Dalton Transactions

An international journal of inorganic chemistry

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Coligand Modulated Oxidative O-demethylation of Methylether Appended Tetradentate N-Ligand on Co(II) Complexes

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Two Co(II) complexes of the formula $CoL^{OMe}X_2$ (X = Cl⁻ (1a); X = I⁻ (1b)), where L^{OMe} is 2-methoxy-N,N-bis(pyridin-2-ylmethyl) aniline were synthesized and their structure, spectroscopy and reactivity were studied. Upon oxidation of 1a and 1b, the ligand L^{OMe} undergo demethylation at the metal centre resulting in the formation of Co(III) complexes with modified phenoxide ligand. This is the very first examples of oxidative O-demethylation reported at a Co(II) centre. The oxidative behaviour shows striking dependance on the nature of coligands coordinated to the metal centre. The Co(II) complex 1a with stronger chloro coligands requires a strong oxidising agent like t-BuOOH for oxidative demethylation and the subsequent formation of a mononuclear Co(III) complex with demethylated ligand, CoL^O·Cl₂ (2). On the other hand, the complex 1b with weaker iodo coligands undergoes oxidation in presence of weak oxidant O₂ to form a dihydroxo bridged binuclear Co(III) complex [Co₂(L^O)₂(OH)₂]²⁺ (3) with modified phenoxide ligand. The oxidation of 1b to 3 is monitored and the intermediate Co(II) iodo aqua complex, [CoL^{OMe}I(H₂O)]⁺ and Co(II) diaqua complex, [CoL^{OMe}(H₂O)₂]²⁺ are isolated and characterised.

Introduction

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Modifications of coordinated ligands, such as hydroxylation of aliphatic¹⁻³ and aromatic C-H bonds^{4,5}, N-dealkylation⁶⁻⁸ and Odealkylation are often observed in the oxidation reactions of biomimicking model complexes of non-heme enzymes, which employ either O2 or its activated forms as oxidants. Odealkylation is a well studied reaction in heme chemistry; since it is involved in the catalytic cycle of cytochrome p-450 enzymes and is responsible for the detoxification of xenobiotics.9-12 However, reports about similar reactions in non-heme sites are quite rare. Over the past few decades, studies have been carried out by employing copper and iron complexes of tetra and pentadentate N-ligands with strategically placed alkoxo groups to accomplish metal assisted O-dealkylation.¹³ In most of these reactions, O-dealkylation was observed as a side reaction and a clean conversion was not achieved. Recently, Mandon et al. successfully showed the oxidative O-demethylation at a Fe(II) complex using modified TPA ligand; but isolation of the Fe(III) phenoxide product was found to be difficult, owing to its sensitivity.¹⁴

Karlin *et al.* had studied the copper-dioxygen chemistry of a tetradentate ligand 2-methoxy-5-tert-butyl-N,N-bis(pyridin-2-ylmethyl) aniline (^oL) with methylether append and the results

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^bSophisticated Analytical Instruments Facility (SAIF), IIT Madras, India [#]Present Address: Department of Chemistry, IIT Bombay, Powai 400 076 Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x show that Cu-O₂ adducts of this ligand are capable of C-H bond oxidation of toluene and alkyl benzene.¹⁵ This report indicates that the oxidation reactions of other metal complexes with similar methyl ether appended ligands may be more interesting. Since oxidation reactions at ferrous centres are more significant in bioinorganic point of view, we started our studies with the ferrous complex FeL^{OMe}Cl₂, where L^{OMe} is 2methoxy-N,N-bis(pyridin-2-ylmethyl) aniline. To our delight, it was noted that the complex undergo oxidative Odemethylation in presence of oxidant t-BuOOH. Demethylation was partial and observed only for the chloro analogue. However, the Fe(III) phenoxide product was very stable and could be isolated and characterised both in solid and solution state. The mechanism for O-demethylation.¹⁶

Since methylether appended ligands show different oxidation behavior with copper and iron, it will be of interest to see the reaction of other metal complexes of L^{OMe} with oxidants. A recent report by Kroutil et al. has showed that the cobalamindependent methyl transferase enzymes are capable of reversible C-O-ether bond formation and breakage via a Co^{III} and the highly reactive Co¹ cycle.¹⁷ The advantage of cobalt complexes over copper and iron analogues is their higher stability owing to high CFSE. However, no O-demethylation was reported at Co(II) centers of non heme complexes till date. In this article we describe the O-demethylation of L^{OMe} in Co(II) complexes upon oxidation. Observations suggest that the coligands play an important role in reactivity, which is expected as it is known that coligands can influence coordination number, crystal packing pattern and also magnetic properties.¹⁸⁻²⁰ The reactivity of few other redox

inactive metal (Mn, Ni and Zn) complexes of L^{OMe} are also explored and the details are discussed.

Results and Discussion

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Two Co(II) complexes of the formula $CoL^{OMe}X_2$ (X= Cl⁻, **1a**; I⁻, **1b**) have been synthesized and characterised. On reaction with oxidants, both these complexes underwent oxidative Odemethylation resulting in the formation of Co(III) complexes with phenoxide ligands (Scheme 1). The chloro complex, **1a** required a stronger oxidant like t-BuOOH for oxidation and resulted in the formation of a mononuclear Co(III) complex, **2** whereas the iodo complex, **1b** underwent demethylation in presence of mild oxidant O₂ and formed a dihydroxo bridged binuclear Co(III) complex, **3**. Cobalt was proved to be a better choice on comparison with ferrous complexes, as the oxidation reactions were straight forward and the Co(III)-phenoxide complexes were stable enough to isolate and characterise.



Scheme 1. Representation of oxidative demethylation of Co(II) complexes in presence of oxidants

Sythesis and characterisation of Co(II) complexes

The precursor Co(II) complexes 1a and 1b were synthesized as fine solids in good yield (>75%) by mixing corresponding metal salts and ligand in 1:1 molar ratio in EtOH/MeOH under inert atmosphere. Single crystal X-ray analysis shows that both these complexes are mononuclear (Fig. 1, Table S1). The molecules consist of a Co(II) centre bound by a molecule of L^{OMe} coordinated in a standard tripodal tetradentate fashion. The two other coordination sites are occupied by terminally bound halide coligands, which are cis to each other. The metal centre in each complex adopt an approximate octahedral geometry with one halide trans to anisole oxygen and the other trans to the tertiary amine nitrogen. The square plane of octahedron was made by one of the coligands and the nitrogen atoms from ligand. The anisole O atom from the ligand backbone and the halide coligand trans to it occupy axial positions. The anisole -CH₃ group lies parallel to the square plane as in the Fe(II) analogue.¹⁶ The metal halide bond lengths are non-uniform and the halide trans to the anisole oxygen coordinate weakly due to the trans effect of ether

oxygen. An identical trend was observed for the cleCo(H) complexes of TPAs with similar geometry. The the cleCo(H) complexes of TPAs with five and six coordinated Co(II) complexes with halide coligands, L^{OMe} exclusively formed six coordinated complexes.^{21, 22}



Figure 1. Displacement ellipsoid (50% probability) plots of Co(II) complexes $CoL^{OMe}Cl_2$, **1a** and $CoL^{OMe}I_2$, **1b**. H atoms are not shown for sake of clarity.

