Inorganica Chimica Acta 363 (2010) 3798-3802

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and characterization of a stable paramagnetic hexacoordinated oxochromium(IV) complex with dianionic tetradentate Schiff base ligand salen

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ARTICLE INFO

Article history: Received 10 March 2010 Received in revised form 7 July 2010 Accepted 12 July 2010 Available online 13 August 2010

Keywords: Oxochromium(IV) complex Schiff base ligand Salen EPR and electronic spectra Cyclic voltammetry Electrochemistry

ABSTRACT

A paramagnetic octahedral oxochromium(IV) complex with dianionic tetradentate ligand salen (where H₂salen is *N*,*N*-bis(salicylidene)-1,2-ethylenediamine) has been synthesized. This compound [CrO(OH₂) (salen)] (**1**) is characterized by elemental analysis, magnetic moment measurement, IR, UV-Vis and EPR spectroscopic studies. Measured room temperature (RT) magnetic moment value is 2.96 BM for **1** indicates a d² system with a triplet ground state. The magnetic moment value rules out a large spin–orbit coupling. The RT and LNT powder EPR spectra of **1** in X-band clearly shows two lines, one around g = 1.965 and the other with larger intensity at $g = 4.26 \pm 0.10$. The first line at g = 1.965 corresponds to the $|0> \leftrightarrow |\pm 1>$ transition from the Kramers doublet $|\pm 1>$, while the broad and intense line at low field with the g-value of 4.26 ± 0.10 is due to the forbidden transition $|-1> \leftrightarrow |+1>$. Compound **1** displays two successive reductions at -0.76 and -1.63 V (versus Ag/AgCl), respectively, while it undergoes only one irreversible oxidation as evident from the well-defined anodic wave at +1.48 V in its cyclic voltammogram.

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1. Introduction

Schiff base complexes of Cr(III) involving the ligand H₂salen (*N*,*N*'-bis(salicylidene)-1,2-ethylenediamine) and related ligands derived from different substituted salen are widely used in the catalysis of various organic reactions [1–12]. Also these Cr(III) Schiff base complexes are used in the construction of artificial metalloenzymes [13-15] in bioinorganic chemistry. These Cr(III) Schiff base compounds are found to be capable of catalyzing oxygen atom transfer from reagents such as iodosylbenzene, H₂O₂, etc. to various organic substrates [2,3,16-18]. From the mechanistic studies of these oxygen atom transfer reactions it has been shown that initially a [Cr^VO(Schiff base)]⁺ complex is formed from the reaction of e.g., iodosylbenzene and the Cr(III) Schiff base complex and then there is an electrophilic attack on the substrate by this oxochromium(V) cation. Adam et al. [16] have suggested that a $[Cr^{IV}(OAc)(salen)]^+$ species other than the $[Cr^{V}O(salen)]^+$ complex may also be involved in the catalytic oxidation based on their mechanistic studies of chemoselective oxidation of alcohols to carbonyl products with iodosobenzene diacetate mediated by chromium(III)(salen) complexes. Some of these [CrVO(salen)]+ complexes are synthesized from the corresponding [Cr^{III}(salen)]⁺ complexes and their properties have been studied [2,3,16-18]. Srinivasan and Kochi have reported [3] the synthesis and molecular structures of a number of stable oxochromium(V)salen cations from the corresponding Cr(III)salen cations treated with a slight excess of iodosylbenzene. This oxochromium(V)salen compound on one-electron reduction either electrochemically or chemically produced the corresponding neutral oxochromium(IV)salen species which was found to be transient character [3]. We have been able to stabilize and isolate an oxochromium(IV)salen complex from methanol solution following a similar procedure for the preparation of the recently reported oxochromium(IV)salophen (where H₂salophen is N,N'-bis(salicylidene)-1,2-phenylenediamine) complex, [CrO(OH₂)(salophen)] (2) [19]. Here, we report the magnetic, spectroscopic and electrochemical properties of this compound.

