributing part is metals having variable oxidation states and this redox activity of sulfur functionalized metallo-ligand generally simulates many biological processes [17-21]. In this stand point, different metallo-sulfur oxygenates having bioactivity including various enzymatic action were transformed from several metal bound thiolato complexes [22-24]. Mainly first row transition metals bound sulfur moiety are more effective for developing active sites for oxygenation of some definite sulfur-rich metalloenzymes [25,26], for example deactivation of metallocysteinate enzymes and to the oxidative metabolism of cysteine [27]. The bioactivity is repressed and irreversibly disabled by the reaction of a sequence of metal-thiolates with molecular O_2 of some sulfur populated enzymes [NiFe] hydrogenase and CO-dehydrogenase [28,29].

In modern biology, the post-translational oxygenation of the protein having cysteine-derived sulfur donors with a

permutation of thiolate (RS^-), sulfenate (RSO^-) and sulfinate (RSO_2^-) in the active site of NHase to iron(III) was reported in cellular regulatory processes [30-33]. Design and synthesis of numerous model complexes by which bio-mimicking the active site of such types of valuable enzymes bound oxygenates of sulfur ligands was achieved [34-36]. Interestingly, a large number of chelates including cyclometalated complex having hetero atoms (N, S, P) containing conjugated ligand of noble metals and their numerous derivatives have emerged into an significant category of luminescent molecules, which are applied in the OLED, photovoltaics, sensitized molecules, photocatalysis or phosphorescent bioimaging [37-46]. Notably cyclometalated complexes having noble metals are the originator of singlet oxygen ($^1\Delta_g$) [47]. Singlet oxygen is the important and lowest excited state of molecular oxygen can be developed thermally and photochemically [48,49] and it is involved in array of biological and biomedical processes also extensively applied for oxygenation of different molecules [50,51]. Complexes with ligands having dithiolate and containing hetero atoms especially nitrogen functionality exhibit strong luminescence due to donation from dithiolate to nitrogen ligand systems generating a charge-transfer complex where attached metals play an important role [52,53].

In recent time, a range of metals mediated sulfur oxygenates like sulfenate, sulfinate and sulfonates have been synthesized predominantly by chemical methods from the corresponding thiolates and also some photochemical and/or electrochemically oxidation processes have been reported [54,55]. It is found that metal-thiolato ligands oxidize to corresponding sulfenato and/or sulfinato by the oxygen from air or purging through the solution containing metal-thiolato from external source in presence of light of particular wave length or some sensitizer. From this survey, it is revealed that both the triplet [$^3\Sigma O_2$] and singlet [$^1\Delta O_2$] state of molecular oxygen can effectively oxidize metal-thiolato to different sulfur oxygenated compounds with changeable circumstances (**Scheme-I**) [53,56]. Still, there are some peroxo and activated oxygen donating sources (H_2O_2, dimethyldioxirane, *etc*.) [57-59], can successfully oxygenated the thiolato sulfur center. However, analogous scrutiny of S-centered oxidation of thiolates with platinum group metals (ruthenium, rhodium, palladium, platinum) and noble metal gold are less common [60-62] and only a few reports for osmium [63] and iridium [64] have so far been made. Among platinum group metals a good number of such types of oxygenate can be observed for ruthenium metal in the literature. It is worth of mentioning that such type of heavier noble metal thiolato is also prone to alike oxidation producing metallosulfones under aerobic condition and strictly O_2 atmosphere is not essential.

In this present review, we will limit our discussion in the heavier platinum metal mediated organosulfur compounds and their S-oxygenates reported to date and tries to concentrate on the synthesis of this group of compounds also paying attention to the underlying mechanism as well as their other process of oxygenation as photooxygenation and sensitization methods.

Oxygenated compounds of thiolate-sulfur: The platinum metal bound thiolates are the potential compounds in this study, being highly nucleophilic they developed a new class of oxygen derivatives. Metal-sulfenate; [M-S(=O)] and metal-sulfinate; [M-S(=O)$_2$] are the two major class of oxygenates of metal-thiolates {M-SR} can be converted by oxygenation of sulfur center (Fig. 1). Sometimes metal-sulfonate [M-SO_3^-] is obtained as one of the oxygenated product during sulfur center oxygenation from thiolate compounds [65]. The metal-sulfenato and metal-sulfinato are formed from metal-thiolates by the addition of molecular oxygen in two and four electron oxidation processes, respectively [66]. Comparably metal-sulfenates are less stable than the analogous metal-sulfinates and would disproportionate to metal-thiolate and metal-sulfinates, thus only a few examples of stable transition metal sulfenates [M-(S(=O)R)] are known [67].

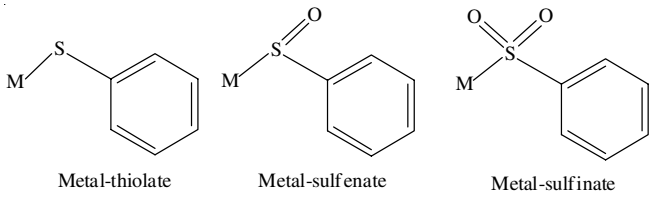
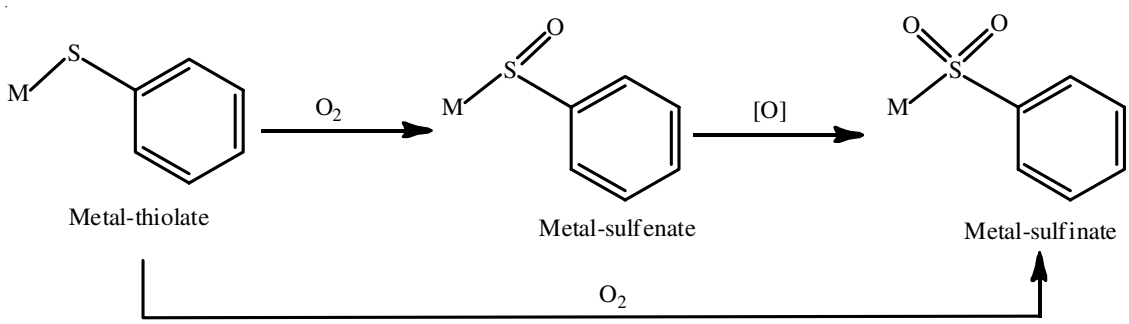


Fig. 1. Metal aryl sulfur motif: metal thiolato, metal-sulfenate and metal-sulfinate

The divalent sulfur of metal-thiolate compounds is oxidized to tetravalent or hexavalent sulfur *via* oxidative addition in presence of molecular oxygen in the oxidation processes. Since molecular O_2 is readily available almost non-toxic and eco-friendly natural species, it is used in a variety of important organic transformations to produce a variety of essential starting materials; which are very reasonable and value added species for industries and modern research. Both the spin state $^3\Sigma O_2$ and/or $^1\Delta O_2$ of molecular oxygen is supposed to oxidize metal-thiolato to sulfenate mostly {(R/Ar)S=O} or sulfinate {(R/Ar)-



Scheme-I: Path of metal-aryl thiolato S-oxygenation

$S(=O)_2$} (**Scheme-I**) [53,56], although $^3\Sigma O_2$ reacts more slowly than $^1\Delta O_2$.