UV-Vis-NIR spectra of these complexes, recorded in CH_2Cl_2 , showed well defined bands at 580 and 592 nm respectively for **1a** and **1b** with ε values in the range 110-160 Mol⁻¹cm⁻¹ (Figure S1). High ε values (>100 Mol⁻¹cm⁻¹) are typical of five coordinated trigonal bipyramidal complexes. Moreover, the splitting pattern of the peaks also matches with the spectra of penta-coordinated complexes.²³ These observations conclude that both **1a** and **1b** exist as penta-coordinated trigonal bipyramidal species in solution when a non-polar solvent like CH₂Cl₂ is used. This may be due to the dissociation of one labile chlorine atom or due to the detachment of anisole moiety from the coordination sphere, which subsequently lead to the formation of a five-coordinated species.

Spectra of the complexes were recorded in variety solvents to understand their solution behavior and both complexes exhibit distinct solution properties (Fig. S2). For **1a**, the λ_{max} was blue shifted to 550 nm in alcohol, on comparison with the spectrum in CH₂Cl₂ (580 nm). The ε values are in the range 50 Mol⁻¹cm⁻¹, typical for six coordinate Co(II) complexes²⁴ and it was concluded that the solid state structure is retaining as such in these solvents. The λ_{max} was further blue shifted to 510 nm with much lower molar absorption coefficients (20-30 Mol-¹cm⁻¹) when H₂O was used as a solvent. This very low value and the blue shift in absorption can be due to the formation of an aqua complex, in which the labile halides were replaced with water molecules. Thus it is noted that, as polarity of solvent increases, the λ_{max} gets blue shifted with lower ϵ values. Similar, but more striking trend was observed for iodo complex 1b (Fig 2, S3) also. Hence it is concluded that both these complexes exhibit solvatochromism and exist as five coordinated species in non-polar solvents like CH₂Cl₂. Whereas in more polar coordinating solvents like H₂O and MeOH, they show properties of regular octahedral complexes and retain octahedral geometry.

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Figure 2. UV-Vis spectra of CoL^{OMe}I₂, **1b** in different solvents.

In literature, UV-Vis studies of five and six coordinated Co(II) complexes of N and O donor ligands are known to show similar solvatochromic behaviour.²⁵ Previously reported cobalt(II) complexes of TPA also showed similar structural changes in solvents.²⁶ ¹H NMR spectra of the six coordinated complex Co(TPA)Cl₂ and five coordinated [Co(TPA)Cl]⁺ were identical, which suggest that the six coordinated complex can undergo chloride dissociation to form five coordinated species in solution.



Figure 3. ¹H NMR spectra of CoL^{OMe}Cl₂, 1a in different solvents.

More evidences for the influence of solvent on the structural and spectral properties of ${\bf 1a}$ and ${\bf 1b}$ are obtained from ${}^1{\rm H}$ NMR studies (Fig 3). The spectrum recorded in CD₃OD showed eleven very sharp signals (two up-field and nine down-field) in the spectral range -60 to 200 ppm. Presence of up-field shifted signals is an indication of significant pseudo contact contribution to isotropic shifts.²⁷ Though spectral width was much lesser in D₂O (-20 to 150 ppm), the pattern was similar confirming that the octahedral geometry is remained more or less same in both these solvents. However, the spectrum in CDCl₃ has only one up-field shifted signal and the other signal was present in the diamagnetic region, indicating the detachment of the anisole -OMe group (vide infra for signal assignment) from the metal centre and the consequent formation of a five coordinated Co(II) complex. Hence it is concluded from ¹H NMR spectra that it is the methyl ether group, which is getting detached from the metal in presence of non-polar solvents and not the coordinated hallde?/C9DT04609G

This observation matches with the conclusion drawn from UV-Vis studies, where spectra of **1a** showed the characteristic features of five coordinated species in CH_2Cl_2 . Further, the ¹H NMR spectrum of **1a** recorded in D_2O is identical with the spectrum of aqua complex $[CoL^{OMe}(OH_2)_2]^+$ recorded in D_2O (vide infra, Fig S15). Based on these observations, the solution speciation of **1a** can be depicted as in scheme 2.



Scheme 2. Solution speciation of 1a in different solvents.

¹H NMR spectra of iodo complex **1b** was recorded in CD₃OD and was compared with that of **1a** to understand the influence of coligands on spectral features (Fig S4). Spectra were similar with eleven sharp signals (two up-field and nine down-field) in a wide spectral window; but some minor differences were noticed as coligand changes. As ligand field strength of the halide decreases, the up-field shift also decrease (-52 ppm for **1a** to -37 ppm for **1b**). The down-field shift and the pattern of the signals did not show any such trend and remained more or less same for both complexes.

Assignment of signals in the paramagnetic ¹H NMR spectrum is challenging owing to the hyperfine shift and broadening of signals.²⁸ All signals in the ¹H NMR spectra of **1a** were unambiguously assigned (Fig. 4) with the help of ¹H-¹H COSY (Fig. S5) and *T1* and *T2* relaxation time measurements (Table S3).²⁹⁻³² Further, to understand the temperature dependence of paramagnetic ¹H NMR signals, variable temperature spectra of **1a** was recorded in the temperature range -85 to +55°C (228 - 328 K). As temperature increased, the most down-field peaks gradually shifted up-field, whereas the up-field peaks showed gradual down-field shift (Fig S6). Curie plots show that the isotropically shifted resonances change linearly as a function of T⁻¹ (Fig S7). Magnetic susceptibility of **1a** and **1b** (CD₃OD, 298 K) indicate μ_{eff} values of 5.2 and 5.4 μ_{B} respectively, consistent with an S = 3/2 ground state.³³



Figure 4. Paramagnetic ¹H NMR spectra of **1a** in CD₃OD at RT (500 MHz) and the assignment of signals

Electrochemistry of Co(II) complexes are also investigated to understand the feasibility of oxidation. CV of **1a**, recorded in

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CH₃CN has a one-electron redox wave (E_{1/2}, 274 mV vs. Fc/Fc⁺) corresponding to metal oxidation. CV of **1b** in CH₃CN shows two redox waves; one at E_{1/2} = 160 mV vs. Fc/Fc⁺ corresponds to the redox couple I⁻/I₂, and the second one at E_{1/2} = -209 mV vs. Fc/Fc⁺ indicating the one electron metal redox couple Co^{2+/3+} (Fig 5).^{34, 35} The Cu(II) complex of L^{OMe} exhibited similar reversible redox processes with a E_{1/2} value of -510 mV vs. Fc/Fc⁺. The lower E_{1/2} value indicates its high reactivity to O₂ and the facile formation of Cu-O₂ complexes. Fe(II) complex of L^{OMe} has much higher E_{1/2} value (-55 mV vs. Fc/Fc⁺) and was stable to air. Hence, the comparatively lower oxidation potential of Co(II) iodo complex **1b**, on comparison with **1a**, indicates that it may be more reactive to O₂.



