

primary sequence of Dfx and Dfx N-term was suspected to be the cause of the pH dependent redox potential. Since Dx does not contain such an homologous residue, but also show a pH dependent redox potential, led us to the search for another conserved ionizable residue. Tyrosine in position 7 could be a plausible candidate, but is also conserved in the Rd sequence. Lys8 and Glu31 are conserved residues in the vicinity of the metal center and are most probably the ionizable sites that influence the pH dependence observed. In *D.gigas* Rd the equivalent position to Glu31 is replaced by an Ala (residue 44). In Rubredoxins the aa sequence position equivalent to Lys 8 is occupied with Val or Ala residues.

FR was a PRAXIS XXI visiting scientist in Portugal. This work was supported by Grants from NIH GM 46865 and Mayo Foundation (FR) and Junta Nacional de Investigação Científica e Tecnológica and PRAXIS XXI (IM and JM). CSA and MJL are supported by PRAXIS XXI grants. Discussions with several European colleagues under contract ERBCHRXCT920014 are acknowledged (JM). Special reference to M.J.Romão for all the extensive collaboration on X-ray studies on Dx and metal substitutions underway.

## REFERENCES

- [1] - Sieker, L.C. and LeGall, J. (1994) in *Methods in Enzymology*, vol. 243, Acad. Press, pp 216-241.
- [2] - Moura, I., Tavares, P. and Ravi, N. (1994) in *Methods in Enzymology*, vol. 243, Acad. Press, pp 203-215.
- [3] - Moura, I., Bruschi, M., LeGall, J., Moura, J.J.G. and Xavier, A.V. (1977) *BBRC*, **75**, 1037-1044.
- [4] - Moura, I., Huynh, B.H., LeGall, J., Xavier, A.V. and Munck, E. (1980) *JBC*, **255**, 2493-2498.
- [5] - Bruschi, M., Moura, I., Sieker, L.C., LeGall, J. and Xavier, A.V. (1979) *BBRC*, **90**, 596-605.
- [6] - Archer, M., Huber, R., Tavares, P., Moura, I., Moura, J.J.G., Carrondo, M.A., Sieker, L.C., LeGall, J. and Romão, M.J. (1995) *JMB*, **251**, 690-702.
- [7] - Devreese, B., Tavares, P., Lampreia, J., VanDamme, N., Moura, J.J.G., VanBeeumen and Moura, I. (1996) *FEBS Lett.*, **385**, 138-142.
- [8] - Czaja, C., Litwiller, R., Tavares, P., LeGall, J., Moura, J.J.G., Moura, I. and Rusnak, F. (1995) *JBC*, **270**, 20273-20277.
- [9] - Ascenso, C.S., Scharf, M., Moura, I. And Moura, J.J.G. (1995) *Portugalix Electrochimica Acta*, **13**, 361-364.
- [10] - Verhagen, M.F.J.M., Voorhorst, W.G.B., Kolkman, J.A., Wolbert, R.B.G. and Hagen, W.R. (1993) *FEBS*, **336**, 13-18.

## COMPARATIVE STUDY OF THE REDOX PROPERTIES OF PLATINUM, PALLADIUM, COPPER AND IRON CAMPHOR DERIVED COMPLEXES

M. Fernanda N.N. Carvalho<sup>a</sup>, Armando J.L. Pombeiro<sup>a</sup> and Rudolf Herrmann<sup>b</sup>

<sup>a</sup> Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

<sup>b</sup> Institut für Organisch-Chemie und Biochemie, Technische Universität München, Lichtenbergstrabe 4, D-85474 Garching, Germany

We have previously prepared several camphorimine complexes using metal sites such as  $\{PdCl_2\}^{(1)}$ ,  $\{FeCl_2\}^+$ ,<sup>(2)</sup> or  $\{CuCl_2\}^{(2)}$  and studied their redox properties by cyclic voltammetry.

We now report the electrochemical behaviour of some new platinum complexes, Table 1, and compare their electronic properties with those of Pd(II), Fe(III) or Cu(II) derived from camphorimine species of type (A) or (B).



Table 1 -Cyclic voltammetric data<sup>a</sup> for  $[PtCl_2L_2]$  (L=A, R=Ph or NMe<sub>2</sub>) and  $[PtCl_2L]$  (L=B, R=NMe<sub>2</sub>) complexes, and for the free camphorimine ligands (L).

| COMPLEX<br>(ligand type) / R group | E <sub>1/2</sub> <sup>ox</sup> | E <sub>1/2</sub> <sup>red</sup> | L<br>type / R                         | E <sub>p</sub> <sup>ox</sup> | E <sub>p</sub> <sup>red</sup> |
|------------------------------------|--------------------------------|---------------------------------|---------------------------------------|------------------------------|-------------------------------|
| (A) / Ph                           | 1.45                           | -1.00 <sup>b</sup>              | (A) / Ph <sup>(3)</sup>               | 1.86                         | -1.54                         |
| (A) / NMe <sub>2</sub>             | 1.34 <sup>c</sup>              | -1.10                           | (A) / NMe <sub>2</sub> <sup>(2)</sup> | 1.48                         | —                             |
| (B) / NMe <sub>2</sub>             | 1.36 <sup>d</sup>              | -1.40                           | (B) / NMe <sub>2</sub> <sup>(2)</sup> | 1.54                         | -1.42                         |

<sup>a</sup> Values in V ± 20 mV vs. SCE measured (at 200 mV s<sup>-1</sup>) at a Pt wire electrode, in 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>] / CH<sub>2</sub>Cl<sub>2</sub>, using [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> (E<sub>1/2</sub><sup>ox</sup>=0.54 V) as internal reference. <sup>b</sup> Another wave is detected at E<sub>1/2</sub><sup>red</sup> = -1.25 V. <sup>c</sup> Irreversible wave (E<sub>p</sub><sup>ox</sup>); another wave is detected as a shoulder at E<sub>p</sub><sup>ox</sup> = 1.20 V. <sup>d</sup> Another wave is detected at E<sub>1/2</sub><sup>ox</sup> = 1.68 V.