Mechanistic interpretation of thiolato sulfur oxygenation: In-depth research has been conducted into thiolate-S oxygenation and its underlying mechanism has been elucidated. It is significant that the initial drifting of non-bonding electron density to dioxygen from thiolato-S occurs during the way of oxygenation. The noble metal thiolato including few soft heavier metals like Ru, Pd and Pt having one or multi S-centers are known to form a range of sulfur oxygenates by sequential oxygenation with singlet oxygen ($^1\Delta O_2$) having appreciable yield [68,69]. The meticulous study explored that a mechanism shown in **Scheme-II** invoke a persulfoxidic species, after the primary addition of dioxygen with metal holding thiolato-S as has been presented in the reaction of $^1\Delta O_2$ with R_2S [70,71], as the common and active originator of both the mono and bis sulfinato products. However, such transformation to sulfinate also passing through the second active intermediate, which was formed rearranging the oxygen atoms of persulfoxide such a way to generate a three membered cycle, termed as thiadioxirane [53,72,73]. Single-site collapse would yield the less stable metal-sulfenate and en route to the stable metal-sulfinate from thiadioxirane either by cleavage of O–O bond and followed by reorganization of oxygen atom through intermolecular pathway. It may also follow the intramolecular orientation of oxygen atom to the sulfinate species after the said reactive intermediate perverted.

The persulfoxide and thiadioxirane are the two important and effective intermediates in the route of sulfenato and sulfinato synthesis, first confirmed by Jensen [74] from their computational studies. Platinum metals sulfones/sulfoxides can be synthesized applying both triplet ($^3\Sigma O_2$) and singlet spin state ($^1\Delta O_2$) of oxygen molecules on specific thiolate compounds which is mentioned earlier, the rate of formation with $^1\Delta O_2$ is 10 times higher than the triplet state [69,75]. The reported $^3\Sigma O_2 \rightarrow {}^1\Delta O_2$ excitation barrier is small only 22.4 kJ/mol and can easily be achieved and compensated by various activation parameters since it follow diffusion controlled rates (Fig. 2) [75]. Although in both the cases the nature of metal-ligand (sulfones) bonding and involvement of different metal electron rich *d*-orbitals are the determining factors to propose a suitable mechanism of this sulfur oxygenation. As for example the heavier transition metals including platinum metals possessing

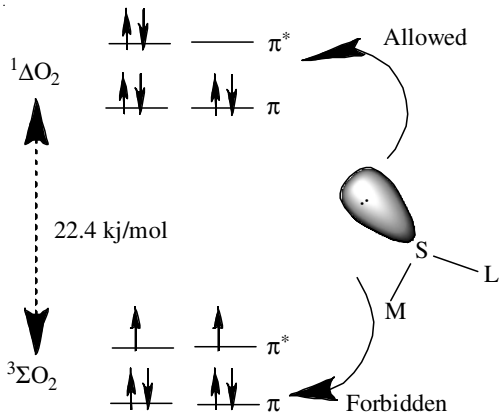
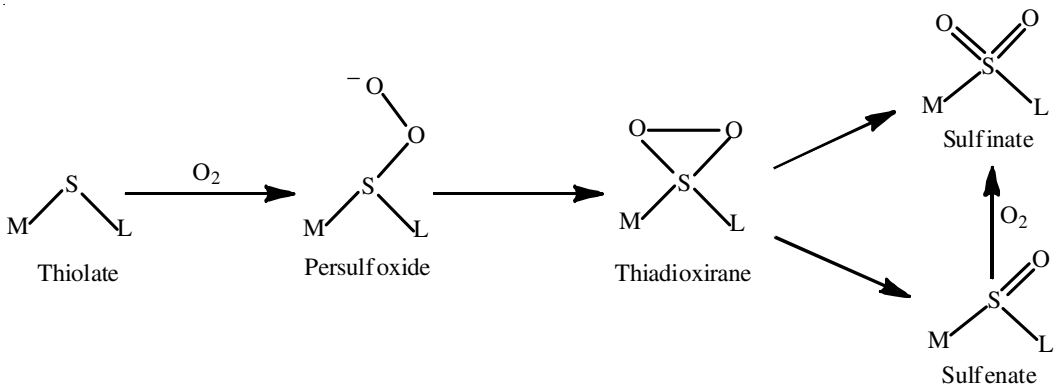


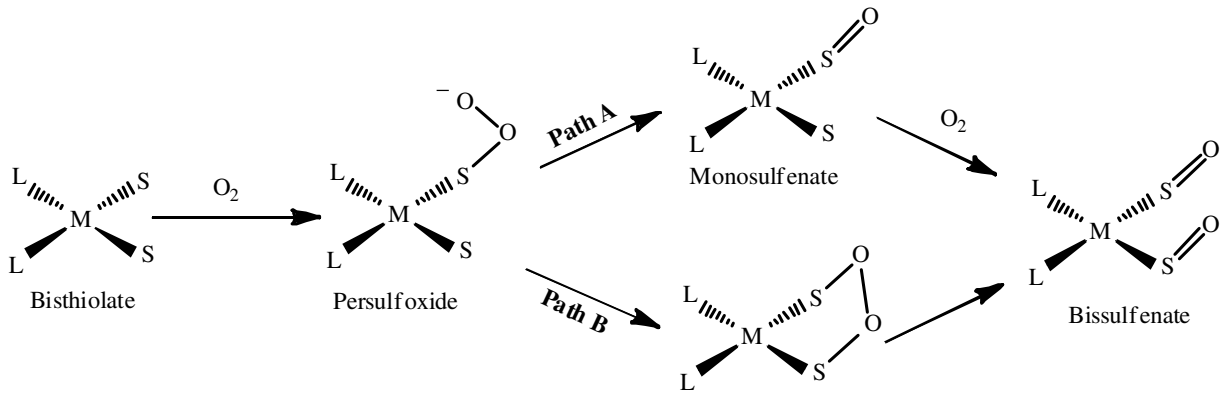
Fig. 2. Interaction of $^3\Sigma O_2$ and $^1\Delta O_2$ with metal-thiolato by spin-forbidden and spin-allowed transformation to metal S-oxygenates

dilated *d*-orbitals due to relativistic effects [76] opperate as a superior contender for back-donation $M(t_2) \rightarrow SO_2(\pi^*)$ as compared to 2nd row (4d) or 1st row (3d) transition metals.

Interestingly, a variety of S-oxygenated products can be obtained in the path of oxygenation reactions with two or more metals bound thiolate functionalities. Besides the six coordinated octahedral compounds, there are a good number of reports of sulfur center oxygenations where four coordinated thiolate compounds having adjacent sulfur site occupied in *cis*-position especially for d^8 metals possessing generally square planar geometry are found in the literature [63,77]. This type of structural arrangement having adjacent sulfur site with respect to metal, facilitate the S-centered oxygenation. It is the dioxygen (O_2) rather single atomic oxygen insertion across the single or neighbouring sulfur of metal-bisthiolato complexes stepwise manner, followed by O–O bond scissions both intramolecular and intermolecular pathway. As a result metal mono-sulfenates and finally metal-bissulfenate complexes were generated following Path A, or *via* a five membered ring $M(SR)_2O_2$, following intramolecular O–O bond cleavage (Path B); which is shown in **Scheme-III**, where it is supposed that in both route passing through a common metal-persulfoxidic intermediate. This is important to observe that the metal linked electron rich monosulfenate and *bis*-sulfenates moieties are comparably less stable and become an appealing intermediate mainly for peroxide species or molecular oxygen attack and ultimately converted to corresponding sulfinate compounds.



