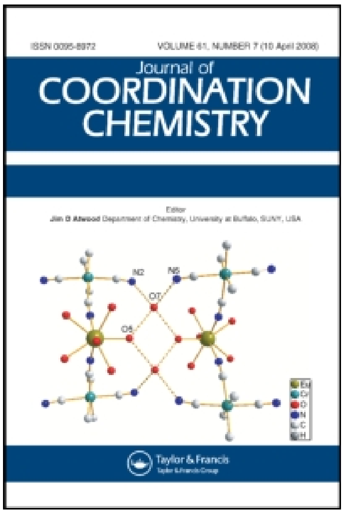

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Electrochemical and Spectroscopic Studies of Co(CREATININE)$_2$Cl$_2$

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To cite this Article Costa, B.S. Parajón , Baró, A.C. González and Baran, E. J.(2002) 'Electrochemical and Spectroscopic Studies of Co(CREATININE)$_2$Cl$_2$', Journal of Coordination Chemistry, 55: 9, 1009 — 1019
To link to this Article: DOI: 10.1080/0095897021000009974
URL: http://dx.doi.org/10.1080/0095897021000009974

J. Coord. Chem., 2002, Vol. 55(9), pp. 1009–1019

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ELECTROCHEMICAL AND SPECTROSCOPIC STUDIES OF Co(CREATININE)$_2$Cl$_2$

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(Received 13 March 2001; Revised 24 August 2001; In final form 17 January 2002)

The electrochemical behavior of Co(creatinine)$_2$Cl$_2$ was investigated by cyclic voltammetry in organic solvents (DMSO and DMF) and in aqueous solution. Analysis of the results indicates that the electroactive species depend on the nature of the solvent. In DMF a single reduction process Co(II)/Co(I) is observed. In DMSO the redox behavior of the complex changes with the scan rate and a two-electron transfer process can be eventually observed. In aqueous solution the complex immediately decomposes giving rise to the aquo-cation. The characteristic peak of the redox couple Cl$_2$/Cl$^-$ is observed as a consequence of the chloride released from the coordination sphere. Analysis of the electronic spectra gave additional support to the proposed mechanisms. The Co–Cl and Co–N stretching bands were clearly identified in the low frequency region of the IR spectrum.

Keywords: Cobalt(II); Creatinine; Cyclic voltammetry; Spectroscopy

INTRODUCTION

Creatinine is the final degradation product of phosphocreatine, a high-energy phosphate that plays an important role in the energetics of muscle tissues [1]. It is also an important end product of nitrogen metabolism in vertebrates and its level in urine and serum is recognized as an indicator of certain diseases [2].

Creatinine (creat), a five-member ring, has different donor groups and exists in imino or/and amino tautomeric forms (Scheme 1, A and B). These characteristics make creatinine an interesting ligand, mono or bidentate, capable of forming complexes of different geometries, reactivity and stability. Even though several authors have investigated transition metal complexes of this ligand [3–10], there is little information about the redox properties of such compounds.

As a part of studies of our laboratory on metal complexes of creatinine and related ligands [3,4], in the present paper we report an electrochemical study by cyclic voltammetry of the Co(creat)$_2$Cl$_2$ complex. We have reinvestigated its redox characteristics in aqueous solution and have attained an insight into its behavior in organic solvents,

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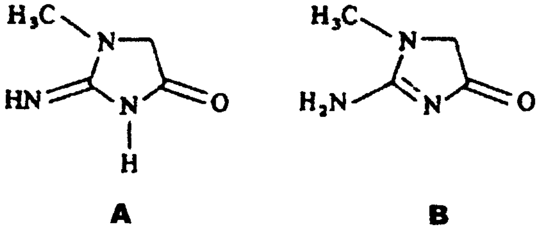
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000009974



SCHEME 1

such as *N,N*-dimethylformamide (DMF) and dimethysulfoxide (DMSO). Complementary electronic spectroscopy measurements of these solutions were performed to give additional support to these results. IR spectra of the solid complex and the ligand were also analyzed.

EXPERIMENTAL

Synthesis of the Complex

The synthetic procedure was similar to that used for the previously reported Cu(creat)$_2$Cl$_2$ complex [3]. Methanolic solutions of creatinine and $CoCl_2 \cdot 6H_2O$ in a 2:1 molar ratio were mixed together. The precipitated blue complex was filtered by vacuum, washed with methanol and dried over P_4O_{10} (yield 74%).

