J. Braz. Chem. Soc., Vol. 9, No. 6, 591-597, 1998.
Printed in Brazil.

Article

Syntheses and Electrochemical Studies of Bis(η^5-Cyclopentadienyl)-(2,3-Quinoxalinedithiolato)Titanium(IV) Derivatives. Comparison with the Electrochemical Properties of Similar Complexes

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M13 9PL

Received: October 23, 1997

Neste trabalho descreve-se a síntese de novos derivados bis(η^5-ciclopentadienil)(2,3-quinoxalina-ditiolato)titanio(IV) e bis(η^5-ciclopentadienil)(1-fenil)(2-metil)(1,2-etenoditiolato)titanio(IV). As propriedades redox destes compostos juntamente com as propriedades de bis(η^5-ciclopentadienil)(ene-1,2-ditiolato)titanio(IV) similares foram medidas em soluções neutras. Todos os compostos exibiram uma redução reversível envolvendo um elétron, sendo que o potencial de redução é dependente da natureza do ligante ditiolato. Um segundo processo de redução é observado para os derivados de 2,3-quinoxalina. As propriedades destes últimos também foram estudadas em meio ácido e a presença de H^+ tem um pequeno efeito em ambos os processos, sugerindo que o mesmo tipo de evento ocorre sob as duas condições.

In this work the syntheses of novel bis(η^5-cyclopentadienyl)(2,3-quinoxaline-dithiolato)titanium(IV) derivatives and bis(η^5-cyclopentadienyl)(1-phenyl)(2-methyl)(1,2-ethenedithiolato)titanium(IV) is described. The redox properties of these compounds along with the properties of similar bis(η^5-cyclopentadienyl)(ene-1,2-dithiolato)titanium(IV) complexes are assessed in neutral solutions. All the compounds exhibited a reversible one electron reduction process, the potential at which the reduction occurs being dependent on the nature of the dithiolato ligand. A second reduction process is observed on the 2,3-quinoxaline derivatives. The properties of the latter are also assessed in acidic solution and the presence of H^+ has a small effect on both processes, suggesting that the same type of event occurs under both conditions.

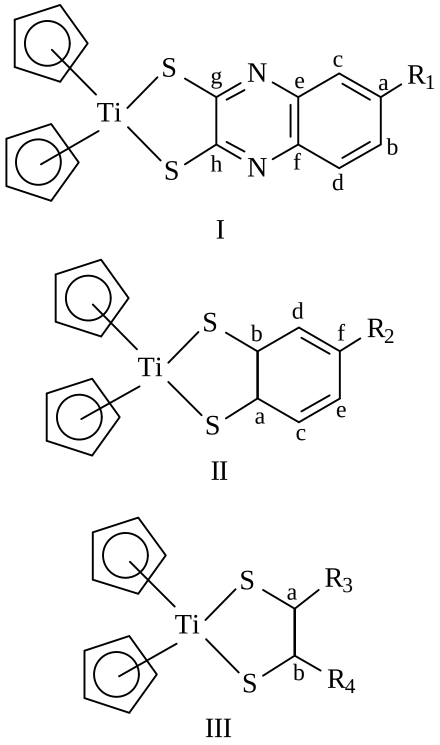
Keywords: *dithiolenes, redox properties, titanium(IV) dithiolato*

Introduction

The recent increased interest in metal-sulphur compounds stems from the recognition of the involvement of metal-sulphur centres in catalyses of biological and non-biological processes[1-7]. Interest in the organometallic chemistry of titanium dates back to the second half of the last century when the first attempt to synthesize organotitanium compounds was made[8]. At that time the sensitivity of these compounds to air and moisture was not taken into account. Only when techniques for working under anaerobic conditions were developed, was the isolation and proper characterization of these compounds possible. Also at this time the action of organotitanium in the polymerization of olefins was demonstrated[9] and later the role of titanium compounds in the fixation of nitrogen was discovered[10]. Since then, the organometallic chemistry of this element has developed considerably.

The syntheses and investigation of bis(η^5 - cyclopentadienyl)(ene-1,2-dithiolato)-titanium(IV) have been pursued since early 1960's. This class of compounds were apparently neglected during the early 1970's and 1980's. However by the end of the last decade they were again of interest, following the discovery of their action as anti-tumor agents[11-15] and also the investigation of their thermodynamic properties[16,17].