Scheme-II: Probable mechanistic path of metal-thiolato S-oxygenation and the intermediates generated



Scheme-III: Plausible mechanistic paths from *cis*-metal-dithiolate to *cis*-metal-bissulfenate *via* persulfoxidic intermediate

Monosulfinate is the primarily product produced from thiadioxyrane, in the route of metal-bissulfinate transformations, for a particular monosulfur center (Path D) which rearranges to furnish bissulfinato product utilising overall two equivalents O_2. Whereas metal-bissulfenate furnished from passing through a five membered cyclic structure $M(SR)_2O_2$, which rearrange to metal-bissulfinate, where SO_2 fragments is generated from identical O_2 molecules (Path C) as shown in **Scheme-IV** and all these intermediates and products can be recognized from the isotopic labelling studies [78]. The possible oxygenated products of the metal bound thiolate and the mechanistic pathway summarized as follows:

(a) Monosulfenate formation at the metal bound thiolate center or at one of the sulfur sites only of a dithiolate, may proceed by both intermolecular and intramolecular oxygen atom transfer *via* a peroxidic/persulfoxide intermediate.

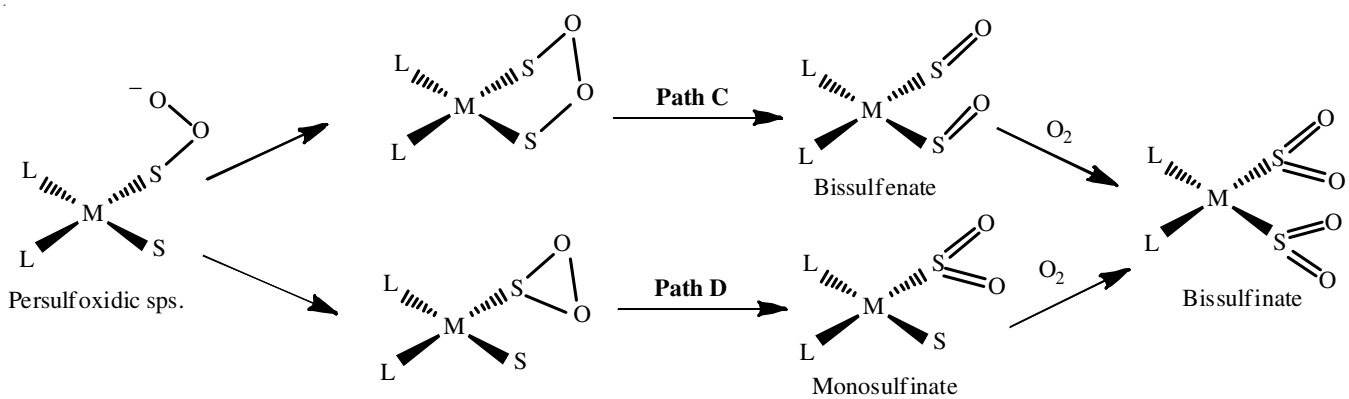
(b) The second sulfenate formation in a dithiolate system generally proceed *via* intramolecular oxygen atom transfer or sequential generation of sulfenate one by one S atoms through persulfoxide and thiadioxirane intermediates.

(c) Whereas formation of mono and/or bissulfinate, there must occur generally intramolecular path *via* collapse of a peroxidic/persulfoxide intermediate or by persulfooxide attack on a sulfenate moiety or secondary photooxidation may be the third preference.

(d) Finally, the mixed sulfenate and sulfinate production in the way of thiolate sulfur oxygenation.

Metal-thiolato oxygenation and characterization: The oxygenation of thiolato S-center mediated by metals and their underlying chemistry are mainly explored for the Ni group having square planar site; due to their potential interaction with the biomolecules together with enzymatic functions. This type of oxygenation were involved in both mono and bisthiolate compounds generating mono-sulfenates [M(RS)(RSO)], disulfenates [M–$(RSO)_2$], mono-sulfinates [M–(RS)(RSO_2)], disulfinates [M–$(RSO_2)_2$] and mixed sulfenate–sulfinate [M–(RSO)(RSO_2)] products [78]. The attention has been intensified in this current study, on the heavier and noble platinum group metals, to investigate its variation of structural features, bioactivities in addition to the optoelectronic properties while these metal-bound thiolate sulfur motif get oxygenated. Remarkably, S-oxygenation of Ru metal is the most studied sulfur-oxygenation chemistry of heavier transition metal after the Ni-group. It is interesting to declare that the syntheses of different S-oxygenates from the analogous thiolates involved mostly in normal aerobic condition under reflux and/or stirring, the majority cases no externally O_2 purging is essential.

Characterization and identification of these oxygenates done by different spectroscopic methods. Redox nature were analyzed by cyclovoltammetric study (CV) and information regarding structural detailing and the mass of the molecular or ionic fragments revealed from XRD and mass spectroscopy. Infrared spectra is most informative for the identification of S-oxygenated complexes for MS(=O) and $MS(=O)_2$ fragments



Scheme-IV: Plausible mechanistic paths from persulfoxidic species to *cis*-metal-bissulfinate *via* monosulfinate or bissulfenate

since it exhibit sharp and strong vibrations in the range 1200-900 cm^{-1} [25,78,79].

The conversion of ruthenium(II) mediated bisthiolato (**1**) ($[Ru^{II}(DPPBT)_3]^-$ where DPPBT = 2-diphenylphosphinobenzene thiolato) to ruthenium(II) bissulfinate (**2**) under stirring condition (Fig. 3) by Grapperhaus *et al.* [54]. Here, metal center oxidation from Ru^{II}-thiolato (**1**) to Ru^{III}-thiolato (**1a**) and followed by the ligand-centered oxygenation generating Ru^{III}-sulfinate (**2a**) under dioxygen environment subsequently *in situ* leisurely reduction of **2a** to Ru^{II}-sulfinate (**2**) yielded without any reducing agent. The metal ion get stabilized due to enhanced interaction of oxygen-metal atoms upon thiolate S-oxygenation, since the donor property of metallo-S group decreases on S-oxygenation [78].

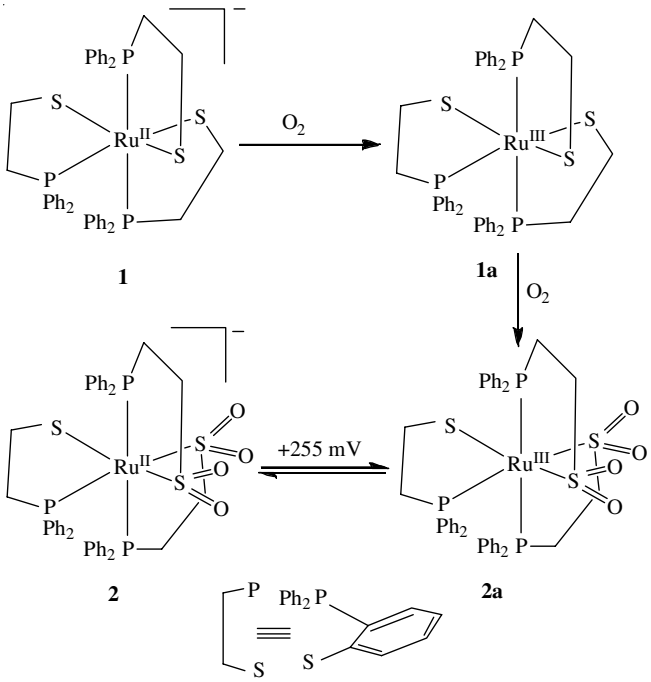


Fig. 3. Stepwise Ru-centered chemical oxidation and ligand–S-centered oxygenation of ruthenium(III) thiolato compound