Anal. Calc. for $C_8H_{14}O_2N_6CoCl_2$ (%) C, 27.00; H, 3.93; N, 23.60. Found: C, 27.22; H, 3.75; N, 23.48.

Unfortunately, it was impossible to obtain single crystals adequate for x-ray crystallographic studies.

Electrochemical Measurements

Cyclic voltammetric experiments were performed with a Bioanalytical System Inc. CV-1B assembly. A standard three-electrode cell was used with a Pt working electrode, a Pt counterelectrode and an Ag/(0.01 M) $AgNO_3$ in CH_3CN reference electrode. The potential of this electrode was calibrated *vs.* NHE using the $[Fe(C_5H_5)_2]^+/[Fe(C_5H_5)_2]$ redox couple as an internal standard, for which a potential of +0.4 V was assumed [11,12]. A small amount of ferrocene was added at the end of each experiment. Potential values are reported in V *vs.* NHE.

All the experiments were performed in high purity (Baker) DMSO and DMF solutions with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. The solvents were dried over 4 Å molecular sieves (Merck) and used without further purification. The supporting electrolyte (electrochemical grade) was purchased from Fluka and used as received.

The electrochemical behavior of the complex was also investigated in aqueous solution using 0.1 M $LiClO_4$ (Mallinkrodt PA grade) as supporting electrolyte.

Prior to each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured. Solid samples were added to the solution and dissolved with stirring. The concentration of the complex was 10^{-3} M. Oxygen was removed by purging the solutions with pure nitrogen (a continuous gas stream was passed over the solutions during the measurements).

Spectroscopic Measurements

The IR spectra were recorded with a Brucker FTIR spectrometer, model 113 v, dispersing the samples either in KBr or in polyethylene pellets. The electronic absorption spectra were recorded in a Hewlett-Packard 8452-A diode array spectrometer, using 10 mm quartz cells.

In order to support the electrochemical studies, solutions of the ligand, $CoCl_2$ and the complex were prepared in DMSO, DMF and water containing the corresponding electrolyte. A 0.1 M solution of the electrolyte was used as a blank.

RESULTS AND DISCUSSION

Infrared Spectrum

The positions of the most characteristic bands in the IR spectra of the free ligand and the complex are compared in Table I. The spectrum of $Co(creat)_2Cl_2$ shows strong analogies with those of other transition metal coordination compounds containing creatinine [5–10]. The band assignment was made on that basis.

The complex spectrum is very similar to that previously reported for the copper–creatinine complex, for which the crystalline structure was determined [3]. This allows us to infer a *quasi*-tetrahedral geometry also for the cobalt compound.

Only a few IR bands for the cobalt complex were already reported by Udupa *et al.* [13]. Their values are in accord with the more detailed analysis presented in this work.

TABLE I Some characteristic IR bands of creatinine and $Co(creat)_2Cl_2$ (values in cm^{-1})

Creatinine	*Co(creat)₂Cl₂*	*Assignment*
3254 vs	3212 s	$\nu_{as}(NH_2)$
3033 vs	3179 w	$\nu_s(NH_2)$
1690 sh	1717 vs	$\nu(C=O)$
1670 vs	1645 vs	$\delta(NH_2) + \nu(C=N)$
1591 vs	1596 s	$\nu(C=N)$
1440 sh	1432 sh/1427 m	$\delta(CH_3)$
1245 vs	1231 m/1226 m	
1212 m	1198 m	$\nu(C–NH_2)$
841 s/813 m	845 m	$(NH_2)_{wagg}$
407 vs	397 s	
	309 s	$\nu(Co–Cl)$
	254 m	$\nu(Co–N)$
246 vs		
218 m	215 w	
198 w	196 vw	
150 m	150 m	
	140 m/134 m	$\delta(Co–lig)$
128 w	121 w	
115 vs		

vs: very strong; s: strong; m: medium; w: weak; vw: very week; sh: shoulder.

