

Electrochemical Behaviour of Acyclic and Macrocyclic Complexes of Nickel(II), Copper(II) and Uranyl(VI)

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Abstract

The electrochemical behaviour of a series of mono-nuclear, homo- and hetero-dinuclear complexes of dioxouranium(VI), nickel(II) and copper(II) ions with acyclic and cyclic compartmental ligands, derived from the condensation of 2,6-diformyl-4-chlorophenol and polyamines of the type $\text{NH}_2-(\text{CH}_2)_2-\text{X}-(\text{CH}_2)_2-\text{NH}_2$ ($\text{X} = \text{NH}, \text{S}$), is reported. The kinetic and thermodynamic aspects governing the electrode mechanism are also discussed with respect to the different ligand designs and their differences in the donor atom sets.

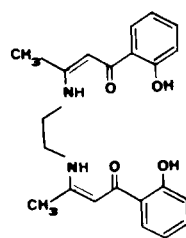
Introduction

Many studies have been published in the recent literature on dinuclear compounds containing similar or dissimilar metal ions, owing to the role played by these metal centers in a variety of fields [1–4]. The simultaneous presence of two metal ions with a suitable geometry and/or distance can give these complexes particular physico-chemical properties (*i.e.*, electric, magnetic, optical, chemical reactivity, etc.) which make them very interesting materials for theoretical studies and practical applications.

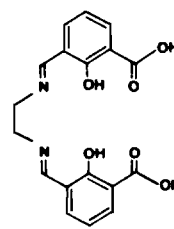
In recent years we have prepared several acyclic binucleating ligands capable of securing two identical or different metal ions in close proximity by condensation of *o*-acetoacetylphenol, β, δ -triketones, 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene, 3-formylsalicylic acid with polyamines [5–8]. More recently we have synthesized cyclic binucleating ligands using 2,6-diformyl-4-chlorophenol and polyamines of the type $\text{NH}_2-(\text{CH}_2)_n-\text{NH}_2$ or $\text{NH}_2-(\text{CH}_2)_2-\text{X}-(\text{CH}_2)_2-\text{NH}_2$ ($\text{X} = \text{NH}, \text{S}$) as precursors [9].

In previous papers we have also investigated the redox properties of transition metal complexes with the above compartmental ligands, namely **1** [10, 11],

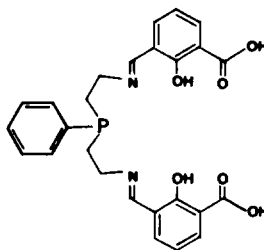
2 [12], **3** [7], **4** [13]. We present here the results of an electrochemical investigation of some transition metal complexes with the set of intercorrelated compartmental ligand **5–11**.



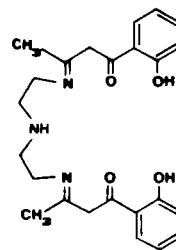
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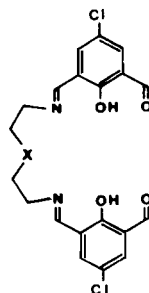
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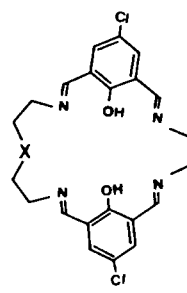
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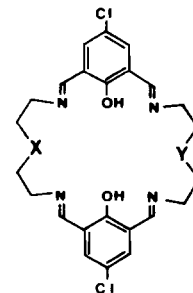
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5, X = NH
6, X = S



7, X = NH
8, X = S



9, X = Y = NH
10, X = Y = S
11, X = S; Y = NH

Experimental

The electrochemical apparatus and most of the materials used have been described previously [10–12]. Unless otherwise specified, the reported potential values refer to an aqueous saturated calomel electrode (S.C.E.). The temperature was controlled at 25 ± 0.1 °C. 2,6-Diformyl-4-chlorophenol was prepared according to literature [14]; ethylenediamine, 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane are commercial (K & K) products and were used without further purifications. The ligands and the mononuclear complexes, and the homo- and heterobinuclear complexes have been prepared according to the established procedures [9, 22].