Figure 5. CVs of **1a** (left) and **1b** (right) in CH₃CN with 0.1 M nBu_4PF_6 as an electrolyte. Scan rate: 0.05 V/s; glassy carbon working electrode, Ag/AgCl/KCl(aq) reference electrode.

As expected based on electrochemical studies, Co(II) chloro complex 1a was stable and did not show any reactivity to air in solid or in solution state even after exposing for longer period of time. Reaction of 1a with stronger oxidant like H₂O₂ resulted in the decomposition of the starting material and did not bring any oxidation. After few trials, it was found that 1a undergo oxidation with t-BuOOH in CH₂Cl₂ medium. On refluxing the blue solution of 1a in CH₂Cl₂ with two equivalents of t-BuOOH, a parrot green solution of Co(III) complex was obtained after 20 h. Based on our studies with the ferrous complexes of L^{OMe}, the possibility of oxidative O-demethylation and the formation of a Co(III) phenoxide complex is expected, which is confirmed by structural and spectral analysis of the product. Solvent removal followed by washing the residue with diethyl ether, the Co(III)-phenoxide complex 2 was isolated as a gray solid in excellent yield (> 95%). The reaction was clean and took place only under specific conditions. On using more than two equivalents of oxidant, the complex got decomposed, whereas less than two equivalents of oxidant leads to longer reaction time. Solvents play an important role in the oxidative Odemethylation and the reaction took place only in chlorinated solvents.

Single crystal X-Ray analysis shows that **2** is mononuclear with distorted octahedral geometry around Co(III) (Fig. 6, Table S4). The most interesting feature is the coordination of the phenoxide O-atom, which is formed as a result of O-demethylation of the anisole append of L^{OMe} during oxidation, with the Co(III) centre. Except the Co-Cl bonds (2.2559(9) Å_{av}) all bonds made to metal are less than 2 Å, which is typical for Co(III) complexes. The square plane of the octahedron is

comprised of two pyridine nitrogens, phenoxide, oxygen and one terminal chloride. The other chloride and tertially and tertially and tertially and tertially and tertially and tertially and the nitrogen take the axial positions. The amine N made longer bond with the metal (1.953(3) Å) on comparison with the pyridines (1.9445(3) Å_{av}). The three trans angles around the metal center showed values of 167.03(13), 178.69(9) and 176.68(9) indicating that the complex is less distorted on comparison with the Co(II) analogue, **1a** and has more perfect octahedral geometry. Similar mononuclear Co(III) complexes with labile coligands such as Cl⁻ or H₂O are known as good catalysts for phosphate ester hydrolysis.^{36, 37}



Figure 6. Displacement ellipsoid (50% probability) plots of Co(III) complex [CoL⁰⁻Cl₂, **2**. H atoms, counter anions and solvents of crystallisation are not shown for sake of clarity

Unlike choro complex **1a**, **1b** was not stable to air and the dull green complex turns red on exposure to moisture, indicating reactivity (Fig S8). Though O-demethylation was expected, reaction of **1b** with t-BuOOH in CH_2Cl_2 resulted in the decomposition of the precursor complex. Similar result was obtained with other strong oxidants like H_2O_2 also. On varying reaction conditions, it was found that **1b** undergoes oxidative O-demethylation in presence of O_2 in CH_3CN-H_2O mixture, yielding Co(III) complex **3** with phenoxide ligand. The oxidized product was isolated as brown-red solid in 40% yield after overnight reaction. However, no reaction was noticed in the absence of O_2 or H_2O .

Single crystal X-ray analysis shows that complex 3 has a binuclear structure in which the Co(III) centers are held together by two hydroxo bridges (Fig. 7, Table S4). The complex is symmetric and has an inversion center that relates one half to the other. The phenoxide ligand Lo- is coordinated in a tripodal fashion around Co(III) and the octahedral coordination is satisfied by coordination with two bridging hydroxo groups. The pyridines make weaker bonds (1.9715(6) Å_{av}) and occupy axial positions of the octahedron. The metal atom lies on the square plane made by two hydroxo groups, phenoxide oxygen and tertiary amine nitrogen. The amine N forms shorter bond with the metal (1.915(5) Å) than the pyridines. This is in stark contrast with that observed for the other Co(III) complex 2. The Co-Co distance is 2.929(3) Å and O-O' distance is 2.423(4) Å which are expected, on comparison Published on 09 January 2020. Downloaded by University of Memphis on 1/9/2020 6:14:18 PM

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with binuclear Co(III) complexes having similar Co $^{\rm III}_2(\mu\text{-OH})_2$ diamond core. 38



Figure 7. Displacement ellipsoid (50% probability) plots of Co(III) complex $[Co_2L^{0-}(OH)]_2$.Cl_{0.75}l_{1.25}.4H₂O.CH₃CN, **3**. H atoms, counter anions and solvents of crystallisation are not shown for sake of clarity

UV-Vis spectra of Co(III) complexes **2** and **3** show well defined d-d bands at 582 (ϵ , 117 Mol⁻¹cm⁻¹) and 519 nm (ϵ , 503 Mol⁻¹cm⁻¹) respectively. In addition, a high energy shoulder was also present around 400 nm in the spectra of both complexes (Fig. S9).³⁹ ¹H NMR spectra of Co(III) complexes **2** and **3** show signals corresponding to 16 protons, whereas the ligand has 19 protons; absence of signals corresponding to three protons provides further evidence for demethylation (Fig. S10). The IR spectrum of dihydroxo bridged binuclear Co(III) complex **3** has strong band at 3343 cm⁻¹, characteristic of the bridging hydroxo group (Fig S11).

Proposed mechanism for O-demethylation

Few examples of N-dealkylation reactions were reported in literature and these reactions are proposed to proceed via the formation of a metal-dioxygen adduct. This metastable intermediate attacks the N-alkyl C-H bond in a rate determining step, resulting in the formation of dealkylated ligand and corresponding aldehyde as byproduct.⁴⁰⁻⁴³ Similar mechanism is expected to operate for O-demethylation also. Though O-demethylation occurs for both 1a and 1b, the difference in the nature of oxidized products confirms that the reaction pathways are different. For 1a, demethylation occurs only in CH₂Cl₂, in which the complex exists as a pentacoordinated species and favors the attack of oxidant. On reaction with t-BuOOH, the pentacoordinated 1a is postulated to form an octahedral Co(III) tertiary butyl peroxo intermediate. Such species are known to afford alkoxy radicals, which can oxidise hydrocarbons.44-47 In the present case, it is proposed that the peroxo intermediate forms a tertiary butoxy radical, which abstract a hydrogen radical from the methoxo group oriented in a favorable position. As a result, a cyclic intermediate forms with the loss of a molecule of butanol. The intermediate on further rearrangement resulted the Co(III) complex 2 with phenoxide ligand and a molecule of formaldehyde (Scheme 3). However, our attempts to detect the presence of formaldehyde were hindered by longer reaction time and comparatively higher reaction temperature.



