Dimerisation of Fe bisdithiolene complexes; An electrochemical study

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Abstract

An electrochemical study of the dimerization of the $[\text{Fe}(\text{qdt})_2]^{2-}$ and $[\text{Fe}(\text{mnt})_2]^{2-}$ iron complexes in dichloromethane, dimethylformamide and acetonitrile, by cyclic voltammetry and ionic conductivity is reported. Ionic conductivity measurements indicate an increased dissociation of the dimers in dimethylformamide and acetonitrile compared to dichloromethane. In $[\text{Fe}(\text{mnt})_2]$ in dichloromethane, only dimer oxidation processes are observed in cyclic voltammetry, while in $[\text{Fe}(\text{qdt})_2]$ both dimeric and monomeric species are involved in redox processes. In acetonitrile and DMF the observed processes correspond to the dissociated monomeric species only. This study demonstrates the major role of the nature of the solvent in the monomer/dimer equilibrium in solution, which appears more easily shifted towards dissociation in the complex with qdt ligands than with mnt and is favoured by N- and O-containing solvents.

Keywords: Iron bisdithiolenes • Cyclic voltammetry • Dimerisation equilibrium • Ionic conductivity

Introduction

Transition metal dithiolene complexes, due to their structural diversity of structures, vivid redox behaviour and rich photo-activity have been a topic of continued research interest for almost 40 years, playing an increasingly important role in different fields such as electrical and magnetic materials,[1,2] catalysis,[3,4] sensors and bio-inorganic chemistry.[5]

In spite of a very rich variety of coordination geometries and oxidation states exhibited by transition metal bisdithiolene complexes, the vast majority of iron complexes with these dithiolene ligands (L) in the solid state have been mostly restricted to a dimerised monoanionic state, formally Fe(III), where these Fe(III) bisdithiolene complexes adopt a square pyramidal, 4+1, Fe coordination geometry due to the formation of dimeric arrangements of distorted square planar $[\text{FeL}_2]^-$ units, $[\text{Fe}_2\text{L}_4]^{2-}$. [6,7,8,9,10,11] A search in the Cambridge crystallographic data base showed that the basal Fe-S bond distances in these dimers are located within the range 2.215-2.255 Å, while the apical Fe-S bond distances lie in the range 2.465-2.515 Å. The first, exception to this dimerisation conformation in Fe bisdithiolene complexes was recently provided by a tetrabutylammonium salt of an iron bi-quinoxaline-2,3-dithiolate (qdt) complex, $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{qdt})_2]$, which showed in solid state a perfect square planar configuration.[12] This square planar coordination is also the geometry presented by all monoanionic Au(III) bisdithiolene complexes,[6,7] where the intramolecular Au-S bond lengths are observed in the range 2.215-2.255 Å with the shortest intermolecular $\text{Au}\cdots\text{S}$ contact strongly dependent on the crystal packing pattern, but always well above the sum of Van der Waals radius.

The rare square planar Fe coordination in (n-Bu₄N) [Fe(qdt)₂] with well isolated complexes was associated with specific cation interactions stabilizing the square planar configuration and hampering the usual dimerization, also found with this ligand in the salt with the (Ph)₄As (TPAs) cation.[5] Another monomeric square planar Fe complex, with the anisyl substituted dithiolene ligand, S₂C₂(p-anisyl)₂, was soon after obtained also in the solid state, but as a mixed crystal, and in solution it was found to be in equilibrium with the corresponding dimer.[13] More recently Weighardt and co-workers reinvestigated the undimerised salt (n-Bu₄N) [Fe(qdt)₂], and obtained additional evidence for the existence in solution of a delicate equilibrium between [Fe(qdt)₂]⁻ monomer and [Fe(qdt)₂]₂²⁻ dimers.[14] Previous work in Fe and Co bisdithiolene chemistry suggested that this dimerisation equilibrium depends on the nature of the solvents.[15,16,17] Under these circumstances the question whether the rare example of the square configuration obtained in (n-Bu₄N) [Fe(qdt)₂] is due to the nature of the qdt ligand, as suggested by other recent examples of more weakly dimerised [Fe(qdt)₂]₂ in some salts,[17] or if it results from particular anion-cation interactions, remains not clear.