In this work the syntheses of new complexes of the general formula $[Cp_2Ti(R\text{-}qdt)]$ (where R = H, CH_3, Br, Cl or F and Cp = η^5-cyclopentadienyl) and $[Cp_2Ti(Me\text{-}sdt)]$ are described. These with $[Cp_2Ti(tdt)]$, $[Cp_2Ti(mnt)]$, $[Cp_2Ti(sdt)]$ and $[Cp_2Ti(bdt)]$ are used in a systematic study involving electrochemistry. Redox properties are assessed.



Structure	R_1	R_2	R_3	R_4	Abbreviation
I	H	-	-	-	$[Cp_2Ti(qdt)]$
I	CH_3	-	-	-	$[Cp_2Ti(Me\text{-}qdt)]$
I	Br	-	-	-	$[Cp_2Ti(Br\text{-}qdt)]$
I	Cl	-	-	-	$[Cp_2Ti(Cl\text{-}qdt)]$
I	F	-	-	-	$[Cp_2Ti(F\text{-}qdt)]$
II	-	H	-	-	$[Cp_2Ti(bdt)]$
II	-	CH_3	-	-	$[Cp_2Ti(tdt)]$
III	-	-	CN	CN	$[Cp_2Ti(mnt)]$
III	-	-	H	Ph	$[Cp_2Ti(sdt)]$
III	-	-	CH_3	Ph	$[Cp_2Ti(Me\text{-}sdt)]$

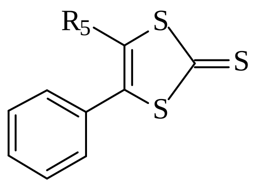
Figure 1. Molecular structures of the complexes synthesized in this work.

Experimental

The various quinoxalinedithiol derivatives were prepared according to methods registered in the literature[18-21]. Styrenedithiol and methylstyrenedithiol were used in the form of their 1,3-dithiol-2-thione (Fig. 2), and were given to the authors by Dr. E.M. Armstrong of the Chemistry Department of Manchester. 1,2-Bezenedithiol and sodium maleonitriledithiolate were given to the authors by Mrs. D. Mather of the Chemistry Department. Finally 3,4-toluenedithiol was obtained from Aldrich (D12,920-8) and used as purchased.

Bis(^{5}-cyclopentadienyl)(dichloro)titanium(IV) - $[Cp_2TiCl_2]$ - and bis(η^5cyclopenta-dienyl)bis(trimethylphosphine)titanium(II) - $[Cp_2Ti(PMe_3)_2]$ - were used as inorganic precursors. The first one was purchased from Aldrich (23,482-6) and used without any previous treatment. The latter was prepared according to Kool *et. al.*[22] and used in the moment it was prepared. The known complexes ($[Cp_2Ti(bdt)]$, $[Cp_2Ti(tdt)]$, $[Cp_2Ti(mnt)]$) were prepared by methods registered in the literature[23,24]. The styrene derivatives ($[Cp_2Ti(sdt)]$, $[Cp_2Ti(Me\text{-}sdt)]$) were made by an alternative method reacting $[Cp_2Ti(PMe_3)_2]$ with the corresponding 1,3-dithiol-2-thione (Fig. 2). This method led to low yields.

Chemical analysis, when possible, enabled the formulation of the complexes and they have been fully characterized by spectroscopic methods. NMR measurements were carried out on a Varian Gemini 200 (for ^1H at 200 MHz and ^{13}C at 50 MHz operating frequencies) and on a Bruker AC300E (for ^1H at 300 MHz and ^{13}C at 75 MHz operating frequencies). Mass spectra were recorded on a Trio 2000 Fisons Instrument. Electrochemical data were obtained using an EG&G Princeton Applied Research 175 universal programmer and an EG&G Princeton Applied Research 178 electrometer. Data were recorded on an Advance Bryans series 6000 XY/t recorder.



$R_5 = H,\ CH_3$

Figure 2. 1,3-dithiolium-2-thione.