Scheme 3. Proposed mechanism for the oxidative Odemethylation of **1a** and the formation of **2**.

The mechanism of conversion of 1b to 3 is likely to follow a different route. It was noticed that 1b undergoes oxidation only in presence of H₂O, suggesting the involvement of an aqua complex as a precursor for oxidation. To understand the mechanistic details and to identify the actual Co(II) precursor which undergoes oxidative O-demethylation, the iodo complex was reacted with H₂O. The red colour of complex 1b in CH₃CN faded to orange on addition of H₂O and to very pale pink in presence of excess H₂O. This can be an indication of the subsequent iodide replacement by H₂O molecules and the formation of Co(II) aqua complexes with formula [CoL^{OMe}(OH₂)I](I), 1c and [CoL^{OMe}(OH₂)₂](I)₂, 1d. However, no such conclusion could be obtained from UV-Vis spectra, as the spectra remained more or less same in H₂O (a broad peak around 500 nm, Fig 2), irrespective of the amount of solvent used. Initial attempts to isolate and crystallize the H₂O coordinated complexes were unsuccessful. However, by exchanging the iodo counter anion with $-ClO_4$, both these complexes could be crystallised as [CoL^{OMe}(OH₂)I](ClO₄), 1c' and [CoL^{OMe}(OH₂)₂](ClO₄)₂, **1d'**. The iodo-aqua complex **1c'** could be synthesised easily, whereas the formation of diaqua complex 1d' required high temperature and longer reaction period. This indicates that the replacement of first iodide is relatively facile on comparison with the removal of second halide.48

Crystal structures confirm that these complexes have regular octahedral geometry around Co(II) as in **1a** and **1b** (Fig. 8). However, an interesting geometric change was noticed for the diaqua complex **1d'**. In all other Co(II) complexes, L^{OMe} was coordinated around the metal in a standard tripodal manner and the N-atoms are meridionally placed. In **1d'**, however, the orientation of N- atoms of the ligand is changed and they form the face of an octahedron maintaining the arrangement of coligands *cis* to each other. Another interesting difference is the change in bond lengths. Similar to **1a** and **1b**, **1c'** also have shorter Co-N(pyridine) bonds (2.115(3) and 2.126(3) Å) and longer Co-N(amine) bond (2.170(3) Å). But for aqua complex **1d'**, the trend was reversed with longer Co-N(amine) bonds (2.153(4) and 2.111(4) Å) and shorter Co-N(amine) bond (2.097(4) Å).

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Figure 8. Displacement ellipsoid (50% probability) plots of Co(II) complexes $[CoL^{OMe}(OH_2)I](CIO_4)$, **1c'** and $[CoL^{OMe}(OH_2)_2](CIO_4)_2$, **1d'**. H atoms, counter anions and solvents of crystallisation are not shown for sake of clarity.

Both agua complexes 1c' and 1d' are characterised in solution by various spectral techniques. The iodo- aqua complex 1c' showed similar solvatochromic behaviour as 1a and 1b. In CH₂Cl₂, 1c' exhibited parrot green color with a strong band in the UV Vis spectrum at 614 nm (ϵ = 235 Mol⁻¹ cm⁻¹). In addition, two weak bands were also present in the NIR region, confirming the formation of a five-coordinated species. On the other hand, the complex was pale pink in EtOH and showed a band at 540 nm with much lower molar extinction coefficient (ϵ =55 Mol⁻¹ cm⁻¹), which is typical for octahedral complexes (Fig S12). Interestingly, both these solutions give similar pale pink blocks of 1c' on crystallization, indicating that the species is same in solid state. No solvatochromic studies could be carried out for the diaqua complex 1d', as it was soluble only in polar solvents like alcohol and H₂O, in which it show features typical for octahedral complexes (490 nm; ε = 32 Mol⁻ ¹ cm⁻¹). λ_{max} for **1c'** and **1d'**, recorded in polar solvents, showed gradual blue shift as the coligand change from weak field iodide (540 nm) to moderate field H₂O (490 nm) (Fig S13).

Paramagnetic ¹H NMR spectra of **1c'** and **1d'** are recorded in CD₃OD and D₂O respectively. The spectrum of **1c'** has eleven signals (two up-field and nine down-field) in the spectral range -40 to 200 ppm, like the other Co(II) complexes (Fig S14). However, the signals were broad and not well defined which could be due to the fast electronic relaxation time. The spectrum of diaqua complex **1d'** also showed eleven signals, which were sharp, in a comparatively shorter spectral window of 180 ppm (-20 to 160 ppm) (Fig S15). Magnetic susceptibility values of **1c'** (CD₃OD, 298 K) and **1d'** (D₂O, 298 K) indicate µeff values of 4.18 and 5.04 µB respectively, consistent with an S = 3/2 ground state.

Complexes **1c'** and **1d'** with $-ClO_4^-$ counter anions are stable and could be stored for months under closed condition; but their iodide counterparts **1c** and **1d** are comparatively more reactive and subsequently get converted to the oxidised complex, **3**. However, it is noted that there is no reactivity when the diiodo complex **1b** is stored in a moisture free environment. The inability to undergo oxidation in the absence of H₂O confirmed that the aqua complex, **1d** is the precursor for oxidation. When the iodo complex **Pb** is treated with 4920 in presence of air, the diaqua complex **1d** forms in situ and reacts with O₂ resulting in the Co(III) complex **3**. The structural analyses of the diiodo and aqua complexes further confirm that the Co(II) diaqua complex is the precursor for oxidation. In the iodo complex **1b**, the $-OCH_3$ group is positioned far away from the coligands. However in the diaqua complex **1d'**, the anisole moiety is rearranged in such a way that it comes in close proximity to the aqua coligands, thereby facilitating the demethylation process.

Oxidation of **1b** is proposed to proceed via the formation of a metastable Co(III)-dioxygen intermediate, which abstract hydrogen atoms from the favourably placed anisole methyl groups.¹ The mechanism then proceed via a pathway similar to that proposed for the conversion of **1a** to **2**, resulting in the formation of Co(III) complex **3** with modified phenoxide ligand and bridging hydroxo groups (Scheme 4).



Scheme 4. Proposed mechanism for the oxidative Odemethylation of **1b** and the formation of Co(III) complex **3**

The experiments on Co(II) and Fe(II) complexes shed light on the O-demethylation reactions of L^{OMe} and it is identified that the redox properties and hard soft nature of metals play crucial role in supporting oxidative O-demethylation. To confirm this point, the oxidation behaviour of few other metal complexes of L^{OMe} is studied. The metals (Mn, Ni and Zn) were selected in such a way that they are less redox active and cannot achieve higher oxidation state under normal conditions, which indicate that they are not expected to support O-demethylation.