In this paper we report a detailed electrochemical study of the dimerization of the [Fe(qdt)₂]₂²⁻ and [Fe(mnt)₂]₂²⁻ iron complexes in various solvents by cyclic voltammetry and ionic conductivity measurements (mnt=malonitrile dithiolate or 2,3-dimercapto-2,3-butenedinitril) aimed at understanding the role of the ligands and solvents in the dimerisation of Fe bisdithiolene complexes. This study shows that the degree of dissociation of these complexes is strongly dependent on the nature of the solvent, the solvents containing N atoms capable to coordinate to Fe strongly favouring the dissociation, which appears more pronounced with the qdt than with the mnt ligand.

Materials and methods

(*n*-Bu₄N) [Fe(mnt)₂], (*n*-Bu₄N) [Fe(qdt)₂] and (TPAs) [Fe(qdt)₂] were prepared and purified following previously described procedures.[12,18] All solvents (acetonitrile, dichloromethane (DCM) and dimethylformamide (DMF)) were distilled and dried just prior to their use using standard procedures.[19]

Cyclic voltammetry was performed at room temperature in 10⁻³ M solutions of the complexes with 10⁻¹ M (*n*-Bu₄N) PF₆ (> 99% Fluka p.a.) as supporting electrolyte, in a single compartment three-electrode cell using a potentiostat (BAS Cell power, CV – 50W software) system under a personal computer control. A platinum disk electrode (0.12 cm²) was used as working electrode. It was polished with 0.05 mm alumina on micro-cloth, thoroughly rinsed with distilled water and acetone prior to use in the electrochemical experiments. The counter electrode was a platinum wire and a silver-silver ion electrode (0.01 M AgNO₃, 0.1 M (*n*-Bu₄N)PF₆) immersed in acetonitrile was used as pseudo-reference. The Ag⁺ ion electrode was separated from the bulk solution by a VycorTM frit. Experiments were conducted under nitrogen atmosphere. All the potentials presented in this work are referred to this pseudo-reference electrode.

Ionic conductivity measurements were performed in 10⁻³ M solutions thermostatised at different temperatures, using a Techno, model 4520, conductimeter.

Results and discussion

The degree of dissociation of the iron complexes in solution can be inferred from measurements of ionic conductivity and comparing results of the Au analogues which are well known to be fully dissociated. Indeed so far all gold monoanionic bisdithiolene complexes have been reported only as isolated square planar coordinated species.[6,7,8] As seen in Table 1 the

conductivity results strongly depend on the nature of the solvent. In dichloromethane there is a significant difference between the conductivity of the Au and Fe compounds for both ligands, which is interpreted as a consequence of the formation of bulkier and less mobile dimeric $[\text{Fe}(\text{S}_2\text{L})_2]^{2-}$ species. The dependence of $[\text{Fe}(\text{qdt})_2]^-$ conductivity in dichloromethane with temperature, approaching that of $[\text{Au}(\text{qdt})_2]^-$, points to a weaker degree of dimerisation upon heating, (dissociation is favoured by higher temperature).

The difference between the ionic conductivity of Fe(III)-bis-dithiolene salts and the gold analogues is much less significant in acetonitrile and DMF, indicating that in these solvents the dimers tend to be dissociated. In acetonitrile the ionic conductivities of the $[\text{Au}(\text{qdt})_2]^-$ and $[\text{Fe}(\text{qdt})_2]^-$ salts are within experimental uncertainty equal indicating that both are fully dissociated. This difference may however be underestimated by the possible presence of conducting impurities, namely Fe hydroxides $\{\text{Fe}^{\text{III}}(\text{OH})\text{O}\}$ which in qdt salts are known to be difficult to remove upon recrystallisation.[14] With the mnt ligand these differences become more significant indicating a smaller degree of dimerisation that decreases at higher temperatures. This certainly results from the iron coordination ability of the nitrogen and oxygen atoms in these solvents, which stabilize the monomers and displace the equilibrium towards dissociation, confirming evidence previously mentioned in other complexes.[15,16,17] These differences in DMF for complexes both with mnt and qdt ligands, are similarly negligible. These results clearly indicate that dissociation equilibrium C_1 is primarily driven by solvent interactions.

Table 1. Molar conductivity Λ_m ($10^2 / \mu S m^2 mol^{-1}$) of TPAs[Au(qdt)₂] vs. TPAs[Fe(qdt)₂] and TBA[Au(mnt)₂] vs. TBA[Fe(mnt)₂] at different temperatures and solvents (dichloromethane-DCM, acetonitrile and dimethylformamide-DMF) indicated.