The bands at 3212 and 3179 cm^{-1} in the complex suggest the presence of the ligand in its amino-tautomer form (see Introduction, Scheme 1, B). The shoulder at 1690 cm^{-1} assigned to $\nu_{(C=O)}$ in the free ligand is shifted to higher frequency upon complexation, appearing as a strong band at 1717 cm^{-1}. This effect was also observed for other creatinine complexes where the ligand is monodentate and co-ordinates through the endocyclic nitrogen [3,14,15].

Other changes in the intensity and position of some creatinine bands are observed in the 600–100 cm^{-1} region in the complex spectrum. Two new bands appear at 309 and 254 cm^{-1}, which can be assigned to $\nu_{(Co-Cl)}$ and $\nu_{(Co-N)}$, respectively, while the one at 140 cm^{-1} could be attributed to a Co–ligand bending mode.

Electrochemical Behavior

The redox properties of this complex were investigated in DMSO, DMF and in aqueous solutions. The electrochemical behavior of the complex appears to be solvent dependent. Our experimental results indicate that:

(a) In DMF the complex undergoes a fast ligand exchange process when dissolved, where two solvent molecules replace both chloro ligands:

$$\mathrm{Co(creat)_2Cl_2 + 2\,DMF \rightarrow [Co(creat)_2(DMF)_2]^{2+} + 2\,Cl^-} \qquad (1)$$

(b) In DMSO the complex is unstable and decomposes to form $[Co(DMSO)_6]^{2+}$

$$\mathrm{Co(creat)_2Cl_2 + 6\,DMSO \rightarrow [Co(DMSO)_6]^{2+} + 2\,Cl^- + 2\,creat} \qquad (2)$$

On the basis of a second experiment in which (TBA)Cl was added to the electrolyte solution in both solvents, one oxidation peak was observed irrespective of the direction of the initial scan. This peak was unequivocally attributed to the oxidation of Cl^- to Cl_2. Thus, the electrochemical measurements reveal that a chemical conversion of the original compound occurs immediately after dissolution through the loss of the chloride ions of the coordination sphere.

(c) Other authors [13] reported a preliminary study of the redox behavior of this and other related compounds by polarography in aqueous solutions with 0.1 M KNO_3 as electrolyte. A reversible two-electron reduction process assumed to correspond to $Co(creat)_2Cl_2$ was reported. Our results indicate that in this medium the species present is the hexaaquo Co(II) complex. This was corroborated by two independent cyclic volammetric experiments, one with the complex and the other with $CoCl_2$. Identical voltammograms were obtained in both cases. UV/vis measurements confirm this observation.

DMF Solution

Cyclic voltammograms (CV) obtained between $+0.15$ and -1.50 V for $[Co(creat)_2(DMF)_2]^{2+}$ (Eq. 1), at different scan rates (v) are shown in Fig. 1. Only one reduction peak is observed on the first cathodic scan. On the reverse scan one oxidation peak

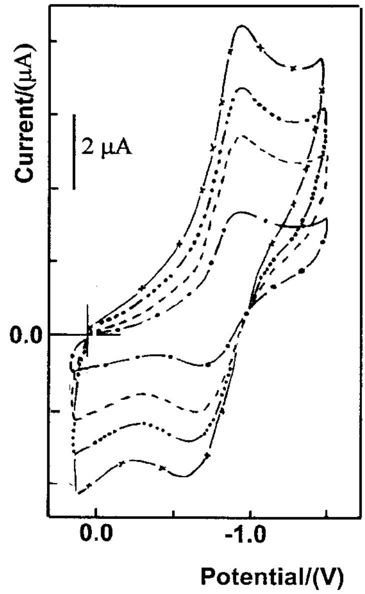


FIGURE 1 Cyclic voltammogram of $[Co(creat)_2(DMF)_2]^{2+}$ in DMF solution at different scan rates ($V s^{-1}$): 0.1 (– • –); 0.3 (– – –); 0.5 (– • • • • • –); 0.8 (–×–).

appears, which becomes less pronounced at smaller scan rates ($v < 0.1\,V s^{-1}$). At $v = 0.01\,V s^{-1}$ the complete lack of this anodic signal is observed (data not shown). This oxidation peak is shifted to a more positive potential as v increases. Moreover, when the cathodic limit is made more negative, no further reduction process can be detected, except the solvent decomposition current.

Figure 2 shows the dependence of the cathodic current (i_{pc}) on the square root of the scan rate ($v^{1/2}$). From the straight line obtained, which goes through the origin, it can be inferred that no chemical reaction precedes the electrochemical process and that the electron transfer is controlled by diffusion.