Syntheses of precursor M(II) complexes were straightforward and all of them were precipitated as stable fine powders in excellent yield by mixing corresponding metal(II) chloride salt and ligand in equimolar ratio in EtOH. The manganese complex $MnL^{OMe}Cl_2$, **1e** was isolated as a flesh colored powder and crystal structure shows that the complex has a geometry identical to the Co(II) complexes **1a** and **1b** (Fig S16, Table S4). To study the oxidation behaviour, the complex was refluxed in CH_2Cl_2 with two equivalent of t-BuOOH for 48 h. No visible changes were observed and the precursor Mn(II) complex **1e** was completely crystallised out from the reaction mixture on cooling, confirming that there is no reaction.

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NiL^{OMe}Cl₂ was isolated as sea green solid in good yield. The crystal structure of the complex is reported and it has a mononuclear structure with distorted octahedral geometry around metal centre as in **1e**.⁴⁹ The complex was characterised by UV-Vis spectroscopy and the spectrum showed two well defined bands at 674 ($\epsilon = 21 \text{ Mol}^{-1} \text{ cm}^{-1}$) and 406 nm ($\epsilon = 48 \text{ Mol}^{-1} \text{ cm}^{-1}$) and a shoulder at 315 nm. Ni(II) complexes are not expected to undergo easy oxidation because of the unstable nature of Ni(III) oxidation products. The complex was dissolved in CH₂Cl₂ and refluxed with an equivalent of t-BuOOH for 48 h. UV-Vis spectrum of the resultant solution showed identical features of the initial Ni(II) complex (Fig S17). The precursor complex **1f** could be fully recovered by washing the residue with diethyl ether.

Reactions were repeated using upto 5 equivalents of oxidant; but no demethylation took place in any case, indicating the inability of Mn(II) and Ni(II) complexes to undergo oxidation. As mentioned earlier, no demethylation is noticed for the Cu(I) complexes of L^{OMe} also. For Cu²⁺, which is a borderline acid, the coordination geometry is effectively satisfied by bonding with soft ether O atom than hard phenoxide O-atom, which explains the observed inertness of Cu(I) complexes to Odemethylation whereas for Ni²⁺ and Mn²⁺ complexes, their inability to achieve and stabilise higher oxidation states resist the reaction. Co²⁺ is a very suitable contestant in this aspect, as it can easily achieve +3 oxidation state and the hard acid Co³⁺ prefers coordination with hard phenoxide oxygen atom over ether O atom. Hence it is proven that the redox properties of metals play significant role in the demethylation of $\mathsf{L}^{\mathsf{OMe}}.$ The electrochemical studies of these complexes further helps to analyze the observed oxidation behavior. Copper complex of L^{OMe} has a very low one electron redox potential (E_{1/2} = -510 mV Vs. Fc/Fc⁺) and undergoes metal oxidation; no Odemethylation was noticed. On the other hand, Iron complex has much higher one electron potential at -55 mV Vs. Fc/Fc+ and undergoes oxidative O-demethylation.¹⁶ Cobalt complexes with comparable CV profiles also undergo oxidative Odemethylation as described before. The electrochemical studies of Mn complex (1e) did not give any useful data. However the CV of NiL^{OMe}Cl₂, 1f shows a redox couple with a high $E_{1/2}$ value of 545 mV Vs. Fc/Fc⁺ (Fig S18). From the electrochemical analysis it is concluded that metals with low redox potential (For Eg: Cu) support metal oxidation whereas those with medium redox potential (Egs: Fe and Co) can assist oxidative O-demethylation. However, metals with very high redox potential (Eg: Ni and Mn) do not aid any type of oxidation. It is interesting to note that the potential of the redox couple O₂/O₂-• in CH₃CN is -1.25 V vs. Fc/Fc⁺.^{50, 51}

In summary, we have reported the first oxidative Odemehylation reactions at Co(II) centers by employing a tetradentate N-ligand with anisole append (L^{OMe}) and halide coligands (Cl⁻ or I⁻). The Co(II) complex, **1a** with chloro coligands, is stable and underwent oxidative demethylation in presence of strong oxidant like t-BuOOH. However, the Co(II) complex, **1b** with iodo coligands is not stable_{vie}to_{Arraic} and oxidised to Co(III) complex with demethylated⁰ Marraic and formation of Co(II) diaqua complexes. The incapability of metals such as Cu, Mn and Ni to carry out oxidative Odemethylation emphasize the importance of metal redox properties in such reactions.

Experimental Section

General Procedures

Unless otherwise stated, all solvents and chemicals used were of commercially available analytical grade, and were used as such without further purification. Co(ClO₄)₂.6H₂O was synthesized by reacting CoCO₃ with HClO₄ in aqueous medium, followed by crystallisation from H₂O. CH₃CN was dried by double distillation over P2O5 and CaH2 after passing through a long column of activated alumina. CH₂Cl₂ was dried by employing standard procedure.⁵² EtOH (99.9%) was purchased from Hayman Ltd and used as such. The deuterated solvents were obtained from Aldrich. Preparation and handling of airsensitive compounds were performed under an argon atmosphere using standard Schlenk techniques. The UV-Vis spectra were recorded on a Jasco V 650 UV-Vis spectrophotometer or Shimadzu 3100 UV- Vis- NIR spectrophotometer. IR spectra were recorded on a Jasco FT/IR-4100 spectrophotometer after making pellets with KBr. ¹H and ¹³C NMR spectral data were obtained from a Bruker 400 MHz/ 500 MHz FT-NMR spectrometers at ambient temperatures by using TMS as an external reference. All electrochemical experiments were performed using a CH Instrument (model CH6003D Electrochemical Analyzer). A three electrode system was used, consisting of a platinum (diameter of the active zone: 2.0 mm) working electrode, a platinum wire counter electrode, and a Ag/AgCl/KCl(aq) reference electrode. The CV measurements were performed in dry acetonitrile solutions containing 0.1 Μ tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, recrystallized from methanol), and 2 mM substrate under N₂ atmosphere at room temperature. Scan rate of 50 mV/s were applied for all the complexes. Ferrocene was used as an internal standard and the $E_{1/2}$ value for Fc/Fc⁺ couple is found at 450 mV vs Ag/AgCl in CH₃CN.