These complexes were also characterized by X-ray fluorescence spectroscopy. By integration of back-scattered X-rays using a scanning electron microprobe, metal ratios were approximated and sample homogeneity was confirmed. A Philips SEM 505 model scanning electron microscope equipped with an EDAX data station was used. Absolute metal percentages were determined by atomic absorption.

Results and Discussion

Mononuclear Complexes

Uranyl(VI) derivatives

The redox properties of the uranyl(VI) complexes I–VIII have been studied by electrochemical techniques.

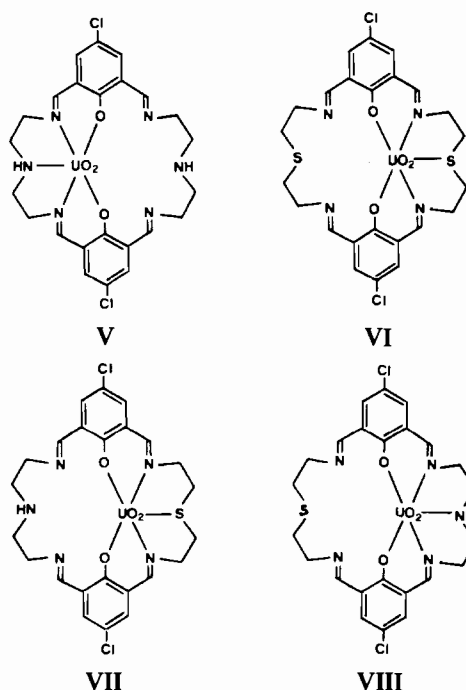
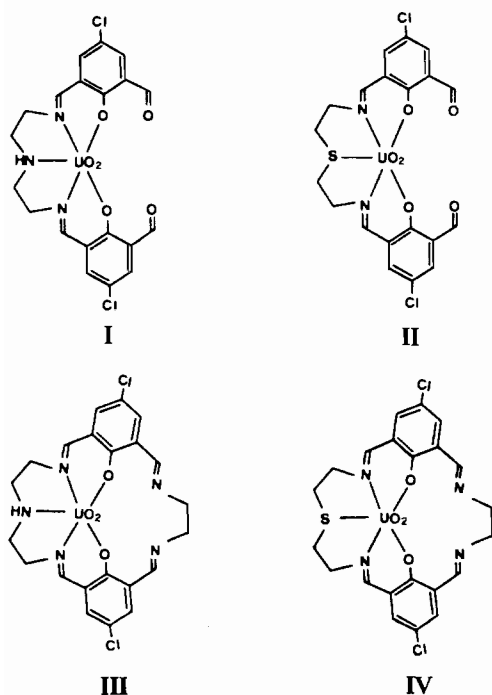


Figure 1 shows the cyclic voltammetric behaviour of I in dimethylsulphoxide (DMSO) solution. A well-formed cathoanodic peak system A/B is present in the potential range from 0.0 V to -1.3 V. Only at potential values higher than -1.7 V are other reduction processes also detectable, which, by comparison with the cathodic behaviour of the corresponding free ligands, have to be attributed to ligand-centered charge transfers. Controlled potential coulometric tests at -1.2 V revealed the cathodic process, occurring at peak A, to involve 1 mol of electrons per mol of I.

Diagnostic criteria [15] from the analysis of cyclic voltammograms recorded at scan rates varying from

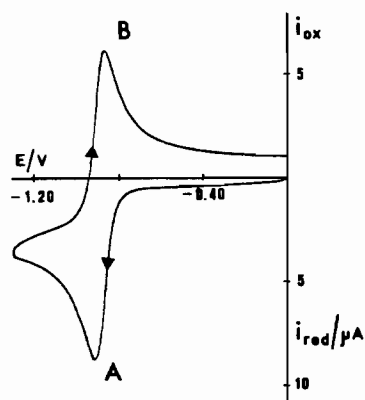


Fig. 1. Cyclic voltammogram recorded at a platinum microelectrode in a DMSO solution containing I (1.16×10^{-3} mol dm^{-3}) and $[\text{NET}_4]\text{ClO}_4$ (0.1 mol dm^{-3}). Scan rate: 0.2 V s^{-1} .