Compound	Solvent	25 °C	35 °C	50 °C
TPAs[Au(qdt) ₂]	DCM	41.0	42.8	-
TPAs[Fe(qdt) ₂]	DCM	26.5	33.2	-
TBA[Au(mnt) ₂]	DCM	58.3	60.1	-
TBA[Fe(mnt) ₂]	DCM	18.7	19.0	-
TPAs[Au(qdt) ₂]	Acetonitrile	119.3	-	144.5
TPAs[Fe(qdt) ₂]	Acetonitrile	111.4	-	144.5
TBA[Au(mnt) ₂]	Acetonitrile	167.5	-	181.0
TBA[Fe(mnt) ₂]	Acetonitrile	149.0	-	171.0
TPAs[Au(qdt) ₂]	DMF	66.1	-	100.5
TPAs[Fe(qdt) ₂]	DMF	61.6	-	99.0
TBA[Au(mnt) ₂]	DMF	75.9	-	99.0
TBA[Fe(mnt) ₂]	DMF	72.5	-	88.0

The degree of dissociation of these iron complexes in different solvents can be also assessed by cyclic voltammetry. Indeed the electrochemical behavior of [Fe(mnt)₂]⁻ and [Fe(qdt)₂]⁻ is also strongly dependent on the solvent, as shown in Figure 1.

Fig. 1. Cyclic voltammograms of $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{qdt})_2]$ (red) and $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{mnt})_2]$ (black) 10^{-3} M solutions in a) dichloromethane b) acetonitrile and c) dimethylformamide, on a platinum electrode at $\nu = 0.10 \text{ Vs}^{-1}$. The potential sweep was started from the open circuit potential in the cathodic direction.

Before any attempt to interpret the cyclic voltammetry results it is important to consider all possible chemical equilibria and electrochemical reactions which may occur in solution, some of them shown in Scheme 1. Part of these reactions, namely the two electron reduction of the $[\text{Fe}_2\text{L}_4]^{2-}$ dimers to form dianionic monomers $[\text{FeL}_2]^{2-}$, and the subsequent oxidations of the dimers $[\text{Fe}_2\text{L}_4]^{2-}$ up to monoanionic, neutral, and even cationic dimeric species, (at potentials $E^0_{1/2}$, $E^1_{1/2}$, $E^2_{1/2}$, $E^3_{1/2}$, respectively in scheme 1) have been previously considered in several studies of iron bis-(dithiolene) complexes, especially in cases where these species could be isolated.^{20,21} However these studies, which were made mainly in dichloromethane, never considered the possible equilibria C_1 and C_2 between dimers and monomers and the monomer

redox processes, (shown at potentials $E_{1/2}^5$, $E_{1/2}^6$ in the lower part of scheme 1), which are expected to be also present in solvents favoring dimer dissociation.

Scheme 1. Possible equilibria and electrochemical reactions involving the iron-bisdithiolene complexes.

In dichloromethane both complexes reveal in cyclic voltammetry an apparently similar electrochemical behavior, with two anodic irreversible pair of waves and one cathodic process at negative potentials that seems to be more reversible in $[\text{Fe}(\text{mnt})_2]$. However the anodic behaviour of these two species with increasing sweep rate is distinct pointing to different mechanisms. In the case of $[\text{Fe}(\text{mnt})_2]^-$, the shape of the voltammogram is typical of two consecutive oxidations occurring at close potentials. It can be seen that i_{p2} is always higher than i_{p1} (Fig. 2) on the time scale of the experiments. The graphical representations of the anodic peak currents against the mean square root of sweep rate, plotted on the inset of figure 2, reveal that process 1 is controlled by diffusion as expected for an irreversible system where the electroactive species are in the bulk of the solution for a non-stirred electrode, ruling out any possible experimental complications, common in platinum/sulphide complexes interfaces, such as adsorption processes.

All these findings point to the absence of chemical equilibria during the direct potential scan. Furthermore, since the dimer is the initial species in solution, as suggested by the conductivity measurements, the processes 1 and 2 can be assigned to the couples $[\text{Fe}_2\text{L}_4]^{2-} / [\text{Fe}_2\text{L}_4]^-$ and $[\text{Fe}_2\text{L}_4]^- / [\text{Fe}_2\text{L}_4]^0$ respectively. During the reverse sweep a cathodic wave detectable at higher

sweep rates, suggests that the product of the second oxidation is being consumed in a chemical equilibrium following an EC mechanism. The mechanism that follows the second oxidation process is still unclear but it remains out of the scope of the present study.