Preparation of ligand and complexes

L^{OMe} (2-methoxy-N, N-bis(pyridin-2-ylmethyl)aniline). Toluene solution (3.0 mL) of picolinic aldehyde (4.0 g, 37.3 mmol) was taken in an air free addition funnel and o-anisidine (4.6 g, 37.3 mmol) in toluene (3.0 mL) was added drop-wise with continuous stirring under N₂. Formed red oil and orange supernatant was stirred under inert atmosphere for an hour. The supernatant was decanted and solvent removed under reduced pressure to obtain the imine as orange oil (7.8 g, 99%). The imine was dissolved in MeOH (15 mL) and reduced by adding NaBH₄ (1.4 g, 37.0 mmol) in small portions over a period of 24 hours under ice cold condition. After complete addition, the solution was kept stirring overnight under N₂. The reaction was stopped, solvent removed and excess NaBH₄ was quenched by adding 6N HCl and the reaction mixture was then

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made basic with 4N NaOH. Extraction to CH₂Cl₂ followed by solvent removal yielded the secondary amine as yellow orange oil (7.1 g, 90 %). The amine was dissolved in CH₃CN (40 mL) and treated with picolyl chloride (4.3 g, 33.7 mmol) under inert atmosphere. To this reaction mixture, solid Na₂CO₃ (1.85 g, 17.5 mmol) was added in small portions with continuous stirring. The reaction mixture was kept heating at 50°C for three days. Solvent was removed and the crude product obtained was purified by column chromatography using silica gel. Elution with petroleum ether removed the un-reacted 2° amine and picolyl chloride, whereas elution with ethyl acetate/hexane (1:1) yielded L^{OMe} (1.3 g, 48%) as off-white rectangular crystals (Rf = 0.25, silica gel, ethyl acetate/hexane 1:1). Yield: 48%. ¹H NMR (CDCl₃): 3.84 (s, 3H), 4.51 (s, 4H), 6.77 (m, 1H), 6.89 (m, 3H), 7.08 (m, 2H), 7.50 (d, 2H), 7.57 (m, 2H), 8.49 (d, 2H). ¹³C NMR (CDCl₃): 55.56 (-CH₂), 58.76 (-OCH₃), 111.72 (Ph), 120.76 (Ph), 120.80 (Py), 121.84 (Ph), 122.36 (Py), 136.45 (Py), 139.30 (Ph), 149.00 (Py), 152.82 (Ph), 159.82 (Py). L^{OMe} was synthesized by Lucas et al.¹⁵, by using a slightly different procedure.

Co^{II}L^{OMe}Cl₂, 1a. To a dark blue solution of CoCl₂.6H₂O (179.0 mg, 0.75 mmol) in EtOH, L^{OMe} solution (228.5 mg, 0.75 mmol) in EtOH was added drop wise with stirring at room temperature. After stirring for 4 h at RT, the precipitated dark purple powder was separated and dried (Yield: 276.0 mg, 85%). Purple needles were obtained from CH₂Cl₂ overnight, by evaporation. Anal.Calcd for C₁₉H₁₉Cl₂CoN₃O: C, 52.43; H, 4.40; N, 9.66. Found: C, 52.40; H, 3.85; N, 9.58. UV-Vis (λ_{max} , nm; ϵ , M⁻¹ cm⁻¹): 582 (113), 1234 (6) (CH₂Cl₂); 584 (79), 1256 (5) (CH₃CN); 548 (43), 1302 (6) (EtOH or MeOH); 502 (25), 1056 (6) (H₂O). FTIR (KBr, cm⁻¹): 2923, m, v(C-C); 1605, s, v(C=N_{py}); 1498, 1444, s, v(C=C_{ar}); 1249, s, v(C=O). μ (CD₃OD, 298 K): 5.19 μ B/Co(II). ¹H NMR (500 MHz, CD₃OD): -51.37, -25.95, 6.60, 12.76, 28.66, 48.98, 50.40, 70.03, 76.50, 151.48, 187.89.

CollLOMel2, 1b. To a freshly prepared dark green solution of Col₂.6H₂O (80.3 mg, 0.19 mmol) in EtOH, ligand solution (59.0 mg, 0.19 mmol) in EtOH was added drop wise with stirring under N_2 , yielding purplish red clear solution. On stirring under N₂ for overnight, orange red supernatant and grey green precipitate formed. The precipitate was separated, dried and yield of the dull green powder noted (88.5 mg, 75%). Bright green block shaped crystals were obtained from CH₂Cl₂ after a day, by vapour diffusing diethyl under N2. Anal.Calcd for C19H19I2CoN3O: C, 36.92; H, 3.10; N, 6.80. Found: C, 37.08; H, 2.56; N, 6.66. UV-Vis (λ_{max} , nm; ϵ , M⁻¹ cm⁻¹): 360 (2495), 514 (96), 560 (136), 594 (143), 1446 (11) (CH₂Cl₂); 376(1289), 520 (75), 1176 (8) (CH₃CN); 362 (673), 536 (51), 1130 (5) (MeOH); 370 (1583), 540 (72), 1278 (6) (EtOH). FTIR (KBr, cm⁻¹): 2912, m, v(C-C); 1604, s, v(C=N_{py}); 1496, 1441, s, v(C=C_{ar}); 1245, s, v(C-O). μ (CD₃OD, 298 K): 5.40 μB/Co(II). ¹H NMR (500 MHz, CD₃OD): -37.55, -20.39, 7.44, 13.78, 28.58, 40.05, 56.56, 69.99, 76.29, 141.40, 189.99.

[Co^{II}L^{OMeI}(H₂O)](ClO₄), 1c'. The dull green precipitate of 1b (100 mg, 0.16 mmol) was suspended in EtOH and treated with an equivalent of NaClO₄ (20 mg, 0.16 mmol). The reaction mixture was stirred overnight to obtain bright pink solution and thin white precipitate which was filtered off. The pink-red

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solid obtained by removing solvent from the supernatant was dried well and yield noted (70 mg, 70%). Paile phile blocks were obtained after two days from CH₂Cl₂ or EtOH by slow evaporation. Anal.Calcd for C₁₉H₂₁ClCoIN₃O₆: C, 37.76; H, 3.17; N, 6.95. Found: C, 37.99; H, 1.45; N, 6.21. UV-Vis (λ_{max} , nm; ϵ , M⁻¹cm⁻¹): 530 (53), 1174 (7) (EtOH); 556 (146), 496 (87), 610(233) (CH₂Cl₂). FTIR (KBr, cm⁻¹): 3399, v(-OH₂); 1120, 627, v(ClO₄⁻); 770, v(pyridyl-CH). ESI-MS (m/z, H₂O): 399 (100%, [L^{OMe}Co(OH₂)(OH]⁺); 491 (93%, [L^{OMe}Co(I])⁺); 426 (85%, [L^{OMe}Co(EtOH)(OH]⁺). μ (CD₃OD, 298 K): 4.18 μ B/Co(II). ¹H NMR (CD₃OD): δ ^{-31.69, -14.96, 8.79, 12.06, 17.83, 32.45, 42.91, 59.97, 73.14, 80.54, 147.39, 194.09 (CDCl₃): -27.22, -15.35, -2.50, 18.02, 69.82, 80.24, 116.56, 210.31.}