0.02 V s⁻¹ to 50 V s⁻¹ indicated the peak system A/B to be due to the uncomplicated one-electron charge transfers UO₂²⁺/UO₂⁺, near reversible in character ($\Delta E_p = 68$ mV at 0.2 V s⁻¹). This cathodic picture holds both at platinum and mercury electrodes and is typical for the uranyl(VI) complexes studied here.

TABLE I. Redox Characteristics of the Mononuclear Uranyl(VI) Complexes in DMSO-0.1 M [NEt₄]ClO₄ Solution

Compound	$E_{UO_2^{2+}/UO_2^+}^{\circ}$ (V) (vs. SCE)	ΔE_p (mV) ^a
I	-0.89	68
II	-0.80 ^b	62
III	-1.05	76
IV	-0.97 ^c	118
V	-1.00	127
VI	-0.82	81
VII	-0.95	72
VIII	-0.95	78

^a On a platinum electrode at 0.2 V s⁻¹. ^b Potential value computed at 1 V s⁻¹. ^c Potential value computed at 5 V s⁻¹.

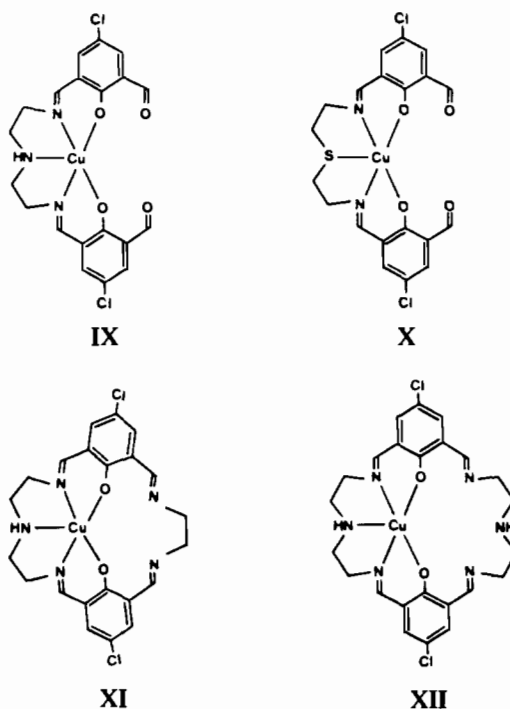
Table I summarizes the redox parameters for I–VIII derivatives. The degree of reversibility of the UO₂²⁺/UO₂⁺ electrode process can be approximately evaluated through the parameter ΔE_p at a fixed scan rate, taking into account that a constant value of 59 mV is expected for a completely reversible one-electron charge transfer. Only for derivatives IV and V is there a significant departure from the reversibility criterion. In addition, for the compounds II and IV the anodic-to-cathodic peak current ratio is lower than unity at 0.02 V s⁻¹ and increases with scan rate, reaching the unity value only at scan rates of 1 V s⁻¹ and 5 V s⁻¹, respectively. These data are indicative of a chemical reaction following the one-electron charge transfer. We think this chemical complication is due to the decomplexation of the electrogenerated uranyl(V) complexes. According to the method of Nicholson and Shain [16], a half-life of about 13 s and of 8 s can be calculated for the electrogenerated uranyl(V) complexes of II and IV, respectively.

An examination of the redox potentials allows us to conclude that some features are important in the thermodynamic access to the uranium(V) complexes. First of all, the redox ability of the metal center located in a compartment is affected by the atom donor set of the neighbouring compartment. In fact, within the two series I–III–V–VII and II–IV–VI–VIII, characterized by a N₃O₂ and N₂SO₂ coordination, respectively, the reduction potential follows the order I > VII > V > III and II > VI > VIII > IV. In addition, the comparison of the redox potentials of

the couples I–II, V–VI, VII–VIII, which differ only by the fifth coordination to the uranyl(VI) group through a nitrogen or a sulfur atom, indicates that a sulfur atom is less electron-donating towards uranium than a nitrogen atom; VII and VIII reduce at the same potential value. This may be explained either by considering that, as previously suggested, all atoms of the two compartments contribute to the redox behaviour, or, by assuming that the two different preparative routes really lead to the same product. Finally, it must be considered that compounds II and IV are not able to lodge the uranyl(V) ion. In this connection it must be taken into account that the cathodic reduction to uranyl(V) forces an enlargement of the N₂SO₂ compartment. Since in II the adjacent O₂O₂ compartment is open, the induced enlargement of the cavity leads to the expulsion of the U(V) ion. In IV the second O₂N₂ compartment is shut, but is probably much too rigid to bear the electroinduced stereochemical rearrangements. In the other cases, the two cavities are sufficiently flexible to minimize the effects of the structural changes. The very similar compounds I and III do not undergo the decomplexation reaction; this is probably attributable to the previously cited electronic effects, which strengthen the U–N bond to an extent sufficient to hold the uranium(V) ion coordinated.