In another study, Lever *et al.* [80] reported the synthesis of less common monosulfinates (**3**) L(S·SO_2) of Ru(II) and the spontaneously interconversion to Ru^{II}-disulfinates (**4**) L(SO_2·SO_2) in solution under aerobic condition (Fig. 4). Irradiation with white light [81] or applied hydrogen peroxide as external oxidant, that initiated and speed up the S-oxygenation reaction. They were able to synthesize Ru^{II}-$(bpy)_2$dithiolato L(S·S) [L = 1,2-benzenedithiolate)] starting from *cis*-Ru$(bpy)_2Cl_2$ and benzene-1,2-dithiol in inert argon medium, but were abortive to purify or isolate the compound, since it was prone to oxidation in the uncommon Ru^{II}-monosulfinates L(S·SO_2) in presence of air [81]. Although, any mono or bis sulfenate products were not reported. In infrared spectra, the newly appeared strong vibrations of S=O symmetric stretch at 989 cm^{-1} (calcd. 983 cm^{-1}); antisymmetric S=O stretch at 1119 cm^{-1} (calcd. 1105 cm^{-1}), which are in the expected ranges [82,83]. An exclusive "family" of S-oxygenated complexes synthesized by the restricted oxygenation of Ru^{II}-$L_{dithiolato}$ (**5**) [25] [L = bmmp-TASN] with distinct time frames by limited dioxygen amount and the products, which varies on the extent of oxygenation of thiolato sulfur (Fig. 5). It is important to observe that starting from Ru^{II}-dithiolato (**5**), they succeeded to synthesize monosulfinate [(bmmp-O_2-TASN)-Ru(PPh_3)] (**6**) [~ 5 min], oxygenates having both sulfenate/sulfinate functionality [(bmmp-O_3-TASN)Ru-(PPh_3)] (**7**) [14] (~ 15 min to 12 h) with *bis*-sulfinate [(bmmp-O_4-TASN)Ru(PPh_3)] (**8**) (~ 120 h) and also the oxygenated products can be interchanged to one another with changing reaction environment [14,25]. The partial oxygenated Ru-$S_{sulfinato}$ (**6**) [S·SO_2] from Ru^{II}-dithiolato (**5**) owing to rapid oxygenation was observed with increasing covalent nature of sulfur-metal group which is attributable to the interactions of π-π* orbitals among t_{2g}-rich metal ions and the thiolate sulfur atoms, which boost up the oxygenation processes [84].

Steric interactions of bulky coligands (PPh_3) around the active site made the further oxygenation more slower rate of thiolate compound (**6**) to metal-sulfenate and sulfinate (**7**) [SO·SO_2] and metal-bissulfinate (**8**) [SO_2·SO_2] than the previous steps [14]. The IR stretching bands of sulfinate in the expected range are confirmed the O=S stretches of both symmetric and asymmetric nature for sulfinate functionality. Again Ru–$S_{sulfinato}$ bond length in partially oxygenated compounds **6** and **7** were reported as 2.2473(6) and 2.2548(9) Å respectively, which are reduced than the corresponding Ru–$S_{thiolato}$ (**5**) distance 2.3754(10) Å, found from X-ray crystallographic data.

An uncommon observation of monomeric Ru^{II}-sulfinato $[(bpy)_2Ru(aesi\text{-}N,S)]^+$ (aesi = *o*-aminoethanesulfinate) (**10**) from a dimeric chelate of Ru^{II}thiolato (**9**), $[Ag\{(bpy)_2Ru(aet)\}_2]^{3+}$ (aet = 2-aminoethanthiolate) in air, after eradicated Ag^+ from $Ru^{II}Ag^{I}Ru^{II}$ linear trinuclear fragment reported by Konno *et al.* [79] (Fig. 6). They also synthesized similar type of optically active isomeric Δ and Λ-monomeric Ru^{II}-sulfinate compounds $[(bpy)_2Ru(D\text{-}Hpsi\text{-}O,S)]PF_6$ from their corresponding isomeric ΔΔ (**11a**) and ΛΛ (**11b**)-dimeric Ru-thiolate-bridged attached with Ag^+, containing a $Ru^{II}Ag^{I}Ru^{II}$ trinuclear motif.

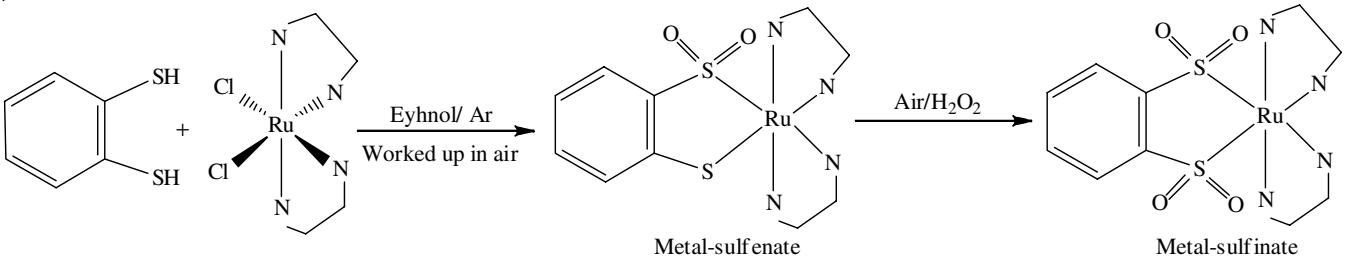


Fig. 4. Formation of Ru-bissulfinates (**4**) through Ru-monosulfenates (**3**)

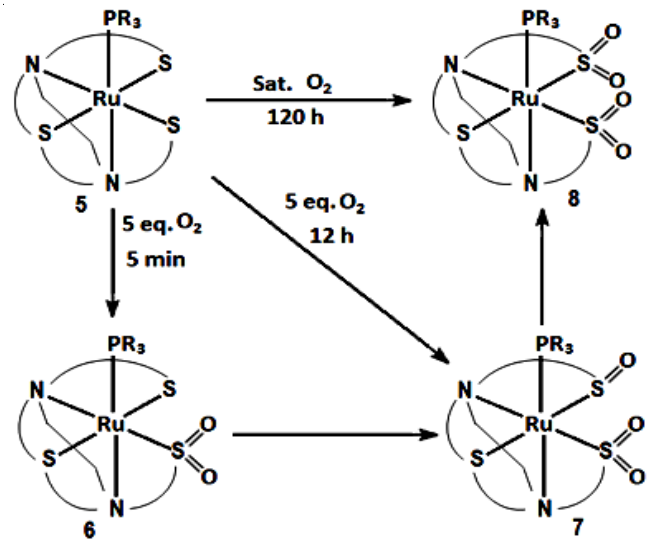


Fig. 5. Conversion of Ru-thiolate (**5**) to Ru-monosulfinates (**6**), Ru-bissulfinates (**8**) and Ru-sulfenate-sulfinates (**7**)