For this redox couple the i_{pa}/i_{pc} ratio increases from 0.66 to 0.99 as v is raised from 0.01 to $1\,V s^{-1}$. This effect and the constant $i_{pc}/v^{1/2}$ value obtained are indicative of a coupled chemical reaction following the charge transfer process (EC mechanism) [16,17]. This reaction can be observed at low v values, when the time scale of the experiment and the half-life of the chemical reaction become comparable. On the other hand, the difference in the peak potential and its dependence with v indicate that the charge transfer process is not reversible (ΔE values > 60 mV).

Differences in the redox behavior were observed when the voltammograms of the complex were compared with those of $CoCl_2$. The CV of the latter compound, at $v = 0.1\,V s^{-1}$, displays one reduction peak at -0.9 V and one oxidation peak situated at more positive potential than obtained with the complex. This last contribution is narrow and symmetrical, typical of species which are electrodesorbed from the electrode surface. Thus, on the forward scan, the reduction path involves an adsorption process. Changes on the electrode surface and deposit of metallic cobalt were evident. Moreover, when the scan was stopped for a few seconds at the end of the reduction peak, an enhancement of the anodic contribution was observed indicating that more adsorbed product is formed.

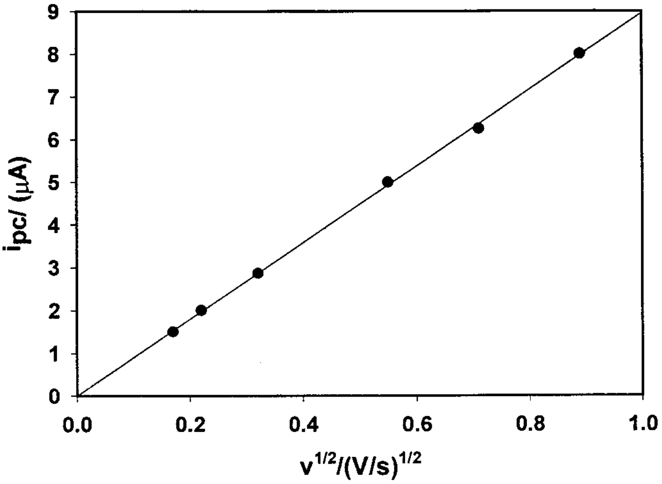


FIGURE 2 Dependence of the cathodic current peak (i_{pc}) on the square root of the scan rate ($v^{1/2}$) for $[Co(creat)_2(DMF)_2]^{2+}$.

In contrast, the shape of the voltammograms for the complex and their dependence on the experimental variables do not show evidence of adsorption phenomena. When the potential was held a few seconds at the end of the reduction peak, no deposit of metallic cobalt was observed.

The experimental data indicate that in the $CoCl_2$ solution reduction involves a two-electron charge transfer from Co(II) to Co(0), with adsorption on the electrode. This means that the Co(I) state once formed is reduced immediately to Co(0). It has no opportunity either to oxidize on the reverse scan or to diffuse away from the electrode.

For the complex, experimental evidence for Co(0) was not found. The linear relation between i_p and $v^{1/2}$ is taken as an acceptable criterion of charge transfer/diffusional control [17]. The reduction peak can then be attributed to a one-electron charge transfer from Co(II) to Co(I). This last species undergoes subsequent chemical reaction. This chemical reaction could be a change in the geometry of the coordination sphere with inclusion of solvent molecules:

$$[Co(creat)_2(DMF)_2]^{2+} + e^- \rightleftharpoons [Co(creat)_2(DMF)_2]^{1+} \qquad (3)$$

$$[Co(creat)_2(DMF)_2]^{1+} + xDMF \rightarrow [Co(creat)_2(DMF)_{2+x}]^{1+} \qquad (4)$$

The absence of a second reduction step suggests that the Co(I) species, surrounded by donor nitrogen atoms, is protected from reduction. Further reduction will be retarded with respect to the Co(I) state of the species formed in the $CoCl_2$ solution and probably lies at more negative potential than the decomposition limit of the solvent.