Preparation of Complexes

[Cp_2Ti(R-qdt)] (where R = H, CH_3, Br, Cl or F)

The preparation of each of the various derivatives of bis(η^5-cyclopentadienyl)-(2,3quinoxalinedithiolato)titanium(IV) complexes followed the same procedure. Metallic sodium (46 mg, 2 mmol) was dissolved in dry methanol (10 mL) in a Schlenk tube under a dinitrogen atmosphere. After the effervescence ceased, 2,3-quinonalinedithiol (194 mg, 1 mmol) (or the equivalent weight of the substituted derivative) was added and the solution stirred for 15 min whereupon it became orange. The solvent was removed under reduced pressure and solid bis(η^5-cyclopentadienyl)(dichloro)titanium(IV) (225 mg, 0.9 mmol) was introduced into the Schlenk tube. Dry diethylether (20 mL) was added with a syringe and the resulting suspension was stirred overnight at room temperature. The red-brown slurry became green. The solvent was then removed under reduced pressure and the complex dissolved in dry dichloromethane (20 mL) producing a green coloured solution and a yellow precipitate which was removed by filtration. The dichloromethane was removed under reduced pressure, leaving a green crystalline powder. Purification was achieved by repeated recrystallization in dry dichloromethane. Yields: [Cp_2Ti(qdt)] 65%; [Cp_2Ti(Me-qdt)] 68%; [Cp_2Ti(Br-qdt)] 42%; [Cp_2Ti(Cl-qdt)] 52%; [Cp_2Ti(F-qdt)] 68%. The compounds are extremely soluble and stable in dichloromethane; fairly soluble and stable in acetone. They dissolve in chloroform and acetonitrile but decompose quickly in these solvents. In the solid state they are stable, decomposing with moisture after *ca.* six weeks.

Chemical analysis

[Cp_2Ti(qdt)] Calculated for $C_{18}H_{14}N_2S_2Ti$ (found) C: 58.4 (58.9) H: 3.8 (3.9) N: 7.6 (7.2) S: 17.3 (17.5) Ti: 13.0 (12.6); [Cp_2Ti(F-qdt)] Calculated for $C_{18}H_{13}N_2$ FS_2Ti (found) C: 55.7 (55.7) H: 3.3 (3.4) N: 7.2 (7.2) S: 16.5 (16.4) Ti: 12.6 (12.5); [Cp_2Ti(Me-qdt)] calculated for $C_{19}H_{16}N_2S_2Ti$ (found) C: 59.4 (59.0) H: 3.3 (3.4) N: 7.3 (7.0); [Cp_2Ti(Cl-qdt)] calculated for $C_{18}H_{13}N_2$ ClS_2Ti (found) C: 53.4 (53.0), H 3.2 (3.0), N 6.9 (6.4) ; [Cp_2Ti(Br-qdt)] calculated for $C_{18}H_{13}N_2$ BrS_2Ti (found) C: 48.1 (47.6), H 2.9 (2.6), N 6.2 (5.9). Because of the amount of the organic starting material, [Cp_2Ti(Me-qdt)], [Cp_2Ti(Cl-qdt)] and [Cp_2Ti(Br-qdt)] were obtained in an amount only sufficient for CHN, but they were fully characterized spectroscopically.

300 MHz ^{1}H-NMR (values in ppm - for labeling of protons refer to Fig. 1)

Spectra recorded in CD_2Cl_2. (R_1 = H) H_b 7.63(dd,1H), H_c 7.90(dd,1H), H_{Cp} 6.35(s,10H); (R_1 = CH_3) H_b 7.47(dd,1H), H_c 7.67(s,1H), H_d 7.79(d,1H), H_{Cp} 6.45(s,10H), H 2.32(s,3H); (R_1 = Br) H_b 7.68(dd,1H), H_c 8.05(s,1H), H_d 7.77(d,1H), H_{Cp} 6.50(s,10H); (R_1 = Cl) H_b 7.55(dd,1H), H_c 7.88(s,1H), H_d 7.84(d,1H), H_{Cp} 6.50(s,10H); (R_1 = F) H_b 7.39(dd,1H), H_c 7.52(s,1H), H_d 7.90(d,1H), H_{Cp} 6.50(s,10H).