Fig. 2. Room temperature cyclic voltammograms of $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{mnt})_2] 10^{-3} \text{ M}$ in dichloromethane with $10^{-1} \text{ M } (n\text{-Bu}_4\text{N}) \text{PF}_6$ as supporting electrolyte on platinum electrode at different sweep rates (ν indicated in the range $0.01\text{-}3 \text{ Vs}^{-1}$). The potential sweep was started from the open circuit potential in the anodic direction. Electrode area: 0.12 cm^2 . The inset shows the dependence of anodic peak currents with square root of scan rate for oxidation processes 1 and 2.

In the case of $[\text{Fe}(\text{qdt})_2]^-$ the ratio between the two peak intensities strongly depends on the scanning rate (Fig. 3) denoting a chemical equilibrium,[22] certainly the equilibrium C1, between monomeric and dimeric species: $2 [\text{FeL}_2]^- \leftrightarrow [\text{Fe}_2\text{L}_4]^{2-}$. The graphical representations of the anodic peak currents against the square root of sweep rate are plotted on the inset of figure 3 for processes 1 and 2 and reveal a linear behaviour typical of diffusion controlled processes which is a further evidence for the existence of two different potential independent

species. These results are in good agreement with the conductivity results which point to a stronger degree of dissociation for $[\text{Fe}(\text{qdt})_2]$, even in dichloromethane.

It should be mentioned that although two anodic waves are detected for complexes with both ligands in dichloromethane, they correspond to different processes that can be ascribed, on increasing potential, to $[\text{Fe}(\text{mnt})_2]_2^{2-}/[\text{Fe}(\text{mnt})_2]_2^{-}$; $[\text{Fe}(\text{mnt})_2]_2^{1-}/[\text{Fe}(\text{mnt})_2]_2^0$ involving only dimeric species for mnt and to $[\text{Fe}(\text{qdt})_2]_2^{2-}/[\text{Fe}(\text{qdt})_2]_2^{-}$; $[\text{Fe}(\text{qdt})_2]^{-}/[\text{Fe}(\text{qdt})_2]^0$ involving dimeric and monomeric species for qdt. Particularly with the qdt ligand the ratio between the two peak intensities strongly depends on the scanning rate (See fig 3), denoting as above mentioned a chemical equilibrium,[22] which is ascribed to equilibrium C1 in scheme 1, between monomeric and dimeric species $2 [\text{Fe}(\text{qdt})_2]^{-} \leftrightarrow [\text{Fe}_2(\text{qdt})_4]^{2-}$.

Fig. 3. Study of the anodic processes. Room temperature cyclic voltammograms of $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{qdt})_2]$ 10^{-3} M in dichloromethane with 10^{-1} M $(n\text{-Bu}_4\text{N}) \text{PF}_6$ as supporting electrolyte on platinum electrode at different sweep rates (v indicated in the range $0.01\text{-}3 \text{ Vs}^{-1}$). The potential sweep was started from the open circuit potential in the anodic direction. Electrode area: 0.12 cm^2 .

At negative potentials, two processes appear for the mnt complex with peak heights ratio that is a function of the scan rate (see Fig 4). This might indicate that the product of the dianion

dimer reduction, $[\text{Fe}(\text{mnt})_2]_2^{3-}$, is unstable and dissociates into $[\text{Fe}(\text{mnt})_2]_2^{2-}$ and $[\text{Fe}(\text{mnt})_2]^-$. Under these circumstances the first pair of waves at -0.39 V is ascribed to the couple $[\text{Fe}(\text{mnt})_2]_2^{2-} / [\text{Fe}(\text{mnt})_2]_2^{3-}$ while the second one at -0.53 V, which becomes more prominent at lower scan rates, is ascribed to the couple $[\text{Fe}(\text{mnt})_2]_2^{2-} / 2[\text{Fe}(\text{mnt})_2]^{2-}$. With the qdt ligand the reduction processes occur at more negative voltage (-0.8 V), the second one being less prominent pointing to the larger instability of the dianionic monomeric species $[\text{Fe}(\text{qdt})_2]^{2-}$.