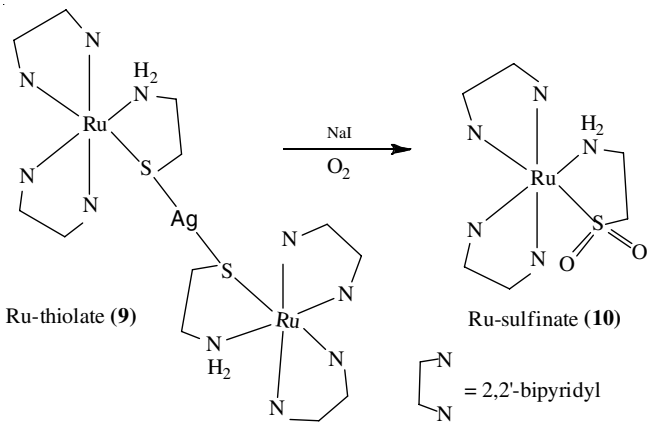


Fig. 6. Formation of Ru-sulfinates (**10**) formation from Ru-thiolates [S and Ag bridged] (**9**) by the removal of Ag^+ ion

A cyclometalated Rh-sulfinate (**12**) (Fig. 7) was obtained as byproduct during the course of synthesis of analogous Rh-thiolate from benzaldehyde thiosemicarbazones ligand and Wilkinson catalyst under aerobic condition [60]. A series of such Rh-sulfinates also reported by varying the substituent [R-Ar, where R = H, Me, OMe, Cl, NO_2] in the aromatic ring. The rhodium coordinated hydride ligand influences sulphur oxidation by increasing the electron density on thiolate group, thereby making it susceptible to oxygenation by dioxygen.

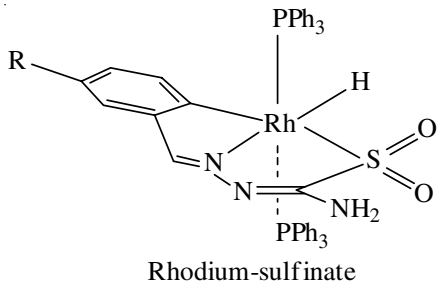


Fig. 7. Cyclometalated Rh-sulfinate (**12**) [R-Ar, where R = H, Me, OMe, Cl, NO_2]

The first case of Ir mediated organosulfinate (**14**) synthesized from its corresponding organothiolato compound (**13**) in regular aerobic circumstances under boiling was reported by Das *et al.* [64] which is shown in Fig. 8. Unfortunately, no monooxygenated Ir-sulfenate products was obtained and confirmed by the FTIR and DFT study. Although the same organosulfur oxygenates with rhodium were not produced under same condition, it is due to the superior metal to ligand back donation and hence stabilization of the soft dilated iridium orbitals compare to analogous rhodium organosulfur compounds. Due to the importance of PPh_3 in oxidative transformations, such reactions were carried out in an excess PPh_3 environment.

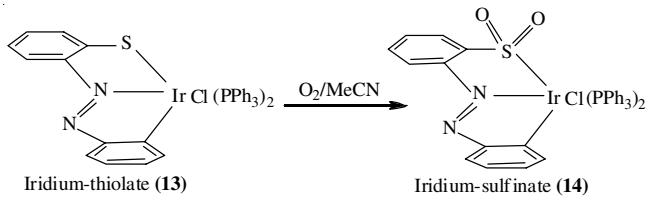


Fig. 8. Ir mediated organosulfinate (**14**) synthesis from analogous organothiolato compound

Moreover, it has been recognized that the similar type of oxidation reactions observed for another toxic heavier metal Os-sulfur compound, in which Os-sulfinate $[Os(aesi)(bpy)_2]^+$ (**16**) (aesi = 2-aminoethanesulfinate), can be obtained in normal aerobic condition, as compared to ruthenium analogue as mentioned by Tamura *et al.* [63]. Interestingly in air, the D_2O solution of amine sulfinate compound slowly transformed into corresponding imine sulfinate, of bis(bipyridine)osmium(II) (**17**) in the exposure of ambient light, with retention of the coordination environment about an Os^{II} center (Fig. 9). Again similar type of oxidized product also generated under the

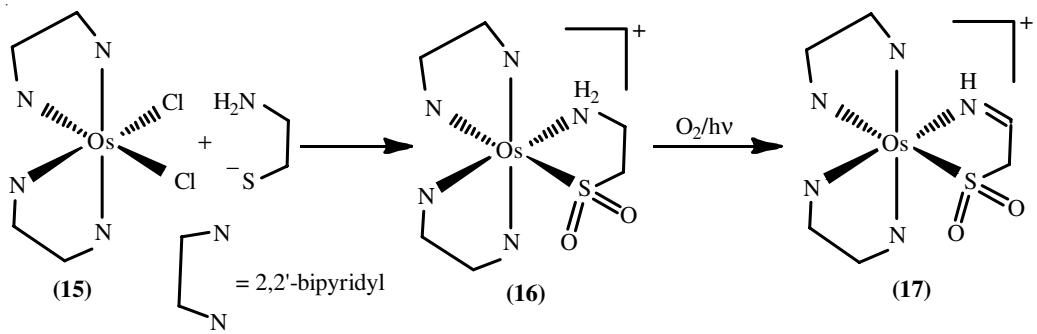


Fig. 9. Formation of Os-sulfinate $[Os(aesi)(bpy)_2]^+$ (**16**) and corresponding imine sulfinate (**17**)

irradiation of D_2O solution of **16**, with a high pressure Hg lamp in air for 1.5 days, maintaining the temperature at 0 ºC and also **16** was readily converted to **17** applying Ag^+. All these spectral signals for new products **17** were remain absent when all these transformation preformed in dark, which strongly implies that that photosensitive nature of **16**. It should be noted that similar photoinduced transformations are not found for its ruthenium counterparts.

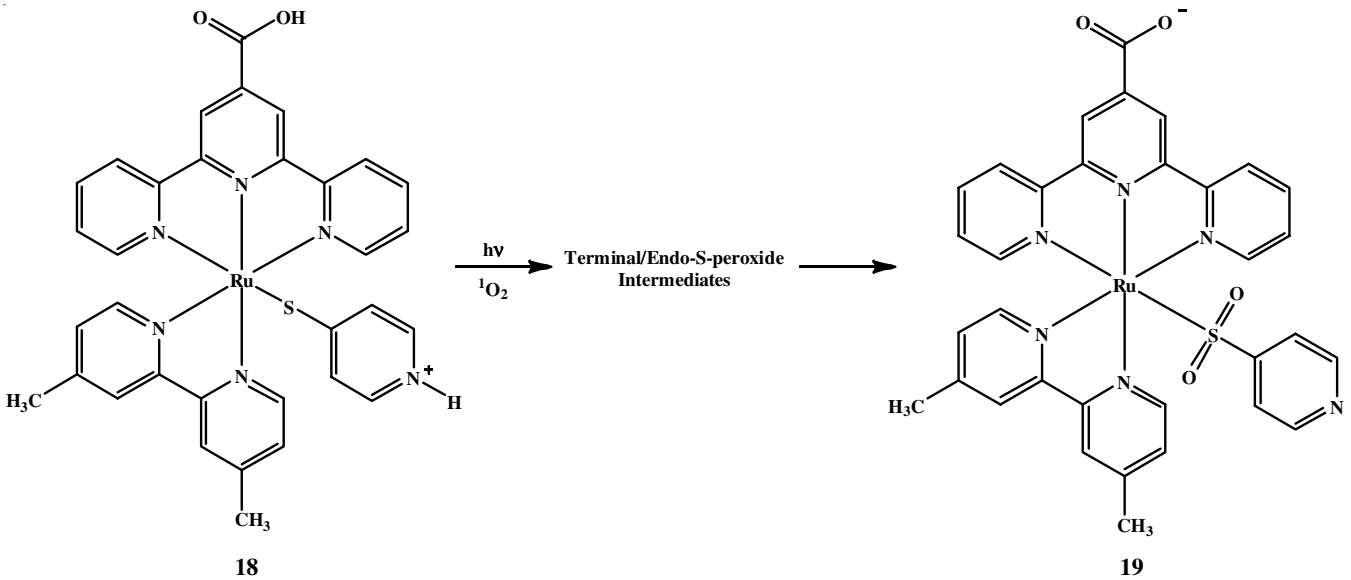
There is a limitation of photoinduced S-center oxygenations of metal-thiolato to the sulfonated molecule [54]. Sulfur compounds like thioanisoles, thiophene and many other diverse non-aromatic organosulfur compounds where the photooxidation reactions were achieved [61,85] applying $^1\Delta O_2$ mediated by H_2O_2 [86] or by irradiation of solution of organosulfur compounds saturated by air in occurrence of a sensitizer [87].