50 MHz ^{13}C-NMR (values in ppm - for labeling refer to Fig. 1)

Spectra recorded in D^6-acetone. (R_1 = H) $C_{a,b}$ 126.7, $C_{c,d}$ 117.1, $C_{e,f}$ 129.2, $C_{g,h}$ 129.7, C_{cp} 118.3; (R_1 = CH_3) C_a 128.1, C_b 127.8, C_c 117.0, C_d 116.8, C_e 129.7, C_f 128.8, C_g 131.8, C_h 131.6, C_{Cp} 118.0 C 24.0; (R_1 = Br) C_a 119.9, C_b 119.6, C_c 119.5, C_d 118.1, C_e 130.9, C_f 121.6, C_g 132.4, C_h 131.1, C_{Cp} 118.3; (R_1 = Cl) C_a 119.9, C_b 119.6, C_c 119.1, C_d 116.4, C_e 127.8, C_f 121.5, C_g 130.8, C_h 129.8, C_{Cp} 118.2; (R_1 = F) C_a 140.1, C_b 133.1, C_c 117.8, C_d 129.3, C_e 127.4, C_f 131.4, C_g 136.5, C_h 134.9, C_{Cp} 116.7. The resonances of the carbons of positions **a**, **b**, **c**, **d**, **e**, **f**, **g** and **h** in the fluorine derivative showed C-F coupling and the chemical shift values refer to the centre of the doublet. The coupling constants are (values in Hz): $^1J_{F,Ca}$ 95, $^3J_{F,Cb}$ 75, $^2J_{F,Cc}$ 75, $^3J_{F,Cd}$ 57, $^2J_{F,Ce}$ 61, $^4J_{F,Cf}$ 31.

Mass spectrometry

The CI spectra exhibit the expected patterns consistent with the isotopic distribution[25] of Ti. The fragmentation pattern of [Cp_2Ti(Br-qdt)] and [Cp_2Ti(Cl-qdt)] also reflects the isotopic distribution of bromine and chlorine. CI MH^+: m/z (relative intensity): (R_1 = H) 369(8%), 370(8%), 371(42%), 372(25%), 373(17%); (R_1 = CH_3) 383(4%), 384(6%), 385(28%), 386(25%), 387(8%); (R_1 = Br) 447(10%), 448(17%), 449(93%), 450(62%), 451(100%), 452(58%), 453(26%); (R_1 = Cl) 403(6%), 404(5%), 405(17%), 407(17%), 408(12%), 409(3%); (R_1 = F) 387(5%), 388(8%), 389(20%), 390(10%) 391(7%).

[Cp_2Ti(Me-sdt)] and [Cp_2Ti(sdt)]

The entire process was carried out under an argon atmosphere because the bis(η^5cyclopentadienyl)bis(trimethylphosphine)titanium(IV) is highly air-sensitive. This compound (*ca.* 1 mmol) was prepared, in a Schlenk tube, according to a method introduced by *Kool et. al.*[18] In a second Schlenk tube 1-pheny-l,2-methyl-1,3-dithiolium-2-thione (Fig. 2, R_5 = CH_3) (220 mg, 1 mmol), or the equivalent weight of 1-phenyl-1,3-dithiolium-2-thione (Fig. 2, R_5 = H), was dissolved in dry tetrahydrofuran (10 mL) and maintained at -77 °C. The solution in the first Schlenk tube was transferred to the second one through a cannula. The mixture was stirred overnight, allowing the solution to attain room temperature, whereupon the solution became deep green. The solvent was removed under reduced pressure and the remaining powder was dissolved in dichloromethane (10 mL). Final purification was achieved by column chromatography on silica (120 x 2 cm, Merck 60) and inert atmosphere. A green band was collected by elution with 1:9 (v/v) dichloromethane:n-hexane. A green solid was obtained by evaporation of the solvents. Yield: [Cp_2Ti(Me-sdt)] 21% and [Cp_2Ti(sdt)] 10%. They are soluble and stable in dichloromethane and acetone. They dissolve in acetonitrile but decompose quickly in this solvent. The solids are rather stable, but decompose with moisture.

Chemical analysis

[Cp_2Ti(Me-sdt)] Calculated for $C_{19}H_{18}S_2Ti$ (found) C: 63.5 (63.3), H: 5.0 (5.3), S 17.9(17.7), Ti 13.4 (13.2); [Cp_2Ti(sdt)] calculated for $C_{18}H_{16}S_2Ti$ (found) C:62.8 (62.4), H: 4.7 (5.0).

200 MHz ^{1}H-NMR (values in ppm - for labeling refer to Fig. 1)

Spectra recorded in $CDCl_3$. ($R_3 = CH_3$, R_4 = Ph): $H_{d,e,f}$ 7.55 (m, 5H), H 2.40 (s, 3H), H_{Cp} 5.8-6.1 (broad line, 10H); (R_3 = H, R_4 = Ph): H_a 7.72 (s, 1H), $H_{d,f}$ 7.20 (m, 3H), H_{Cp} = 5.89 (broad line, 10H).