[Co^{II}L^{OMe}(H₂O)₂](ClO₄)₂, 1d'. The dull green precipitate of 1b (150 mg, 0.24 mmol) was suspended in EtOH and treated with aqueous NaClO₄ solution (60 mg, 0.49 mmol). The dark orange reaction mixture was heated at 60° C for 2 hours. Cooled to room temp, solvent removed and the product was extracted to CH₃CN. The residue obtained from CH3CN was dissolved in deionised water and heated overnight again at 60° C. The red oil obtained after solvent removal on keeping closed for three days yielded the diagua complex as brown red crystalline solid (Yield: 87 mg, 60%). Pale pink blocks were obtained from butanol after a week by vapour diffusion of diethyl ether. Anal.Calcd for C₁₉H₂₃Cl₂CoN₃O₁₁: C, 38.08; H, 3.87; N, 7.01. Found: C, 38.23; H, 2.28; N, 6.80. UV-Vis (λ_{max}, nm; ε, M⁻¹cm⁻¹; H₂O/ MeOH]: 492 (32), 1074 (5). FTIR (KBr, cm⁻¹): 3400, v(-OH₂); 1089, 626, v(ClO₄-); 770, v(pyridyl-CH). ESI-MS (m/z, [L^{OMe}Co(OH₂)(OH]⁺); 463 H₂O): 399 (100%, (87%, [L^{OMe}Co(ClO₄)]⁺); 426 (85%, [L^{OMe}Co(EtOH)(OH]⁺. μ (D₂O, 298 K): 5.04 μB/Co(II). ¹H NMR (D₂O): -14.25, -7.43, 10.73, 15.51, 25.26, 26.17, 46.65, 54.72, 63.68, 146.68, 156.02.

Mn^{II}L^{OMe}Cl₂, 1e. To a pale pink solution of MnCl₂.4H₂O (156.0 mg, 0.79 mmol) in EtOH, L^{OMe} solution (244.3 mg, 0.8 mmol) in EtOH was added drop wise with stirring at room temperature. After stirring for 2 h at RT, the precipitated flesh colour powder was separated and dried (Yield: 310 mg, 90%). Faint pink coloured blocks were obtained from $\mathsf{CH}_2\mathsf{Cl}_2$ after overnight, by evaporation. Anal. Calcd for C19H19Cl2MnN3O: C, 52.92; H, 4.44; N, 9.74. Found: C, 52.56; H, 3.95; N, 9.85. NI^{II}L^{OMe}Cl₂, 1f. To a solution of NiCl₂.6H₂O (85.1 mg, 0.36 mmol) in EtOH, ligand solution (111.2 mg, 0.36 mmol) in EtOH was added drop wise with stirring under N2. The reaction mixture was stirred for two hours and the precipitated apple green product was separated (128.3 mg, 82%). Dark green block shaped crystals were obtained from CH₃NO₂ after a day, by slow evaporation. Anal.Calcd for C19H19Cl2NiN3O: C, 52.46; H, 4.40; N, 9.66. Found: C, 52.18; H, 3.74; N, 9.39. UV-Vis (λmax, nm; ε, M⁻¹ cm⁻¹, CH₂Cl₂): 406 (48), 674 (21), 982 (9), 1312 (6). FTIR (KBr, cm-1): 2930, w, v(C-C); 1604, s, v(C=Npy); 1446, s, v(C=Car); 1012, s, v(C–O). ¹H NMR (500 MHz, CD₃NO₂): 2.09, 4.33, 7.15, 13.45, 22.17, 43.11, 51.25, 113.13, 138.82.

Zn^{II}L^{OMe}Cl₂, 1g. To the colourless solution of ZnCl₂ (101.6 mg, 0.75 mmol) in EtOH, L^{OMe} solution (226.2 mg, 0.74 mmol) in same solvent was added drop wise with stirring at room temperature. Precipitated white solid was separated and dried (Yield: 311 mg, 95%). Anal.Calcd for C₁₉H₁₉Cl₂ZnN₃O: C, 51.67;

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H, 4.34; N, 9.51. Found: C, 51.88; H, 3.82; N, 9.62. ¹H NMR (400 MHz, CDCl₃): 3.88 (3H, s), 4.93 (2H, s), 6.74 (2H, d), 7.04 (1H, d), 7.09 (2H, t), 7.38 (2H, t), 7.44 (1H, d), 7.69 (2H, t), 9.31 (2H, d).

L^{o-}Co^{III}Cl₂. H₂O, 2. To the dark blue solution of 1a (211.3 mg, 0.48 mmol) in CH₂Cl₂, 6M t-BuOOH, (122 uL, 0.73 mmol) was added under N_2 with stirring. The reaction mixture was refluxed at 40°C for 20 h, yielding dark green solution with little grey precipitate. Solvent removed and the sticky grey residue was washed thrice with diethyl ether to remove excess t-BuOOH and any butanol formed. Dried well and the yield of the fine grey powder was noted (195.0 mg, 95%). Parrot green needles were obtained after three days from CH₃CN solution by slow evaporation. Anal.Calcd for C₁₈H₁₆Cl₂CoN₃O: C, 51.45; H, 3.84; N, 10.00. Found: C, 50.98; H, 3.41; N, 9.84. UV-Vis (λ_{max} , nm; ε, M⁻¹ cm⁻¹; CH₃CN): 415 (217), 584 (117). FTIR (KBr, cm⁻¹): 3529, 3404, br, v(-OH₂), 1609, m, v(C=N_{py}); 1585, m, 1480, s, v(C=C_{ar}); 1283, m, v(C–O). ¹H NMR (400 MHz, CD₃CN): 4.63 (2H, d), 5.68 (2H, d), 6.48 (2H, t), 6.74 (1H, t), 7.35 (2H, d), 7.52 (2H, t), 7.61 (1H, d), 7.88 (2H, t), 9.45 (2H, d). ¹³C NMR (400 MHz, CD₃CN): 58.59 (-OCH₃), 60.05 (-CH₂), 121.96 (Py), 122.77 (Py), 123.02 (ar) 127.59 (ar), 128.30 (ar), 129.22 (ar), 136.45 (Py), 139.08 (ar), 148.94 (Py), 159.82 (py).

[CoLo-(OH)]2.Cl0.75l1.25.4H2O.CH3CN, 3. The in situ prepared Co(II) iodo complex 1b (166 mg, 0.27 mmol) was suspended in CH₃CN and millipore H₂O was added till a bright red clear solution forms. The reaction mixture was purged with O_2 and heated overnight at 60°C. Cooled to room temperature and kept open to get dark brown rectangles of 3 (125 mg, 62%) after 3 days. Isolated product was washed well with CH₃CN and H₂O separately, to remove impurities. Dark red needles were obtained after overnight from CH₃CN-H₂O mixture by evaporation. Anal.Calcd for C₃₆H₃₄Co₂I₂N₆O₄: C, 43.84; H, 3.47; N, 8.52. Found: C, 44.28; H, 2.89; N, 8.98. UV-Vis (λ_{max}, nm; ε, M⁻¹ cm⁻¹; CH₃CN+H₂O): 519 (503), 375 (1313). FTIR (KBr, cm⁻¹): 3536, s, v(-OH), 3343, br, v(-OH₂), 1609, s, v(C=N_{py}), 1491, s, 1435 s, v(C=Car); 1246, m, v(C-O). ¹H NMR (CD₃CN+D₂O, 400 MHz): 4.90 (2H, d), 5.90 (2H, d), 6.25 (1H, d), 6.53 (1H, t), 6.70 (1H, m), 6.95 (2H, t), 7.52 (2H, d), 7.65 (1H, d), 7.86 (2H, m), 7.99 (2H, d).