A photooxidation of $[Ru(Hmctpy)(dmbpy)(\kappa SSpyH)]^{2+}$ (**18**) (Hmctpy = carboxy-substituted terpyridine, dmbpy = methyl-substituted bipyridine), a thiolate sulfur, to the corresponding partial S-oxygenated compound, $[Ru(mctpy)(dmbpy)(\kappa S\text{-}SO_2py)]$ (**19**) involving $^1\Delta O_2$ under exposure of UV-vis light in acetonitrile [88]. Again, the ligand system contained ruthenium metal since Ru-compounds are extremely photosensitive and exhibit a variety of absorptive and emissive properties. An extremely satisfying mechanism was proposed of this self-sensitized photooxidation process of thiolate compound **18** to sulfinate product **19**, *via terminal/endo* S-peoxideic intermediates, as shown in Fig. 9 [53,89].

It is important to point out that the photooxidation of ruthenium-sulfides by singlet oxygen ($^1\Delta O_2$) to corresponding sulfinate rather than sulfenate (Fig. 10) and is highly solvent dependent. The transformations were facilitated in aprotic solvents like acetonitrile and DMF [88]. However, in presence of water or alcohols (protic solvents), hydrogen-bonding interactions with the intermediate predominate, and so this kind of S-oxygenation is hindered. Again, the small life time of singlet oxygen ($^1\Delta O_2$) in presence of protic solvent is another fact [90].

Monsour *et al.* [55] extensively reviewed the Type-II photooxidation of metal thiolates of a range of transition metals and mainly focused on the platinum group metals. Also they had compared these types of photooxidation reactions along the mechanistic approaches of metal thiolates with the organic sulphides. The process of sensitization of singlet oxygen including possibility of self-sensitized photooxidation reactions of thiolato ligands were also reported. According to their survey photooxidation of Pt-thiolate compounds having mono or 1,2-dithiolate S center(s) sometimes called dithiolene, can be classified in three groups *viz.* (i) arylthiolato compounds generated sulfinate as exclusive product, (ii) a mixture of sulfenate and sulfinate products were obtained from mainly alkylthiolates and (iii) self-sensitized reactions, where H_2O_2 removed as associated product in slightly higher pH and a very agreeable mechanism of formation of H_2O_2 also proposed. Sensitized photooxidation reactions of Pt^{II}-sulfur compounds as mentioned above are comprehensively studied by Selke *et al.* [53]. Palladium dithiolates show almost akin S-centered reactivity with singlet oxygen generating similar type of oxygenated products [69,71,78]. The oxygenated products obtained in such types of photooxidation reaction are shown in Fig. 11.

Platinum(II) centers are subsequently very important that a large amount of organometallic photosensitizers attaching thiolate ligands are mostly Pt(II) complexes. Generally, dithiolate moiety and a diimine ligand are the two main potential motif of target ligand to behave as sensitizers. It is mostly the ligand→ligand charge transfer (LLCT) arises from metal/dithiolene group to the diimmine moiety of the ligand upon irradiation, which was termed as "mixed-metal-ligand-to-ligand" transition by Eisenberg *et al.* [91] because the contributions from both metal atom and the dithiolene moiety to the HOMO of this system found after theoretical analysis. These dithiolate and diimine ligand with Pt(II)/Pd(II) are the brand organometallic compounds, which are famous for sensitize the formation of $^1\Delta O_2$ from ground-state oxygen $^3\Sigma O_2$ and photoinduced



18 **19**

Fig. 10. Proposed mechanism of the formation of Ru-sulfinate (**19**) from Ru-thiolate (**18**)