2. Results and discussion

2.1. Infrared spectra

The infrared and far infrared spectra of the chromium complex $[CrO(OH_2)(salen)]$ (1) have been recorded using KBr and polyethylene pellet, respectively. The broad band around 3450 cm⁻¹ region indicates the presence of water [20] in complex 1. The very strong



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and sharp band at 1630 cm⁻¹ due to v(C=N) in the IR spectrum of the free ligand is found to be shifted to 1620 cm⁻¹ in complex **1**. The medium but prominent band at 1025 cm⁻¹ in the spectrum of complex **1** may be attributed to v(C=O) [19–21]. This band is absent in the IR spectrum of the corresponding *trans*-[Cr^{III}(OH₂)₂ (salen)]⁺ reported by Srinivasan and Kochi [3]. Two medium intensity bands at 477 and 457 cm⁻¹ in the far infrared spectrum of **1** may be assigned as v(Cr-N) while a medium intensity peak at 316 cm⁻¹ may be assigned as v(N-Cr-N) [20,22]. The bands at 421, 395 and 384 cm⁻¹ may be originating due to v(Cr-O) while a medium intensity peak at 213 cm⁻¹ may be assigned as v(O-Cr-O) [20].

2.2. Magnetic moment

The room temperature magnetic susceptibility measurement shows that the μ_{eff} value for complex 1 is 2.96 BM (at 25 °C). Since the spin–orbit coupling constant value reported for Cr(IV) in the literature [23] is around 160 cm⁻¹, we can interpret this room temperature susceptibility value for 1 as indicating two unpaired electrons and ³F to be the ground state for the free ion and hence supposed to be a ${}^{3}T_{1g}(F)$ for the complex (in O_{h}) [24–26]. However, the complex as indicated by its electronic and EPR spectra is expected to be tetragonal with low symmetry D_{4h} , and the ${}^{3}T_{1g}$ (in O_{h}) will be split into E_{g} and A_{2g} (in D_{4h}) [25]. Thus, in D_{4h} symmetry, d_{xz} , d_{yz} transform as E_{g} containing an electron in each orbital.

The brown compound **1** is readily soluble in methanol, toluene, CCl_4 , CH_3CN , CH_2Cl_2 , DMF; poorly soluble in diethyl ether, and insoluble in water. Conductivity measurement of **1** in CH_3CN solution shows the compound is non-electrolyte. Thus, based on its elemental analysis, IR spectrum, magnetic moment value and conductivity measurement, and in analogy to trnas-[$Cr(OH_2)_2(salen)$]⁺, the proposed structure for **1** is shown in Fig. 1 below.

2.3. Electronic spectra

The electronic spectrum of $[CrO(OH_2)(salen)]$ (1) has been recorded in CH₃CN solution. The spectrum is shown in Fig. 2, and the electronic spectral band positions are listed in Table 1. The electronic spectral band positions of the corresponding reported $[CrO(OH_2)(salophen)]$ (2) [19] are also presented for comparison.

The two new lower energy bands at 560 nm ($\varepsilon = 131$) and 485 nm ($\varepsilon = 248$) appeared in the visible region of the electronic spectrum of complex **1** in CH₃CN are absent in the spectrum of the free ligand H₂salen. These two bands may be attributed to d– d transitions [26–28]. The other expected higher energy d–d transition [26,28] is probably masked by the strong CT transitions. The higher energy bands in the region between 218 and 315 nm are comparable to those in the free ligand spectrum, and are most likely associated with intraligand $\pi \rightarrow \pi^*$ transitions [29].

It is to be noted here that the lowest energy d–d transition for the corresponding reported [19] [CrO(OH₂)(salophen)] (**2**) in CH₃CN was observed at 600 nm (ε = 116). The next higher energy band appeared at 480 nm (ε = 1267) exhibited a large solvatochromic shift to 464 nm (ε = 1874) in DMF and was attributed to a charge transfer (CT) transition [19]. This band is found to be more



Fig. 1. Structure of compound 1.