Fig. 4. Room temperature cyclic voltammograms of $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{mnt})_2]$ 10^{-3} M in dichloromethane with 10^{-1} M $(n\text{-Bu}_4\text{N}) \text{PF}_6$ as supporting electrolyte on platinum electrode at different sweep rates (v indicated in the range $0.01\text{-}3 \text{ Vs}^{-1}$). The potential sweep was started from the open circuit potential in the cathodic direction. Electrode area: 0.12 cm^2 .

In acetonitrile two distinct behaviors are observed depending on the ligand; For mnt only one anodic wave is detected even at scanning rates as high as 2 Vs^{-1} , pointing to the absence of dimers (fig. 5a), as expected from the conductivity measurements but for qdt a second wave starts to be detected at 0.1 Vs^{-1} pointing to the presence of chemical equilibrium C1. The comparison of these waves of qdt in both dichloromethane and acetonitrile solvents (see fig. 6)

indicates that, the second anodic wave corresponds to the dimer oxidation since in acetonitrile the dimers are less concentrated species as pointed out by the conductivity results. The wave detected at 0.1 Vs^{-1} in dichloromethane, is only detected at 0.4 Vs^{-1} in acetonitrile.

In acetonitrile the two processes at both negative and positive voltages become less pronounced and the voltammograms are dominated mainly by a simple pair of waves (see fig 1). These results are consistent with a larger degree of dissociation of both the $[\text{Fe}(\text{mnt})_2]_2^{2-}$ and $[\text{Fe}(\text{qdt})_2]_2^{2-}$ complexes in acetonitrile. The process at negative potentials become more irreversible, as a consequence of the larger instability of the dianionic monomeric species $[\text{FeL}_2]^{2-}$. A similar situation is observed in DMF, however in this solvent the potentials appear shifted to lower potentials. The study of the anodic processes on acetonitrile and dimethylformamide points to complete dissociation of mnt and a partial dissociation of qdt (fig. 5).

Fig. 5. Study of the anodic processes. Room temperature cyclic voltammograms of a) $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{mnt})_2] 10^{-3} \text{ M}$ and b) $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{qdt})_2] 10^{-3} \text{ M}$ in acetonitrile with $10^{-1} \text{ M } (n\text{Bu}_4\text{N}) \text{PF}_6$ as supporting electrolyte on platinum electrode at different sweep rates v indicated. The potential sweep was started from the open circuit potential in the anodic direction. Electrode area: 0.12 cm^2 .

Fig. 6. Comparison of room temperature cyclic voltammograms of $(n\text{-Bu}_4\text{N}) [\text{Fe}(\text{qdt})_2] 10^{-3} \text{ M}$ in dichloromethane (in black) and acetonitrile (in blue) with $10^{-1} \text{ M } (n\text{Bu}_4\text{N}) \text{PF}_6$ as supporting electrolyte on platinum electrode at sweep rates v a) 0.05 Vs^{-1} and b) 0.1 Vs^{-1} . The potential sweep was started from the open circuit potential in the anodic direction. Electrode area: 0.12 cm^2 .

Conclusions

In conclusion our electrochemical studies show that in solution there is an equilibrium between $[\text{Fe}(\text{L})_2]_2^{2-}$ dimers and $[\text{Fe}(\text{L})_2]^-$ monomers, with the dimer dissociation degree being strongly dependent on the nature of the solvent. In $[\text{Fe}(\text{mnt})_2]$ in dichloromethane, only dimer oxidation processes are observed in cyclic voltammetry, while in $[\text{Fe}(\text{qdt})_2]$ both dimeric and monomeric species are involved in redox processes. In acetonitrile and DMF the observed processes correspond only to the dissociated monomeric species. The dimer dissociation is more pronounced in the iron complex with the qdt than with the mnt ligand and it is significantly favoured in nitrogen and oxygen containing solvents such as acetonitrile and DMF compared with dichloromethane. This stabilization of the monomers is ascribed to the ability of nitrogen and oxygen atoms of such solvents to apically coordinate the Fe atom of the dithiolene complex in addition to its four bisdithiolene sulfur atoms.

The major role of the solvent interactions in the monomer/dimer equilibrium put into evidence by this study is certainly identical to the solid state interactions responsible for the recently reported formation in some salts of iron bisdithiolene complexes with the unusual square planar[12,13] or poorly dimerised[17] geometries.

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Graphical Abstract

An electrochemical study demonstrates the major role of the nature of the solvent in the equilibrium between monomer and dimer of iron bisdithiolene complexes in solution

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