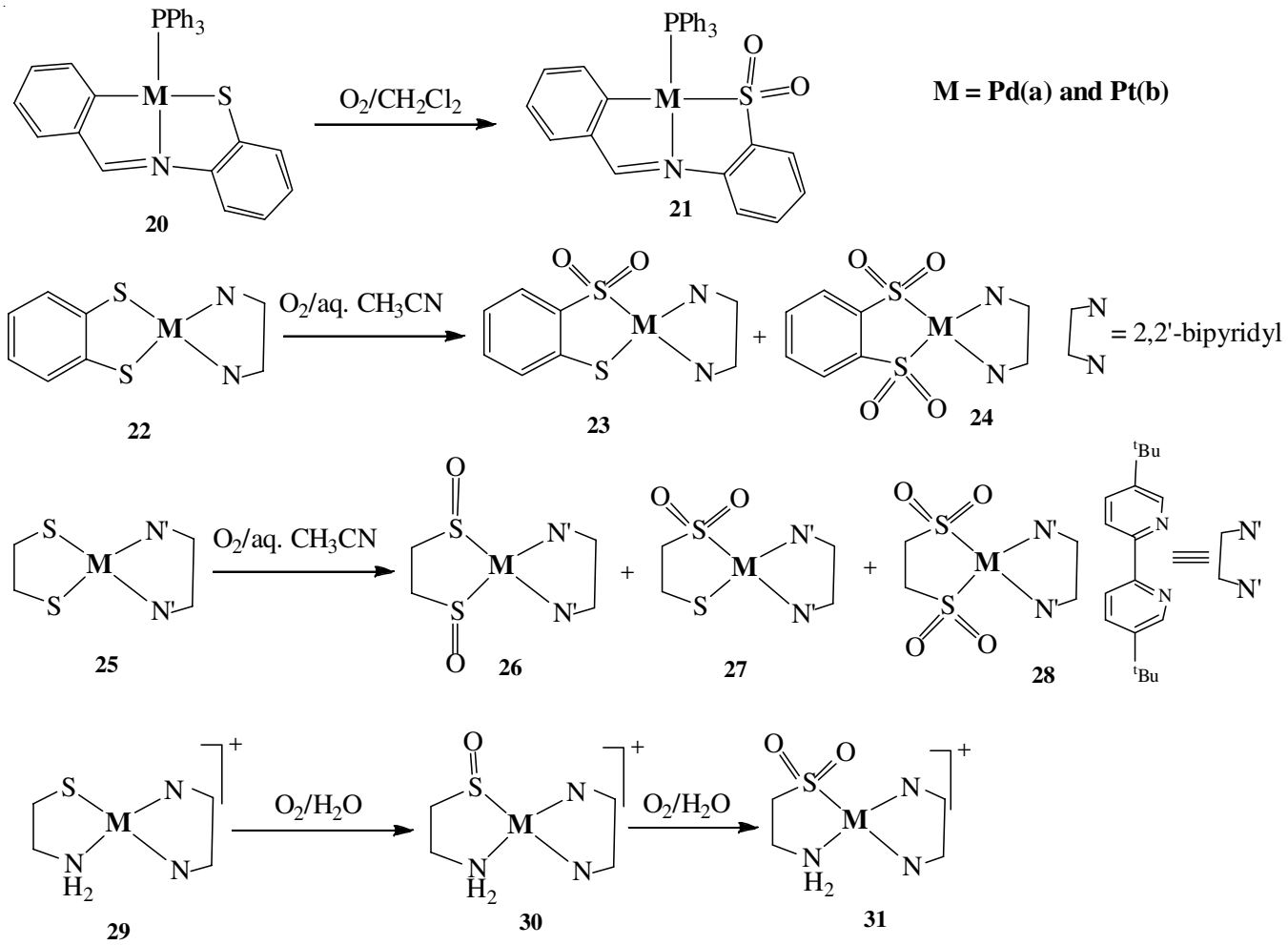


Fig. 11. Sulfenate, sulfinate and mixed sulfenate-sulfinate products of Pd^{II} (a) and Pt^{II} (b), generated by photooxidation reactions

decomposition of thiolate system utilizing the singlet oxygen is the fundamental step in the course of the reaction. A similar type of photooxidation of thiolates having Ni(II) and Pd(II) have been reported by Darensbourg *et al*. [69,78].

Dithiolates precursor are further interesting due to their course of sequential oxygenation of sulfur center and in terms of nature of dioxygen spin state. The primary oxygenation to the sulfur center of such dithiolate compounds attaching both lighter and heavier transition metals are accomplished applying equally singlet and triplet state of oxygen; however the monosulfinates are mostly inactive towards $^3\Sigma O_2$ but labile with respect to $^1\Delta O_2$ yields the disulfinate products. This findings is established not only with 3d-transition metal thiolates like Fe, Co, Ni but also heavier soft metals as Pd, Pt show the same result.

Ir-cyclometalated thiolate [Ir-(benzene-1,2-dithiolate)-$(ppy)_2]^-$ ($[IrSS]^-$) is the first example of anionic dithiolate (**32**) compound of iridium was introduced by Nguyen *et al.* [92], which were subjected to stepwise oxygenated to monsulfinate (**33**) ($[IrSSO_2]^-$) applying air as a source of oxygen and this partially oxidized compound were further oxygenated to bis-sulfinate product (**34**) ($[IrSO_2SO_2]^-$) using oxygen or hydrogen peroxide. Interestingly, both the mono and bis oxygenated compounds are anionic complexes. As these oxygenates formed by the coupling of dithiolates being redox-active part with the $[Ir(ppy)_2]^+$ moiety having luminescent character, hence this combined part served as sensing molecule because of the oxygen or reactive oxygen species (ROS) [93].

Similar type of singlet oxygen photosensitized reaction of C^N^S-cyclometalated compounds [94] incorporating Pd(II) and Pt(II) disulfide-Schiff base type ligand system, afforded the analogous sulfinate products. Due to the strong theoretical (DFT) results, mechanism of the photooxidation reaction by reactive $^1\Delta O_2$, and an approachable pathway from the cyclometalated thiolate complex to similar stable sulfinate products and the involved intermediates can be provided.

The S-oxygenation reactions of palladium thiolates with singlet oxygen are extremely similar to that of platinum thiolate compounds. The rate of photooxidation by sensitization of singlet oxygen of Pd-thiolate compounds are generally higher that the corresponding Pt-analogous, as per spectroscopic and electrochemical studies, the lower energy of HOMO of the Pd-thiolate compare to Pt-thiolate is responsible for the result since the oxygenation of sulfur with oxygen is generated by attack of the HOMO of thiolate on the $^1\Delta O_2$ molecule [55].

Properties of M–S and M–SO_2 bond: The sulfur center oxidation of metal mediated thiolate compounds mainly for platinum group metals display rich chemistry involving in the M-L bonding. This can be revealed from the different structural

feature of both thiolate and the oxygenated compounds, which can be investigated by the crystallographic analysis. Using the M–S bonding data of both in thiolato and S-oxygenated species, the underlying chemistry and the active site reactivity can be obtained. A decrease in the M–S bond distance in M-sulfinato than M-thiolato analogue are as expected and can be ascribed due to the following effects: (i) the electron–electron repulsion between the metal (t_2) and 3*p*-orbital of sulfur get reduced upon oxidation, (ii) the ionic interaction involving platinum metals and sulfinato-S increased, owing to the small radius of the oxidized sulfur in (M–SO_2) as compared to the thiolato sulfur (M–S); and (iii) exclusion of electrons are implicated in the interaction of d_π-p_π (antibonding nature) orbitals among the *d*-orbitals of metals and 3*p* of sulfur due to M(t_2) → SO_2(π^*) back donation than M-$S_{thiolato}$ [64]. These reasons are very effective to increase the substrate/new precursor lability for the sulfur oxygenated products and also their bioactivity as the hydrolytic behaviour at the NHase and SCNase active sites get increased [95]. Such change in metal-S=O bond nature are investigated by IR SO stretching frequency measurement and a few of them are listed in Table-1.

Bioactivity and bioapplications of M-S-oxygenates: Transition metal sulfur compounds are famous for their bioactivity especially catalytic activity of many active enzymes. Interestingly *o*-dithiolates attaching platinum group metals and few 3d-metals like Fe^{II}, Ni^{II}, Zn^{II} and their sulfenate [SO·SO] [96,97] and sulfinate [78,83,98] analogues are found to be biologically active. The potential moieties M-S, M-SO (mono and di) and M-SO_2 (mono and di), are enormously much efficient to adopt the irregular active site in the metalloenzyme like nitrile hydratase [99] as well to the study of their models for the metalloenzymes [100]. Platinum group metals sulfur compounds attaching the arenes together with their oxygenates are known to interact with biomolecules like DNA. Such type of interaction with biomolecules like DNA for Ru^{II}-arene compounds containing Ru^{II}-thiolato, sulfenato and sulfinato functionality are also investigated [36]. The metal-sulfur bond lability is altered by the oxygenation of arene attaching sulfur site as well as the different kinetic effect of other coligands presence, which persuade the H-bonding interaction with the polar biomolecules like DNA [101,102].