Fig. 2. Electronic spectrum of [CrO(OH₂)(salen)] (1) in CH₃CN.

intense compared to the weak d–d transition observed at 485 nm (ε = 248) for **1**. This could be due to substitution of the ethylenediamine bridge of **1** with *o*-phenylenediamine in **2** which causes a larger π charge delocalization in the latter resulting in a more intense band which is CT in nature. The second and third expected d–d transitions for **2** were obscured by the strong CT transitions [19].

It may be pointed out here that in the UV–Vis spectrum of the reported chromium(III) complex with the same ligand salen, $[Cr(OH_2)_2(salen)]ClO_4$, the lowest energy band was reported by Kanthimathi et al. [30,31] at 485 nm (ε = 275) while that for other $[Cr(OH_2)_2(salen)]^+$ cations reported by Coggon et al. [32] were observed in the range 482–500 nm; and for the five coordinate oxochromium(V) cation, $[CrO(salen)]^+$ [3] the lowest energy band was observed at 566 nm (ε = 1200), respectively, clearly reflecting the differences in their electronic structures with that of compound **1** presumably containing a Cr(IV) ion.

2.4. EPR results

The powder EPR spectra for the complex **1** were recorded at Xband frequency both at RT and LNT (Fig. 3a–c) and also at Q-band frequency at RT (Fig. 4). When this compound is dissolved in DMF, this solution does not exhibit any EPR signal at RT. However, when this DMF solution is frozen as a glass at LNT, strong EPR signal is observed (Fig. 3d). It may be pointed out here that the powder EPR spectrum displayed by compound **1** at X-band frequency is found to be drastically different from the X-band EPR spectrum of [Cr(OH₂)₂(salen)]Cl reported by Koner et al. which displayed an intense line at g = 1.965 [33].

The EPR of the chromium (IV) complexes can be interpreted by the simple Spin Hamiltonian,

$$\bar{H} = \beta B \cdot g \cdot S + S \cdot D \cdot S \tag{1}$$

with S = 1, g and D being tensors and the contributions from hyperfine interaction being neglected. Compound 1 has been studied using powder both at RT and LNT (Fig. 3a and c) and frozen DMF solution (Fig. 3d) at LNT in X-band, and powder at RT in Q-band (Fig. 4). Measurement at two different frequencies gives us a clear idea on the understanding of the origin of these unusually broad lines. The RT and LNT powder spectra in X-band clearly present two lines, one around g = 1.965 and the other with larger intensity at $g = 4.26 \pm 0.10$ what could be termed as a half-field line. The first line at g = 1.965 corresponds to the $|0 > \leftrightarrow| \pm 1>$ transition from the Kramers doublet |±1>. However, the broad and intense line at low field, i.e., with the g-value of 4.26 ± 0.10 is due to the forbidden transition $|-1 > \leftrightarrow|+1$. While the large intensity is caused by fairly large D value, substantial broadening could be caused by dipolar interaction between nearby paramagnetic species noting that the powder is a condensed paramagnetic lattice. The intensities of such

Table 1

Electronic spectral band positions in nm (cm⁻¹) of (a) [CrO(OH₂)(salen)] (1) in CH₃CN and (b) [CrO(OH₂)(salophen)] (2) in CH₃CN [19].