Copper(II) derivatives

The electrode behaviour of the copper(II) mononuclear complexes IX–XII has been investigated.



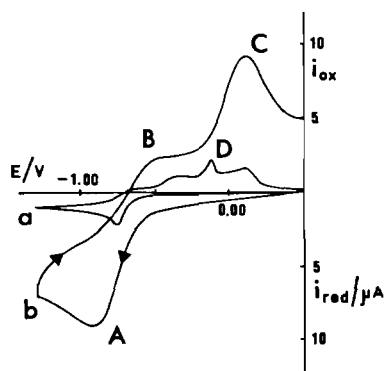
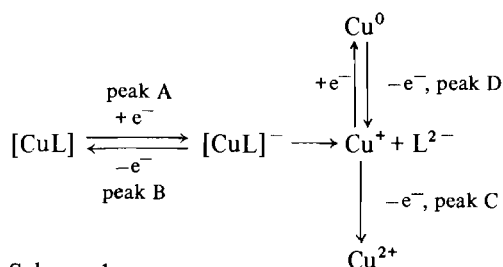


Fig. 2. Cyclic voltammograms recorded at two different scan rates in a DMSO solution containing IX (1.08×10^{-3} mol dm^{-3}) and $[\text{NEt}_4]\text{ClO}_4$ (0.1 mol dm^{-3}). (a) Scan rate: 0.01 V s^{-1} ; (b) scan rate: 0.50 V s^{-1} . Platinum working microelectrode.

Figure 2 shows the cyclic voltammetric response obtained at a platinum microelectrode from a DMSO solution of IX, which is typical for all copper(II) complexes of the present study. At scan rates higher than 0.1 V s^{-1} the cathodic peak A is accompanied, in the reverse scan, by the directly associated re-oxidation peak B, and the more anodic peak C. At decreasing scan rates peak B tends to disappear, and at 0.01 V s^{-1} the stripping peak D takes place, clearly due to the reoxidation of some electrodeposited copper metal. Indeed this voltammetric picture is quite common to many mononuclear copper(II) complexes $[\text{CuL}]$ [12], and it has been explained according to the e.c.e. mechanism (Scheme 1).



Scheme 1.

It must be taken into account that the expulsion of copper(I) ions from the complex at the potentials of peak A is thermodynamically followed by reduction to copper metal because free copper(I) ions in DMSO reduce at about -0.12 V [17]. We succeeded to prevent nearly all of the decomplexation reaction which follows the first quasi-reversible charge transfer, and hence to compute a reliable formal electrode potential for the couple IX/ $[\text{IX}]^-$, using a mercury electrode and high potential scan rates. In fact, the degree of reversibility of the charge transfer at a mercury electrode was higher than that at a platinum electrode (for instance, at 0.5 V s^{-1} , ΔE_p is

equal to 450 mV at Pt electrode and 210 mV at Hg electrode); in addition, at the highest scan rate of 50 V s^{-1} , $(i_p)_B/(i_p)_A$ ratio reaches the value of 0.95, with a ΔE_p of 360 mV. In spite of the sluggishness of the charge transfer, one can likely assume that a transfer coefficient α of 0.5 (or not very different) is involved in the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ step, so that the shifts of both the cathodic and the directly associated anodic peaks are symmetric in respect to the standard potential [18]. In addition, the half-life of the electrogenerated copper(I) complex could be evaluated through the Nicholson's method at slow scan rates. Only for compounds XI and XII it was impossible to prevent the cited chemical complication at an extent sufficient to compute reliable formal electrode potentials.