DMSO Solution

Cyclic voltammograms of the compound present in this solution (Eq. 2) are shown in Fig. 3. On the forward scan one cathodic peak is observed in the potential range

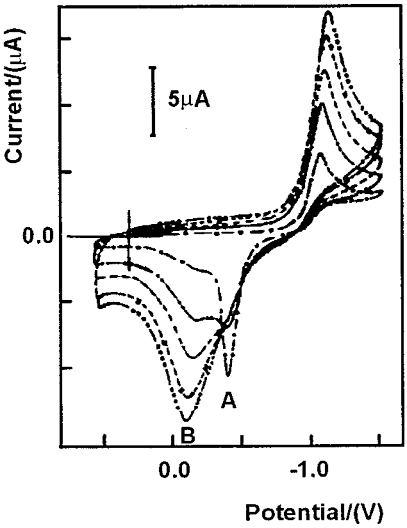


FIGURE 3 Cyclic voltammogram of the compound generated in DMSO solution, $[Co(DMSO)_6]^{2+}$, at different scan rates: 0.1 (– • –); 0.3 (– •• –); 0.5 (– – –); 0.8 (–×–); $1\,V\,s^{-1}$ (–• • ••–).

between $+0.6$ and $-1.5\,V$, at every scan rate analyzed (0.01–$1\,V\,s^{-1}$). On the reverse scan, the shape of the oxidation curve depends on the scan rate:

- At $v \leq 0.1\,V\,s^{-1}$, one oxidation peak (A) and a shoulder at a more positive potential are evident. This peak is sharp and symmetric, typical of stripping of surface deposits.
- At intermediate scan rate ($0.1 \leq v \leq 0.3\,V\,s^{-1}$) another peak (B) appears at more positive potential. This wave has a characteristic of an irreversible electrode reaction for a species in solution.
- At $v > 0.3\,V\,s^{-1}$, the first oxidation peak (A) vanishes and only the second one (B) remains.

Figure 4 shows the plot of i_{pc} *vs.* $v^{1/2}$. In contrast with the results observed for DMF solution (Fig. 2), two straight lines with different slopes are obtained suggesting that two non-equivalent processes are involved. A transition between both events is evident in a scan rate range from 0.1 to $0.3\,V\,s^{-1}$, which correspond to a $v^{1/2}$ value of 0.31 and 0.55, respectively. Even when this plot refers to the i_{pc} behavior, these results are in agreement with the anodic response discussed above.

Comparative measurements, at scan rates that differ by an order of ten, show that at $v > 0.3\,V\,s^{-1}$ the first oxidation peak A appears, as a minor contribution, only if the cathodic limit is shifted to more negative values (Fig. 5).

On the other hand, the response obtained with $CoCl_2$, under identical experimental conditions, indicates that the electroactive species is the same in both cases (Eq. 2).

The observed behavior suggests that the initial coordination sphere of the complex does not remain intact upon reduction. While the more stable Co(II)–DMSO complex is six-coordinate, Co(I) shows a tendency to form five-coordinate complexes [18]. Thus, a partial loss of ligands due to the change of the metal center oxidation state may occur.

It is evident that both oxidation peaks correspond to different steps that take place on the forward scan. It is interesting to consider the dependence on the time scale of the

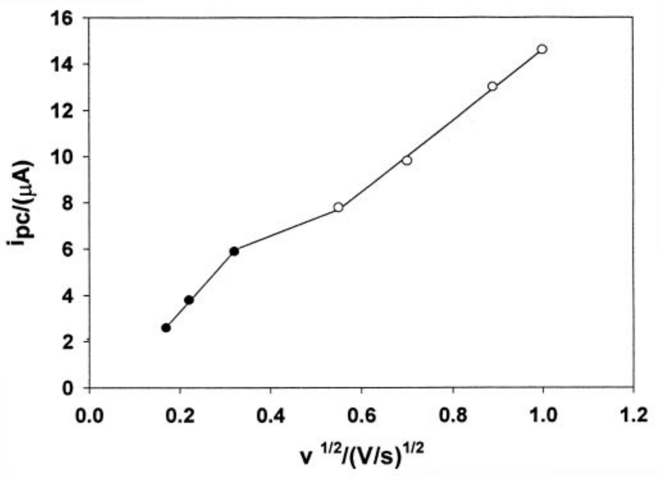


FIGURE 4 Dependence of the cathodic current peak (i_{pc}) on the square root of the scan rate ($v^{1/2}$) for $[Co(DMSO)_6]^{2+}$.