(a) [CrO(OH ₂)(salen)] (1) in CH ₃ CN				(b) [CrO(OH ₂)(salophen)] (2) in CH ₃ CN			
Band position		ϵ , M^{-1} cm ⁻¹	Assignments	Band position		ϵ , M^{-1} cm ⁻¹	Assignments
nm	(cm^{-1})			nm	(cm^{-1})		
560	(17,857)	131	$d \rightarrow d$	600	(16,667)	116	$d \rightarrow d$
485	(20,618)	248	$d \rightarrow d$	480	(20,833)	1267	CT
391	(25,575)	2649	СТ	373	(26,810)	3588	CT
315	(31,746)	3607	$\pi ightarrow \pi^{*}$	330	(30,303)	6405	$n \rightarrow \pi^{*}$
272	(36,765)	8259	$\pi ightarrow \pi^{*}$	316	(31,646)	7074	$\pi ightarrow \pi^{*}$
250	(40,000)	16,543	$\pi ightarrow \pi^{*}$	292	(34,247)	8683	$\pi ightarrow \pi^{*}$
218	(45,872)	18,918	$\pi ightarrow \pi^{*}$	207	(47,619)	20,025	$\pi ightarrow \pi^{*}$



Fig. 3. EPR spectra of [CrO(OH₂)(salen)] (1) recorded at X-band frequency (a) Powder at RT with DPPH, (b) Powder at RT without DPPH, (c) Powder at LNT without DPPH, and (d) Frozen glass in DMF at LNT without DPPH.



Fig. 4. Powder EPR spectrum of $[CrO(OH_2)(salen)](1)$ recorded at Q-band frequency at RT without DPPH.

forbidden transitions ($\Delta Ms = \pm 2$) are proportional to $(D/hv)^2$ and from its intensities it can be guessed that the 2D value could be just comparable to the X-band frequency. The Q-band powder spectrum at RT very clearly supports the above interpretation: (i) the clearly separated anisotropic lines at higher frequency due to $g_{II} = 1.734$ and $g_{\perp} = 1.997$ giving a g-average of 1.91, close to 1.965 decided from an unresolved spectrum in X-band; (ii) as expected, the above referred forbidden line ($\Delta Ms = \pm 2$) at $g \sim 4.3$ has a much reduced intensity in correspondence to measurement at higher frequency. We estimate from the relative intensities of this line at two different frequencies a D value of ~0.3 cm⁻¹.

2.5. Electrochemical results

The redox behavior of compound **1** has been studied in CH₃CN containing 0.1 M Et₄NClO₄ (TEAP) at a glassy carbon working electrode, platinum auxiliary electrode, and a Ag/AgCl reference electrode using cyclic voltammetry (CV). The cyclic voltammogram shows two cathodic waves at -0.76 and -1.63 V, respectively (Fig. 5a). The reductive response at -0.76 V is found to be coupled to a weak and broad anodic peak (figure not shown) around -0.65 V (Δ E_P = 110 mV) suggesting a quasi-reversible electron



Fig. 5. Cyclic voltammogram of $[CrO(OH_2)(salen)]$ (1) in CH₃CN containing 0.1 M TEAP at a scan rate of (a) 20 mV s⁻¹, (b) 100 mV s⁻¹.

transfer process for this step. For an initial positive scan, on the other hand, a well-defined oxidative wave is observed at +1.48 V. No corresponding cathodic peak is observed on scan reversal (Fig. 5b). Moreover, this anodic wave is shifted to +1.65 V in the second cycle and is found to be very broad (figure not shown) indicating oxidative degradation of the compound. Similar oxidative degradation was also observed for the corresponding salophen complex **2** [19].

In the electrochemical studies of $[Co^{II}(salen)]$ in DMSO using cyclic voltammetry and coulometry by Ortiz and Park [34] two nearly reversible redox couples were observed at 0.03 and -1.13 V (versus Ag/AgCl) corresponding to Co(III)/Co(II) and Co(II)/Co(I), respectively. Thus the first reduction observed at -0.76 V (versus Ag/AgCl) for **1** in the present case is associated with metal-centered Cr(IV)/Cr(III) reduction. It should be noted here that the free ligand H₂salen is reduced only at a potential -1.77 V (versus SCE) as observed by Isse et al. [35] from their electrochemical studies for the reduction of H₂salen in DMF. The Cr(IV)/Cr(III) couple for the reported tetraphenylporphyrinato oxochromium(IV) compound [CrO(TPP)] in CH₂Cl₂ was observed at -1.12 V (versus SCE) [36]. The second reduction waves for **1** and **2** are surprisingly found to be at the same potential ca. -1.63 V (versus Ag/AgCl) under similar experimental condition strongly