75 MHz ^{13}C-NMR. (values in ppm - for labeling refer to Fig. 1)

Spectra recorded in D^6-acetone. ($R_3 = CH_3$, R_4 = Ph) C_a 156.4, C_b 156.9, C_c 127.2, C_e 129.4, C_f 128.6, C 27.3, C_{Cp} 112.9 and 108.7. Due to low yield, [Cp_2Ti(sdt)] was not produced in suffucient amount for a ^{13}C spectrum.

Mass spectrometry

CI: MH^+ m/z (relative intensity). ($R_3 = CH_3$, R_4 = Ph) 357(19%), 358(12%), 359(100%), 360(27%), 361(20%); (R_3 = H, R_4 = Ph) 342(9%), 343(15%), 344(80%), 345(13%), 346(11%).

Redox Properties of [Cp_2Ti(ene-1,2-ditiolato)]

The series of bis(η^5-cyclopentadienyl)(ene-1,2-dithiolato)titanium)(IV) complexes have been studied for their redox properties. Measurements were carried out in dichloromethane solution at a sample concentration of 10^{-2} mol/L at room tempertaure using [BuN_4][BF_4] as the supporting electrolyte at 0.2 mol/L concentration and dinitrogen atmosphere. Potentials were registered against a Standard Calomel Electrode. Electrochemical quantities ($E_{1/2}$, ΔE, i_{pc}/i_{pa}) were calculated according to methods registered in the literature[26,27]. Values of ΔE were compared with that of ferrocene used as internal standard. This procedure allows the evaluation of the number of electrons involved in the reaction. The reversibility of the system was also tested by observing the process at a series of scan rates.

Figure 3 displays the corresponding cyclic voltammograms and Table 1 summarizes the electrochemical data for the series [Cp_2Ti(tdt)], [Cp_2Ti(bdt)], [Cp_2Ti(mnt)], [Cp_2Ti(sdt)] and [Cp_2Ti(Me-sdt)]. The electrochemistry of [Cp_2Ti(tdt)] and [Cp_2Ti(mnt)] has already been reported[28,29]. The value of $E_{1/2}$ here registered for [Cp_2Ti(mnt)] is in good agreement with that recorded earlier[27]. However the value for [Cp_2Ti(tdt)] is different (-0.5 V) than that previously published[28]. The reason for this may be due to different experimental conditions used by Dessy *et. al*[28]. Their measurements were carried out in dimethoxyethane using a Ag/Ag_2ClO_4 reference electrode. The ΔE presented here are close to the values measured for ferrocene in the same solution and under the same conditions and the ratio i_{pa}/i_{pc} are all close to unity.

The redox properties of [Cp_2Ti(R-qdt)] (where R = H, CH_3, Br, Cl or F) have also been investigated, both in neutral and acidic solution in diclhoromethane. Figure 4 displays the cyclic voltammograms for [Cp_2Ti(qdt)], which is representative of the series, in neutral solution (parts A and B of the figure) and acidic solution (parts C and D of the figure). Table 2 summarizes the cyclic voltammetric data for the series [Cp_2Ti(R-qdt)] (where R = H, CH_3, Br, Cl or F) in neutral and acidic solution. The cyclic voltammograms registered in neutral solution present two waves, revealing two reduction processes (labelled E^m and E^l). The first reduction process was inspected in more detail by recording the cyclic voltammogram in the region between 0.0 V and 0.9 V (part B of Fig. 4). The values of ΔE_p^m were

Table 1. Cyclic Voltammetric data for [Cp_2Ti(ene-1,2-dithiolato] at a scan rate of 100 mVs^{-1} in dichloromethane neutral solution. Supporting electrolyte [NBu_4][BF_4]. Experiments conducted with SCE.

Complex	$E_{1/2}$ (V)	ΔE_p(V)*	ΔE_p(V)**	n	i_{pa}/i_{pc}
[Cp_2Ti(tdt)]	-1.19	0.090	0.096	1	1.1
[Cp_2Ti(bdt)]	-1.18	0.095	0.083	1	1.0
[Cp_2Ti(mnt)]	-0.74	0.093	0.090	1	1.1
[Cp_2Ti(sdt)]	-1.32	0.090	0.085	1	0.9
[Cp_2Ti(Me-sdt)]	-1.37	0.099	0.106	1	0.9

(n) number of electrons. (*) value for the complex. (**) value for ferrocene at the same solution.
Scan rate: 100 mV s^{-1}. Values corrected for SCE.