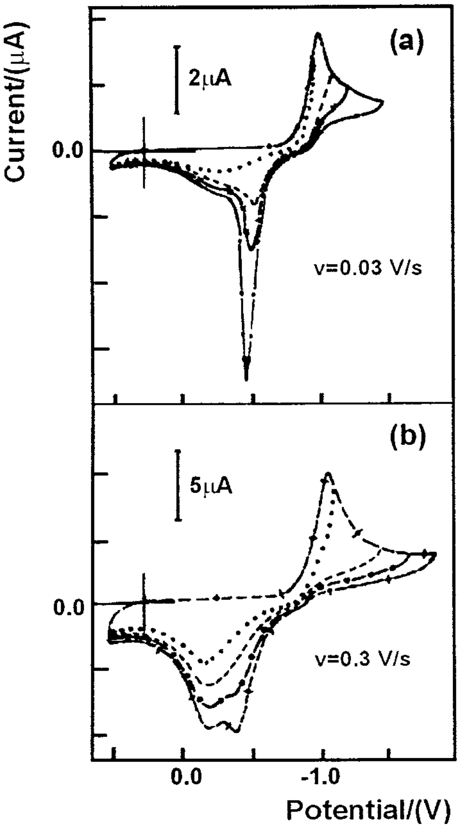
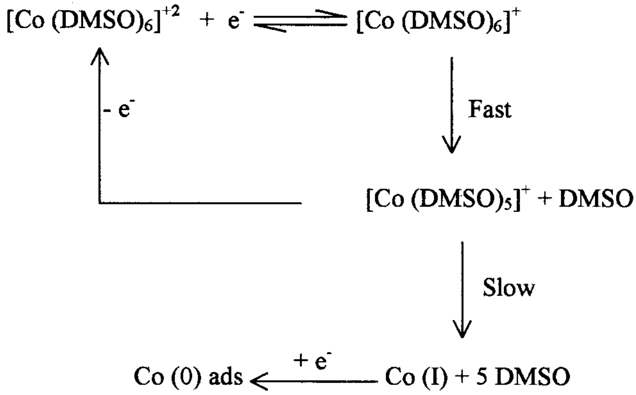


FIGURE 5 Comparison of the cyclic voltammograms obtained for the species $[Co(DMSO)_6]^{2+}$ at two different scan rates and cathodic limit (Ec): (a) $v = 0.03\,V\,s^{-1}$, Ec = − 1.5 V; (b) $v = 0.3\,V\,s^{-1}$, Ec = − 1.9 V.

experiment. By decreasing v, only a very small fraction of the second anodic contribution B remains suggesting that, on the forward scan, the compound responsible of this peak decomposed by a relatively slow homogeneous chemical reaction. The product of this chemical reaction undergoes an other electron transfer process and produces the species that can be adsorbed on the electrode surface. Deposit of metallic cobalt was observed in this case and peak A corresponds to the electrodesorption of this species.



SCHEME 2

In contrast, the experimental evidence indicates that at $v > 0.3\,\mathrm{V\,s^{-1}}$ the compound is reduced to Co(I) by transfer of one electron. A release of one solvent molecule occurs by a fast chemical reaction to produce a pentacoordinate species (see Scheme 2). This species requires a higher anodic potential for its oxidation than those obtained at smaller values of v.

Electronic Spectroscopy

In order to clarify the nature of the transformations observed in the electrochemical measurements, the electronic spectra were also investigated. Solutions of the ligand, the complex and $CoCl_2$ were prepared in the same conditions as those for the electrochemical experiments. The results obtained with each solvent can be summarized as follows:

(a) *DMF* In this solvent a light blue solution of the complex is obtained. The spectrum was recorded at different times during 30 min showing changes within this period. The last one as selected as that which corresponds to the conditions in the electrochemical measurements. The positions of the bands are compared with those obtained with a $CoCl_2$ solution (Table II).