suggesting that the cathodic wave observed at -1.63 V (versus Ag/AgCl) for **1** is also associated with a metal-centered reduction and is most likely due to the Cr(III)/Cr(II) couple. The Cr(III)/Cr(II) couple for the reported *trans*-[Cr(OH₂)₂(salen)]⁺ in DMSO was observed at -1.34 V (versus SCE) [30,31], for [CrCl(TPP)] in CH₂Cl₂ it was observed at -1.10 V and for [CrO(TPP)] in CH₂Cl₂ it was found at -1.51 V (versus SCE), respectively [36].

The oxidative degradation of 1 may be explained as follows. It should be mentioned here that for the recently reported [CrO(OH₂)(salophen)] (2) an initial positive scan yielded two irreversible oxidation waves at +1.03 and +1.47 V (versus Ag/AgCl), respectively, but the second cycle yielded only a very broad oxidation wave around +1.50 V with large anodic current indicating oxidative degradation of the compound followed by electrode pollution [19]. It appears from the cyclic voltammogram of 2 that it undergoes two successive metal centered oxidations leading to a Cr(VI) species probably followed by a chemical change, thereby making the process completely irreversible and possibly with the electrode depositions of this oxidized species. The oxidation wave observed for 1 is found to be even at a slightly higher positive potential than that of the second oxidation peak for 2. Thus it is possible that compound 1 undergoes an irreversible two-electron oxidation, as evident from high positive potential with large anodic current, directly to a Cr(VI) species followed by some chemical change and electrode deposition. The postulation of a single step two-electron oxidation for 1 is also rationalized from the fact that the reported Cr^VO/Cr^{IV}O potential of the salen complex, [CrO(salen)]⁺ in CH₃CN, ($E_{1/2}$ = +0.47 V versus SCE), is at much less positive potential [3], and it is highly unlikely that the coordination of a water molecule trans to the oxo group in the corresponding Cr(IV) compound (1) will cause such a drastic change in the Cr^{IV}O/Cr^VO oxidation potential, though it is apparent that the presence of a water molecule trans to the oxo group has dramatically changed the stability of **1** in the present case as evident from the following observations.

The electrochemical behavior of the oxochromium(V)salen cation in dimethyl sulfoxide solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte was studied by Srinivasan and Kochi using cyclic voltammetry (CV). The compound displayed a well-defined quasi-reversible one-electron reduction, but the cathodic wave was found to diminish upon repetitive CV scans, indicative of the gradual disappearance of the oxochromium cation. The reductive degradation of oxochromium(V) was also observed in acetonitrile solution and the large anodic current observed on the reverse scan was symptomatic of electrode pollution and a brown deposit caused this electrode deposition. They also found a similar brown precipitate that was formed during the chemical reduction of the oxochromium(V) cation with ferrocene. This transient brown species was tentatively ascribed to a neutral chromium(IV) derivative by these researchers. Thus it appears that the oxoCr(IV) species generated electrochemically or chemically from the corresponding oxochromium(V)salen cation was unstable under those experimental conditions.

3. Conclusions

It has been possible to stabilize a paramagnetic oxoCr(IV) complex in the solid state with the Schiff base ligand H₂salen. Complex 1 is remarkably stable and no apparent decomposition or transformation to other compounds is observed for this compound. This observation is consistent with its low reduction potential. It is very puzzling that the coordination of a water molecule trans to the oxo group has resulted in such a dramatic change in its stability as well as in its redox behavior. However, the Cr(IV) oxidation state in the

compound **1** is clearly evident from the magnetic moment and its other properties which are highly inconsistent with that of the corresponding reported Cr(III) compound and oxochromium(V) compound. Several attempts to prepare single crystal for this Cr(IV) compound was unsuccessful, so X-ray structural determination has not been possible. So, all the studies were confined to powder samples and solutions.