X-ray crystallography

Complex **1a** was crystallised in orthorhombic system with space group $P2_12_12_1$. Asymmetric unit was formed by a molecule of complex and half water molecule. Complex **1b** was crystallised in monoclinic system with space group $P2_1/c$ and the iodo aqua complex **1c** was crystallised in triclinic system with P-1 space group. The asymmetric unit of **1c** consist of a molecule of complex and a $-CIO_4^-$ counter anion which is disordered. The diaqua complex **1d** is crystallised in monoclinic system with space group $P2_1/c$. The asymmetric unit consists of a molecule of complex, two molecules of $-CIO_4^-$ counter anions which are disordered and a molecule of H_2O as solvent of crystallisation. Just as the Co(II) chloro complex **1a**, The Mn(II) chloro complex **1e** also crystallised in orthorhombic system with space group $P2_12_12_1$. The asymmetric unit

contains a molecule of complex and half molecule of the solvent of crystallisation as in **1a**. The Co(III) Chrono Complex **2** was crystallised in orthorhombic system with space group *Pna21*. The asymmetric unit consisted of a molecule of complex and a H₂O molecule as solvent of crystallisation. The Co(III) dihydroxo complex **3** crystallises in orthorhombic system with *Pnma* space group. The complex is highly symmetrical and the asymmetric unit contain just half molecule of complex. The charge is neutralised by 1.36 l-atoms and 0.64 Cl- atoms. In addition, four molecules of H₂O and a molecule of crystallisation.

X-ray data were collected with a Bruker AXS Kappa Apex II CCD diffractometer equipped with graphite monochromated Mo-K α (λ = 0.7107 Å) radiation. The structures were solved by direct methods using SHELXT-2015, and refined by full-matrix least-squares techniques using the SHELXL-2016 computer program. All hydrogen atoms were fixed at chemically meaningful positions. Molecular graphics were generated using diamond programs.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

S. A thanks CSIR, India for a fellowship. We gratefully acknowledge the single-crystal X-ray diffractometer facility funded by SAIF, IIT Madras and Dept. of Chemistry, IIT Madras.

Notes

data **1a**: $C_{19}H_{19}Cl_2CoN_3O_{1.50}$, M = 443.20, [‡]Crystal Orthorhombic, P2₁2₁2₁, a = 9.5758(2) Å, b = 13.8028(3) Å, c = 15.2197(2) Å, V = 2011.63(7), R_{int} = 0.0137, Z = 4, ρ_{cald} = 1.463 g cm⁻³, μ = 1.134 mm⁻¹, F(000) = 908, T = 298(2) K, R(F² > 2 σ) = 0.0207, wR₂ = 0.0514, 3421 independent reflections, 2θ = 50° and 246 parameters, GOF of F^2 = 1.039. For **1b**: $C_{19}H_{19}Col_2N_3O$, M = 618.10, monoclinic, P2₁/c, a = 12.9288(3) Å, b = 9.5177(2) Å, c = 18.2171(5) Å, β = 108.7800(10)°, V = 2122.32(9), R_{int} = 0.0218, Z = 4, ρ_{cald} = 1.934 g cm⁻³, μ = 3.73 mm⁻¹, F(000) = 1180, T = 296(2) K, $R(F^2 > 2\sigma)$ = 0.0275, wR_2 = 0.0619, 3736 independent reflections, $2\theta = 49.98^{\circ}$ and 247 parameters, GOF of F² = 1.058. For 1c': C₁₉H₂₁ClCoIN₃O₆, M = 608.67, triclinic, P-1, a = 9.0682(3) Å, b = 11.6181(4) Å, c = 12.1412(4) Å, α = $103.0870(10)^{\circ}$, β = $104.1930(10)^{\circ}$, γ = $90.1940(10)^{\circ}$, V = 1205.53(7), R_{int} = 0.0176, Z = 2, ρ_{cald} = 1.677 g cm⁻³, μ = 2.141 mm⁻¹, F(000) = 602, T = 296(2) K, $R(F^2 > 2\sigma) = 0.0312$, $wR_2 =$ 0.0774, 4420 independent reflections, 2θ = 50° and 327 parameters, GOF of F^2 = 1.049. For 1d': $C_{19}H_{25}Cl_2CoN_3O_{12}$, M = 617.25, monoclinic, P21/c, a = 10.8936(5) Å, b = 19.2866(10) Å, c = 13.2468(6) Å, β = 112.981(2), V = 2562.3(2), R_{int} = 0.0356, Z = 4, ρ_{cald} = 1.600 g cm⁻³, μ = 0.944 mm⁻¹, F(000) = 1268, T = 293(2) K, R(F² > 2σ) = 0.0401, wR₂ = 0.1019, 4555 independent reflections, $2\theta = 49.2^{\circ}$ and 430 parameters, GOF of $F^2 = 1.083$.

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For 1e: $C_{19}H_{19.50}Cl_2MnN_3O_{1.25}$, M = 435.71, orthorhombic, P2₁2₁21, a = 9.6360(3) Å, b = 13.9208(4) Å, c = 15.4915(5) Å, V = 2078.04(11), Z = 4, ρ_{cald} = 1.393 g cm⁻³, μ = 0.906 mm⁻¹, F(000) = 894, T = 296(2) K, $R(F^2 > 2\sigma) = 0.0237$, $wR_2 = 0.0526$, 3655 independent reflections, $2\theta = 50^{\circ}$ and 251 parameters, GOF of F^2 = 1.047. For **2**: $C_{18}H_{18}Cl_2CoN_3O$, M = 438.18, orthorhombic, Pna2₁, a = 13.7658(5) Å, b = 15.0676(6) Å, c = 8.9198(3) Å, V = 1850.12(12), Z = 4, ρ_{cald} = 1.573 g cm⁻³, μ = 1.234 mm $^{-1},\ F(000)$ = 896, T = 296(2) K, $R(F^2>2\sigma)$ = 0.0245, wR₂ = 0.0599, 3098 independent reflections, 2θ = 50.96° and GOF of $F^2 = 1.053$. 243 parameters, For C₃₈H₄₅Cl_{0.64}Co₂I_{1.36}N₇O₈, M = 1040.71, orthorhombic, *P*nma, a = 16.0730(4) Å, b = 16.5200(4) Å, c = 16.8530(4) Å, V = 4474.91(19), R_{int} = 0.0322, Z = 4, ρ_{cald} = 1.545 g cm⁻³, μ = 1.771 mm⁻¹, F(000) = 2091, T = 293(2) K, $R(F^2 > 2\sigma) = 0.0555$, $wR_2 =$ 0.1659, 4083 independent reflections, 2θ = 49.60° and 317 parameters, GOF of $F^2 = 1.071$.

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