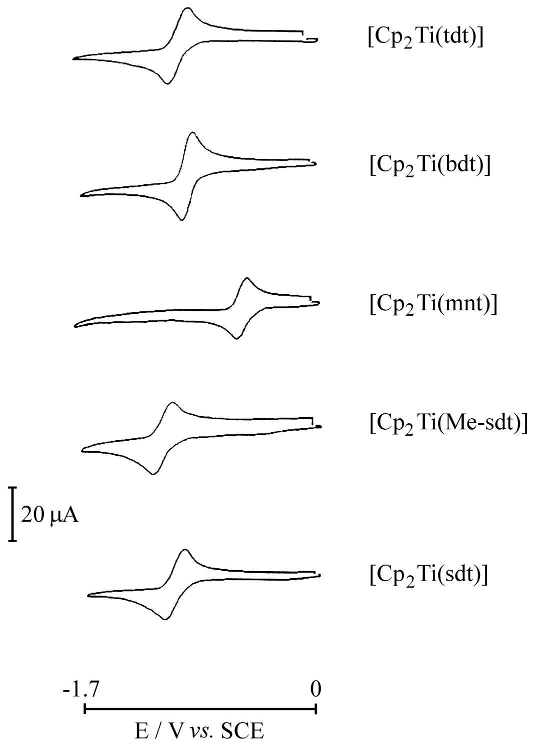


Figure 3. Cyclic Voltammograms for [Cp_2Ti(ene-1,2-dithiolato)] series at a scan rate of 100 mV s^{-1} in CH_2Cl_2 neutral solution. Supporting electrolyte [NBu_4][BF_4].

measured using ferrocene as internal standard as in the previous set of complexes. The values presented in Table 2 are close to the values measured for ferrocene in the same conditions. With the exception of [Cp_2Ti(Br-qdt)], all i_{pa}/i_{pc} ratios are close to the unity. The second redox process of the [Cp_2Ti(R-qdt)] system labelled E^l is not as prominent as the E^m since the currents involved are lower. These low values of the currents and the broad shape of the waves did not allow a reliable measurement of the ratio i_{pa}/i_{pc}.

The electrochemical properties of [Cp_2Ti(R-qdt)] series of compounds have also been studied in acidic solution using 1, 2 and 3 equivalents of acetic acid. The amount of acid employed caused no difference in the voltammograms. Figure 4 shows the cyclic voltammogram obtained with the solution with two equivalents of acid (parts C and D). Here two clear waves are observed for the first and second reduction process (E^m and E^l). The E^m process is still observed at the same potential as in the absence of acid. E^l is also observed at approximately the same potentials, but they are more intense. Weak irreversible processes are observed, specially between E^m and E^l. The first redox process (E^m) was inspected in more detail by recording the cyclic voltammogram in the region between 0.0V and -0.9 V (part D of Fig. 4). Comparison of E^m values in neutral and in acidic solution (Table 2) reveals only small shifts to less negative potentials upon addition of protons,

Table 2. Cyclic voltammetric data for the E^m process [Cp_2Ti(R-qdt)] at a scan rate of 100 mV s^{-1} in dichloromethane neutral solution, and with 2 equivalents of acetic acid. Supporting electrolyte [NBu_4][BF_4]. Experiment conducted with SCE.

Complex	$E_{1/2}^m$ (V)		Δ_p^m (V)		ΔE_p(V)**		i_{pa}/i_{pc}		n
	neutral	acid	neutral	acid	neutral	acid	neutral	acid	
[Cp_2Ti(qdt)]	-0.79	-0.79	0.12	0.12	0.11	0.11	1.0	1.1	1
[Cp_2Ti(Me-qdt)]	-0.81	-0.79	0.11	0.12	0.11	0.11	1.1	1.0	1
[Cp_2Ti(Br-qdt)]	-0.77	-0.74	0.10	0.11	0.11	0.11	0.7	1.1	1
[Cp_2Ti(Cl-qdt)]	-0.76	-0.74	0.10	0.10	0.12	0.12	0.9	0.9	1
[Cp_2Ti(F-qdt)]	-0.91	-0.77	0.12	0.12	0.12	0.12	0.9	1.1	1

(n) number of electrons (*) value for the complex (**) value for ferrocene.

Table 3. Cyclic voltammetric data for the second reduction process (E^l) of [Cp_2Ti(R-qdt)] in dichloromethane neutral solution and with two equivalents of acetic acid. Experiment conducted with SCE. Supporting electrolyte [NBu_4][BF_4].