The ligand does not show any absorption in the measured spectral range. The spectrum of a freshly prepared solution of the complex shows a maximum at 656 nm and shoulders at 620 and 582 nm. It changes with time: the bands get broader and similar to those observed for a $CoCl_2$ solution, suggesting coordination of the solvent to the metal center. This fact is in accordance with the electrochemical results that show that DMF replaces Cl^- ion in the Co(II) coordination sphere. The estimated ε values

TABLE II Electronic spectra of creatinine, its Co(II) complex and $CoCl_2 \cdot 8H_2O$ in DMF and DMSO solutions, 30 min after preparation. Absorbance maxima in nm

DMF		*DMSO*	
Co(creat)₂Cl₂	*CoCl₂*	*Co(creat)₂Cl₂*	*CoCl₂*
		292	
	530	535	535
610	608	616	616
672	676	676	680

(2–$4 \times 10^2\,M^{-1}\,cm^{-1}$) and the position of the bands are typical of tetrahedral Co(II) complexes with N-donor ligands [19].

(b) *DMSO* The spectrum of the free ligand shows an absorption band at approximately 290 nm that looks like a shoulder as it is very close to the solvent cut-off. Both, the complex and $CoCl_2$, give greenish blue solutions and the spectra were very similar to each other. The positions of the bands are also shown in Table II. The results are in accord with dissociation of the complex and the solvolysis process observed in the electrochemical measurements. The autocomplexation reaction that takes place after the loss of creatinine from the coordination sphere occurs in the same way as for the $CoCl_2$ solution [20].

$$2\,CoCl_2 + 6\,DMSO \rightarrow [Co(DMSO)_6]^{2+} + CoCl_4^{2-} \tag{5}$$

The bands at 616 and 676/680 nm are characteristic of $CoCl_4^{2-}$ [21]. In addition, a broad band of lower intensity, which can be attributed to $[Co(DMSO)_6]^{2+}$ [19], is present at approximately 535 nm. The other band corresponding to this species, expected at 684 nm, is not observed, as it lies in the same spectral region as the much more intense $CoCl_4^{2-}$ absorption band.

From analysis of the relative absorbances and taking into account the reported ε values [19], $[Co(DMSO)_6]^{2+}$ is the main species in solution. Only a small fraction of Co(II) is present as $CoCl_4^{2-}$, leaving free Cl^- in solution, giving rise to the electrochemical signal discussed above.

(c) *Water* When the compound is dissolved in water, its color changes immediately from light blue to pink. The spectrum coincides with that obtained with a $CoCl_2$ solution, indicating that the complex turns to $[Co(H_2O)_6]^{2+}$ in water showing the characteristic bands of this species [19].

CONCLUSIONS

The general behavior and especially the IR spectroscopic results suggest that $Co(creat)_2Cl_2$ is *quasi*-tetrahedral similar to the previously investigated Cu(II) complex of the same stoichiometry [3]. The present study also allows qualitative determination of the electrode reaction mechanism of this Co(II) complex although retention of its structure does not occur in the investigated solvents. The compound modifies its coordination sphere, dependent on the nature of the solvent. Once dissolved, the chloro ligands are released from the coordination sphere of the complex. DMSO and DMF are both aprotic solvents that strongly interact with cations but only in DMSO was complete loss of ligands observed. The complex appears to be more stable to solvolysis in DMF solution in which creatinine is retained in the coordination sphere and the loss of the two chloro ligands is followed by the attachment of solvent molecules. These facts are in accordance with a preference of the Co(II) ion to remain surrounded by ligands containing the same donor atom, as far as possible.

The redox process involving the metal center shows different electrochemical response in each solvent, as a consequence of different electrochemically active species. Measurements with $CoCl_2$ solutions in identical experimental conditions corroborate this observation.

In DMF, reduction of $[Co(creat)_2(DMF)_2]^{+2}$ from Co(II) to Co(I) is accompanied with a structural change. The generated Co(I) intermediate is stable on the time scale of the experiment and no deposition of Co(0) on the electrode surface is observed.

The electrochemical response in DMSO was examined in considerable detail in order to establish a mechanism of the reaction. The reduction of the Co(II) species generated in this medium, is complicated by the formation of metallic cobalt on the electrode surface. The Co(I) species produced on the first scan is less stable at slow scan rates; in this case the reduction path to metallic cobalt is predominant and gives rise to the electrodesorption peak observed during the oxidation scan.

Acknowledgements

This work was supported by CONICET and ANPCyT (Pict 06148), B.S.P.C. and E.J.B. are members of the Research Career of CONICET.

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