Table II reports the most significant parameters of the electrode activity of the studied copper(II) complexes. A very rough comparison of the easy access to the reduced form for the starting copper(II) complexes can be tentatively accomplished through the peak potential value, E_p^a , at a fixed scan rate on the same electrode material. Although the set of data is much less significant than that obtained for uranyl-(VI) complexes, it seems that, as regards the different fifth donor atoms, the poor electron-donating ability of the sulfur atom towards the copper(II) centre, in respect to that of the nitrogen atom, is less marked. This can be explained considering that the aminic nitrogen atom is a 'hard' base, while the thio group is a 'soft' base. Hence the nitrogen atom binds more strongly to the 'hard' UO_2^{2+} acid; the effect is quenched in the case of the 'borderline' Cu^{2+} acid [19].

TABLE II. Significant Characteristics for the Reduction of the Mononuclear Copper(II) Complexes, $[\text{CuL}]$, in DMSO-0.1 M $[\text{NEt}_4]\text{ClO}_4$ Solution

Compound	$E_{\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}}^{\circ}$ (V) (vs. SCE)	E_p^a	$t_{1/2}[\text{CuL}]^-$ (s)
IX	-0.76	-0.81	1
X	-0.75	-0.83	6
XI		-1.08	
XII		-0.77	

^aPeak potential values on a mercury electrode at 0.2 V s^{-1} .

Dinuclear Complexes

The dinuclear complexes examined by voltammetric techniques include both heterodinuclear (XIII–XV) and homodinuclear (XVI–XVII) derivatives.

Figure 3 shows the cyclic voltammetric behaviour of XIII in DMSO solution. Two distinct cathodic processes arise, which, from a comparison with the one-electron oxidation of an equimolar amount of ferrocene, have to be attributed to two subsequent

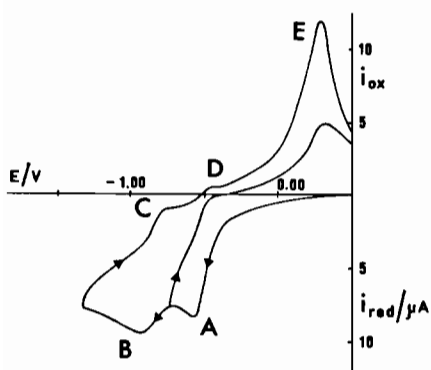
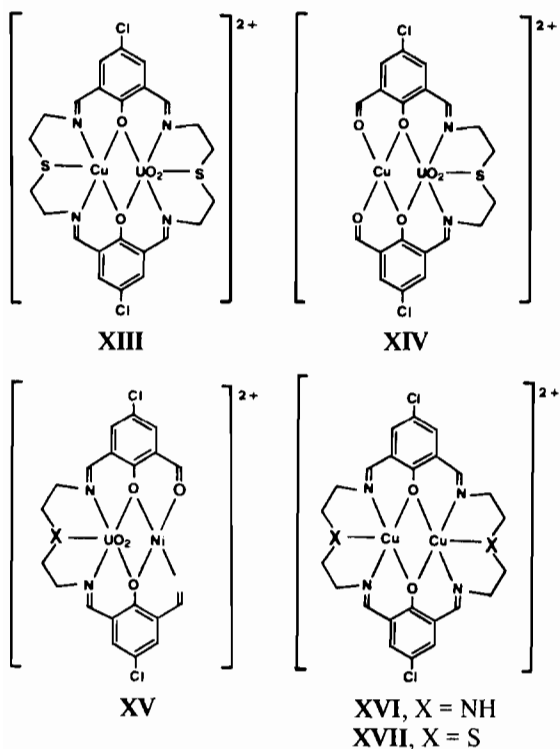


Fig. 3. Cyclic voltammogram recorded in a DMSO solution containing **XIII** (1.3×10^{-3} mol dm $^{-3}$) and [NET $_4$]ClO $_4$ (0.1 mol dm $^{-3}$). Platinum working microelectrode. Scan rate: 0.2 V s $^{-1}$.