Complex	$E_{1/2}^l$ (V)		ΔE_p^l (V)*		ΔE_p (V)**		n
	neutral	acid	neutral	acid	neitral	acid	
[Cp_2Ti(qdt)]	-1.51	-1.53	0.08	0.10	0.11	0.11	1
[Cp_2Ti(Me-qdt)]	-1.54	-1.56	0.08	0.10	0.11	0.11	1
[Cp_2Ti(Br-qdt)]	-1.48	-1.51	0.10	0.11	0.12	0.11	1
[Cp_2Ti(Cl-qdt)]	-1.48	-1.48	0.08	0.10	0.12	0.12	1
[Cp_2Ti(F-qdt)]	-1.50	-1.54	0.09	0.10	0.12	0.12	1

(n) number of electrons (*) value for the complex (**) value for ferrocene.

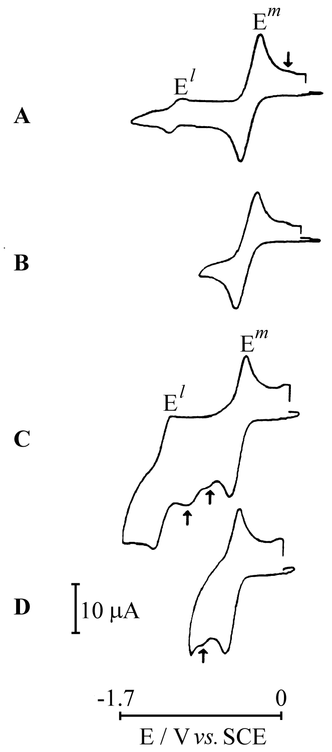


Figure 4. Cyclic voltammograms for $[Cp_2Ti(qdt)]$ at a scan rate of 100 mV s^{-1} in CH_2Cl_2. Supporting electrolyte $[NBu_4][BF_4]$ 0.2 mol/L. A and B - neutral solution. C and D acidic solution (2 meq of acetic acid). Arrows indicate irreversible processes.

except for $[Cp_2Ti(F\text{-}qdt)]$. For this last compound the reduction occurs at a potential 140 mV less negative after acidification. Values of ΔE_p^l (Table 3) are close to the equivalent values obtained for ferrocene in the same conditions. The anodic current is observed as a shoulder and it is not as clear as the cathodic current. The determination of i_{pa}/i_{pc} was therefore not achieved.

Cyclic voltammograms at scan rates of 500, 200, 100, 50 and 20 mV s^{-1} were recorded for all complexes in neutral solution and in the case of $[Cp_2Ti(R\text{-}qdt)]$ (where R = H, CH_3, Br, Cl or F) also in acidic solution. These experiments showed that the compounds exhibit a clear reversible one-electron redox process (E^m).

Conclusion

The potential at which the first reduction occurs varies with the nature of the dithiolene ligand from -0.74 V to -1.37 V (*vs.* SCE) as (in order of increasing negative potential) mnt < qdt < bdt < sdt. A surprising result is that the substituents on the ligand, including the presence of H^+ which is expected to protonate the qdt nitrogen, generally only have a small effect, opposing to the effect observed for similar cobalt complexes[30]. In that kind of complex the addition of acid gave rise to several waves in the second reduction process. The change of the central metal may be the answer for the change in the behaviour of the complexes, showing that the metal-sulphur bond is the key for the understanding of their properties. For the series of substituents on the quinoxaline ring the inclusion of an electron donating group (CH_3) gives a more negative $E_{1/2}^m$ than for unsubstituted ligand, whilst halogen substitution gives less negative values. However $[Cp_2Ti(F\text{-}qdt)]$ has the more negative value which is not expected.

A second reduction process (E^l) is also observed on the qdt series. The addition of acid has also a small effect on their values. Values for ΔE^l are close to the same value obtained for ferrocene in the same solution and under the same conditions. They suggest that E^l is still a one-electron reduction process in the presence of acid. The close correspondence in position and shape of the voltammetric waves for this second redox process in both neutral and acidic solution suggests that the same type of event is occurring under both conditions.

Acknowledgements

The authors wish to thank to CAPES - MEC (Coordenadoria de Aperfeiçoamento do Pessoal do Ensino Superior) for the financial support for the Ph.D. course of JCL, which provided the conditions for this work.

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