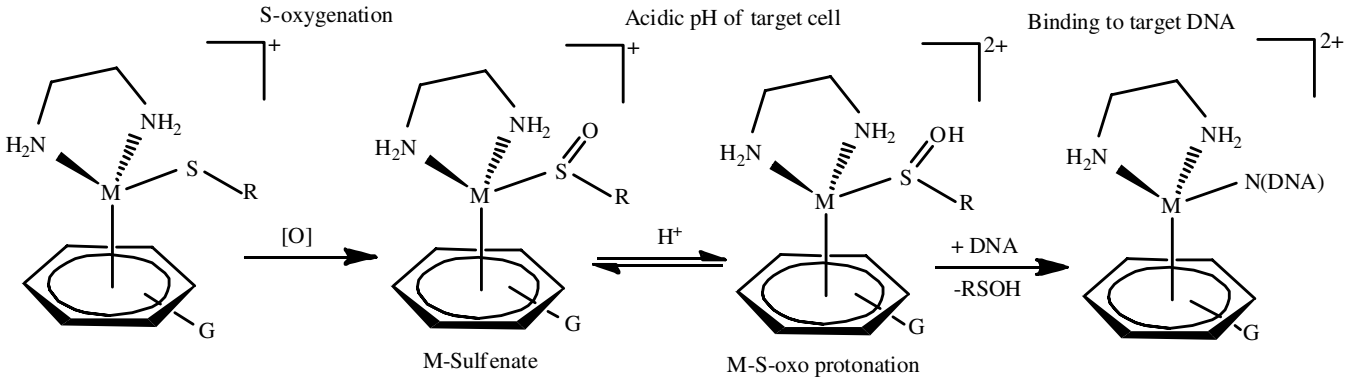
Heavier platinum group metals-incorporated sulfur compounds and their oxygenated derivatives are being toxic and very much imperative in view for the design of new anticancer drugs [103,104]. Ruthenium(II) bound ligand S-centered oxidation, which allowing the binding with DNA (**Scheme-V**), due to enhancing the lability of sulfur group ligand by weakening the metal-sulfur bond. In reality, the sulfur oxygenated species are not adequately biologically active possessing strong metal-sulfur bond formation in oxygenated compounds [105], rather it is the pH dependent H-bonding interactions among the DNA bases and M–SO moiety responsible for bioactivity. These findings generate interest among the researchers that the exploitation of biological fate of platinum group metals based metallodrugs [106-111]. Such heavier metal-sulfur compounds and their oxygenated derivatives being associate with the heavier platinum group metals, are found to be active part to confirm the *in vitro* activity [112-116] and can extend into active precursor for the anticancer drug design [117,118] in the area of biological applications.

Conclusion

The current review on the several transformations of a class of platinum group metals mediated mainly organosulfur compounds to the subsequent oxygenates and offered concentration on their basic chemical nature and impending activities. The sulfur centers mainly thiolate functionality attached to the noble metal center are highly vulnerable for S-centered reactivates. The oxygenation at the metal bound sulfur center is possible in different reaction conditions. Remarkably, numerous

TABLE-1
IR S=O STRETCHING FREQUENCY DATA OF METAL-MEDIATED SULFENATE AND SULFINATE COMPOUNDS

Compound number	Compounds	Functions	IR stretching bands (cm^{-1}) (experimental)	Ref.
2	[Ru(DPPBT-O_2)$_2$(DPPBT)]	O=S=O; O=S=O	1025 and 1119	[54]
2a	[PPN][Ru(DPPBT-O_2)$_2$(DPPBT)]	O=S=O; O=S=O	1017 and 1115	[54]
3	Monosulfinates [Ru(bpy)$_2$(S·SO_2)]	O=S=O	983 and 1105	[80]
4	Ru^{II}-disulfinates [Ru(bpy)$_2$(SO_2·SO_2)]	O=S=O; O=S=O	989 and 1119	[80]
6	Mono-sulfinate [(bmmp-O_2-TASN)-Ru(PPh_3)]	O=S=O	1139 and 1020	[14]
7	Mixed sulfenate/sulfinate [(bmmp-O_3-TASN)Ru(PPh_3)]	S=O O=S=O	1137 and 1020	[14]
8	*Bis*-sulfinate [(bmmp-O_4-TASN)Ru(PPh_3)]	O=S=O; O=S=O	1136, 1120, 1029 and 1015	[14]
10	[(bpy)$_2$Ru(aesi-N,S)]$^+$ (aesi = *o*-aminoethanesulfinate)	O=S=O	1110 and 1010	[79]
11a	ΔΔ, Ru^{II}-sulfinate compounds [(bpy)$_2$Ru(D-Hpsi-O,S)]PF_6	O=S=O	1116 and 1010	[79]
11b	ΛΛ, Ru^{II}-sulfinate compounds [(bpy)$_2$Ru(D-Hpsi-O,S)]PF_6	O=S=O	1119 and 1011	[79]
12	Cyclometalated Rh-sulfinate (12-NO_2)	O=S=O	1157	[60]
14	Ir-mediated organosulfinate [Ir(L^{SO2})Cl(PPh_3)$_2$]	O=S=O	1161 and 1042	[64]
16	Os-sulfinate [Os(aesi)(bpy)$_2$]$^+$	O=S=O	1114 and 1006	[63]
21a	C,N,S-cyclometalated Pd-sulfinate	O=S=O	1178 and 1038	[55]
21b	C,N,S-cyclometalated Pt-sulfinate	O=S=O	1187 and 1038	[55]
30	Pt^{II}(bpy){N,(SO}-aminoethane sulfenate)	S=O	918	[53]
31	Pt^{II}(bpy),{N($SO)_2$}aminoethanesulfinate)	O=S=O	1162 and 1024	[53]
33	^{n}Bu_4N[Ir(ppy)$_2$(Benzene-1-sulfinate-2-thiolate)] [$IrSSO_2$]$^-$	O=S=O	994 and 1136	[92]
34	^{n}Bu_4N[Ir(ppy)$_2$(Benzene-1,2-disulfinate)] [$IrSO_2SO_2$]$^-$	O=S=O; O=S=O	1014 and 1149	[92]



Scheme-V: Proposed mechanism of DNA binding of metal-arene sulfenates. M = platinum group metals, R = any alkyl/aryl substituent, G = any alkyl substituent

thiolate complexes of platinum group metals undergo a diversity of reactions with molecular oxygen or any oxygen sources. Due to their strong nucleophilicity, thiolate compounds are susceptible to oxygenation by the activation of dioxygen from the environment, and the purging of O_2 to the reaction medium, as well as a few other external sources of oxygen like peroxides. But it is evident that sulfur oxygenates are not obtained under strictly inert medium. There are plentiful mechanistic paths for the oxygenation of platinum metals bound thiolate S-center unlike the oxygenation reaction of organic sulphides. Hypothetically, these S-oxygenations could occur through intramolecular and/or intermolecular dioxygen addition. Thorough investigations on the interactions of such thiolates with molecular oxygen mostly $^1\Delta O_2$ producing oxygenates typically metal-sulfinate products, where the functionality bound to the S-atom especially hetero atoms plays a vital role of oxygenation. The symmetrical and unsymmetrical oxygenated products including mixture of oxygenates can be obtained in the case of multiple thiolato-S centers, though sulfenates are generally very rare. This review carefully examines and discusses the thiolato functionality-mediated photooxygenation of platinum metals. The method of sensitization of $^1\Delta O_2$ including possibility of self-sensitized photooxidation reactions of thiolato ligands of different platinum metals are also reported. Impressive bioactivity, enzymatic catalytic activity and significant inter-action with the DNA protein molecule of such type of heavier metal-sulfur oxygenates are also discussed. The interactions with biomolecules and their mechanism of action will be enormously supportive for designing and setting up for the synthesis of many similar organosulfur systems of soft toxic metals. This review will be helpful for the researchers for exploring novel techniques and proposals of preparation of a new class of organosulfur compounds and their oxygenated derivatives mediated by heavier transition metals, which will be effectively used in metal mediated drugs and sensor developments.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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