4. Experimental

4.1. Chemicals

Salicylaldehyde and ethylenediamine (reagent grade) were obtained from Aldrich and were used without further purification. Absolute ethanol (GR) was obtained from Merck, Germany. Potassium dichromate (GR) was obtained from Sarabhai Chemicals, India. Methanol (GR), dichloromethane (GR), toluene (GR), DMF (GR) and acetonitrile (HPLC) were obtained from Merck, India. All other chemicals were of reagent grade and were used as such. Tetraethyl ammonium perchlorate (TEAP) was prepared using a method described in literature [37].

4.2. Preparation of the Schiff base ligand H₂salen

This ligand was prepared by the reaction of 6.1 g (0.05 mol) of salicylaldehyde with 1.5 g (0.025 mol) of ethylenediamine in dry ethanol, and the yellow compound was purified by recrystallization from ethanol. *Anal.* Calc. for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.80; H, 6.08; N, 10.52%. Mp 126 °C. UV–Vis (CH₂Cl₂) [λ_{max} , nm]: 257, 318. IR (KBr pellet, cm⁻¹): 3450br v(O–H), 1635s v(C=N), 1283s v(C–O).

4.3. Preparation of [CrO(OH₂)(salen)] (1)

A 0.294 g (1 mmol) sample of solid potassium dichromate was added to 0.536 g (2 mmol) of H₂salen ligand in 50 mL of methanol with constant stirring at room temperature (RT). Stirring was continued for 90 h while the solution turned from yellow to red brown. The solution was filtered through a G4 sintered glass crucible and the red brown filtrate was evaporated to dryness in vacuum. The brown solid thus obtained was stirred at RT with 100 mL of toluene for 1 h in a stoppered conical flask and filtered. The red brown filtrate was kept for slow evaporation at RT when a brown compound was obtained. This was filtered and washed thoroughly with diethyl ether. This compound was then recrystallized from CH_2Cl_2 and *n*-hexane. *Anal.* Calc. for $C_{16}H_{16}N_2O_4Cr$: C, 54.53; H, 4.58; N, 7.95. Found: C, 55.02; H, 4.61; N, 8.13%.

4.4. Physical measurements

Elemental analyses (C, H and N) were performed in a Perkin–Elmer 240 CHNS/O analyzer. Infrared spectra were measured with a Jasco IR report-100 spectrophotometer using KBr pellet. Far infrared spectra were recorded with a Bruker IFS 66 V spectrometer using polyethylene pellet. Static susceptibility measurements were made with the help of a Princeton Applied Research Vibrating Sample Magnetometer Model 155. Electronic spectra were recorded with a Jasco V-570 UV/Vis/NIR spectrophotometer using a pair of matched quartz cell of path length of 1 cm. EPR spectra were recorded using a Varian E-112 X/Q-band spectrometer. RT solution EPR spectra were recorded in liquid nitrogen temperature (LNT) using a quartz dewar. Diphenylpicrylhydrazyl (DPPH) was used as internal field marker. Electrochemical measurements were done with the help of a PAR Versastat-II electrochemistry system at 298 K under nitrogen atmosphere. A standard three-electrode cell consisting of a glassy carbon working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode was used. Tetraethyl ammonium perchlorate (TEAP) was used as supporting electrolyte.

Acknowledgments

A.P.K. and M.K. thank Professor Sakti Prasad Ghosh, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata for help with the elemental analysis and magnetic moment measurement. A.P.K. thanks Dr. Shyamal Kumar Chattopadhyay of the Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah for help with the electrochemical studies. We thank the SAIF, IIT-Madras for providing EPR and far-infrared facilities. P.T.M. thanks the DST, Govt. of India, respectively for the Research Scheme (SP/S1F18/2000) and Ramanna Fellowship (SR/S1/RFIC-02 /2006).

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