TABLE III. Formal Electrode Potentials (in V, vs. S.C.E.) for the Reduction of each Metal Centre in the Binuclear Complexes, in DMSO-0.1 M [NET $_4$]ClO $_4$ Solution

Compound	UO $_2^{2+}$ in N $_2$ SO $_2$ compartment	Cu $^{2+}$ in N $_2$ SO $_2$ compartment	Cu $^{2+}$ in N $_3$ O $_2$ compartment	Cu $^{2+}$ in O $_2$ O $_2$ compartment	Ni $^{2+}$ in O $_2$ O $_2$ compartment
XIII	-0.84	-0.51			
XIV	-0.58			-0.58	
XV	-0.58				-1.7
XVI			-0.83 ^a		
XVII		-0.93 ^a			

^a Peak potential value at 0.2 V s $^{-1}$ on a platinum electrode for a single two-electron step.

one-electron charge transfers. The peak system A/D is clearly due to the redox couple Cu(II)/Cu(I) of **XIII**, because of the presence of the reoxidation peak E attributable to the oxidation of free copper(I) ions produced by the decomplexation of the electro-generated mixed valent species Cu^IU^{VI}. The $(i_p)_D/(i_p)_A$ ratio, notably lower than unity, is evidence that this reaction is operative. In this picture the peak system B/C must be attributed to the redox couple U(VI)/U(V). A complete analysis of cyclic voltammetric responses with scan rate cannot be performed in that the two peak systems tend to merge, owing to the different degree of reversibility of the relevant charge transfers. Hence, only approximate values can be computed for the potentials of the two redox couples, and these data are reported in Table III.

The voltammetric behaviour of **XIV** is at least in principle similar to that described for **XIII**, but peaks A and B are in this case not well resolved [$(E_p)_A - (E_p)_B = 130$ mV at 0.2 V s $^{-1}$], and at high scan rates (>1 V s $^{-1}$) the voltammetric picture shows only one cathodic peak system. Hence, even if the reduction mechanism involves two one-electron charge transfers at different potentials, not a single two-electron step, we can give only a single potential value for the two redox couples Cu^{II}/Cu^I and U^{VI}/U^V.

Additional proofs of the reduction in two successive one-electron steps of binuclear complexes of type **XIV** come from the compound **XV**. It shows in principle similar to that described for **XIII**, but peaks A and B are in this case not well resolved [$(E_p)_A - (E_p)_B = 130$ mV at 0.2 V s $^{-1}$], and at high scan rates (>1 V s $^{-1}$) the voltammetric picture shows only one cathodic peak system. Hence, even if the reduction mechanism involves two one-electron charge transfers at different potentials, not a single two-electron step, we can give only a single potential value for the two redox couples Cu^{II}/Cu^I and U^{VI}/U^V.

The voltammetric behaviour displayed by the homodinuclear complexes **XVI** and **XVII** is less encouraging than the ones described above. In fact, at mercury electrodes adsorption processes make the cyclic voltammograms unintelligible. At platinum electrodes the reduction process appears as an extremely rounded cathodic peak, to which no reoxidation peak is directly associated even at the highest scan rates. We suggest that this behaviour is

due to two one-electron charge transfers at the same or near the same potentials, followed by a rapid decomplexation of the two copper(I) centers.

The reduction potentials for all the binuclear complexes studied are summarized in Table III. The reduction potentials of the metal centers are in general less negative than those of the corresponding mononuclear complexes, except for UO_2^{2+} . This potential shift can be ascribed to the cationic form of these dinuclear complexes which favours electrostatically the addition of electrons, while in **XIII** the thermodynamic stabilization of the mixed valent species $\text{Cu}^{\text{I}}\text{U}^{\text{VI}}$ enlarges the separation between the potentials of the two redox couples involved.

It must be noted that the electrochemical measurements were carried out in dimethylsulphoxide owing to the low solubility of these compounds in other non-coordinating solvents. Such solvents can, however, coordinate the central metal ion, sometimes giving rise, especially when high temperatures were used for the solubilization of the samples, to undesired complexes with a solvent molecule in the apical position instead of the X donor atom of the ligand. Such a complication does not happen with UO_2^{2+} where the five N_2XO_2 donor atoms are involved in the formation of the very usual and stable equatorial pentacoordination.

Finally, we note that the electrochemistry of the binuclear complexes **XIII–XVII** is indicative of the difficulty of resolving the intriguing dilemma as to whether binuclear complexes reduce in two one-electron steps at the same potential [20] or at different potentials [21].

Acknowledgements

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