The results were obtained by cyclic voltammetry and controlled potential electrolysis commonly in 0.2 M [NBu<sub>4</sub>][BF<sub>4</sub>] / CH<sub>2</sub>Cl<sub>2</sub> solutions, but in some cases in THF, using Pt wire or Pt gauze working electrodes, respectively. All the potential

values are quoted *versus* S.C.E. using  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$  ( $E_{1/2}^{\text{ox}} = 0.54 \text{ V}$ ) as internal reference.

As shown by the values on Table 1, the Pt(II) complexes are easier to oxidize than the corresponding free ligands. In addition, the anodic and cathodic processes, except the oxidation of  $[\text{PtCl}_2\text{L}_2]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{NMe}_2$ ), display a significant reversible character, in contrast with the behaviour observed for the free ligands. These observations suggest a significant contribution of the metal to the HOMO of the complexes. Furthermore, complexes derived from type (A) ligands are easier to reduce than the corresponding free ligands but the compound derived from type (B) ligand ( $\text{R}=\text{NMe}_2$ ) displays a cathodic process at a potential value similar to that measured for the free ligand. Moreover, the reduction process observed on the Pd(II) complex derived from the (B) type ligand ( $\text{R}=\text{NMe}_2$ ), displays (Table 2) a comparable value to that measured for the Pt(II) complex, in agreement with a ligand centred reduction process.

No other complexes with type (B) ligands were obtained, due to side reduction reactions of  $\text{PtCl}_2$  with deposition of Pt(0), thus inhibiting the formation of the expected complexes.

Table 2 Cyclic voltammetric data<sup>a</sup> for complexes  $[\text{PdCl}_2\text{L}_2]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{NMe}_2$ , OMe, OH, NPh or  $\text{NPr}^i$ ;  $\text{L}=\text{B}$ ,  $\text{R}=\text{NMe}_2$  or  $\text{NH}_2$ ).

| COMPLEX<br>(ligand type) / R group | $E_p^{\text{ox}}$ <sup>b</sup> | $E_p^{\text{red}}$ <sup>b</sup> | COMPLEX<br>(ligand type) / R group | $E_p^{\text{ox}}$ <sup>b</sup> | $E_p^{\text{red}}$ <sup>b</sup> |
|------------------------------------|--------------------------------|---------------------------------|------------------------------------|--------------------------------|---------------------------------|
| (B) / $\text{NMe}_2$               | 1.52<br>(1.54)                 | -1.48<br>(-1.42)                | (A) / OH                           | 1.81<br>(1.53)                 | -1.54<br>(-1.68)                |
| (B) / $\text{NH}_2$                | 1.92<br>(1.98)                 | -1.42<br>(-1.42)                | (A) / NPh                          | 1.96<br>(1.86)                 | -1.0<br>(-1.54)                 |
| (A) / $\text{NMe}_2$               | 1.76<br>(1.48)                 | -1.20 <sup>c</sup><br>—         | (A) / $\text{NPr}^i$               | 1.76<br>(1.59)                 | -1.24<br>(-2.12)                |
| (A) / OMe                          | —<br>(1.86)                    | -0.84<br>(-2.02)                |                                    |                                |                                 |

<sup>a</sup> Values in Volt  $\pm 20$  mV, *versus* S.C.E., measured in 0.2 M  $[\text{NBu}_4][\text{BF}_4] / \text{CH}_2\text{Cl}_2$ , unless stated otherwise. <sup>b</sup> In brackets are given the potential values measured for the corresponding processes in the free ligands. <sup>c</sup> In THF.

For the palladium complexes the comparison between the potentials of their redox processes and those of the free ligands suggests that for those with type (B) ligands they are centred at the ligands, whereas for the type (A) case, the metal appears to play a more important role.

The redox behaviour of the palladium complexes is possibly related with the characteristics of the group responsible for coordination, the imine group on type (A) and the sulphonimine group on type (B) ligands, as it was previously demonstrated by X-ray diffraction analysis<sup>(1)</sup> for complexes  $[\text{PdCl}_2\text{L}_2]$  ( $\text{L}=\text{A}$  or  $\text{B}$ ,  $\text{R}=\text{NMe}_2$ ).

As observed for some Pt(II) complexes, the  $[\text{FeCl}_2\text{L}_2][\text{FeCl}_4]$  and  $[\{\text{CuCl}_2\text{L}\}_2]$  compounds display reversible cathodic processes, which occur at potentials, Table 3, comparable to those of the processes  $\text{Fe(III)} \rightarrow \text{Fe(II)}$  at  $\text{FeCl}_3$  ( $E_{1/2}^{\text{red}} = 0.06 \text{ V}$ ), and  $\text{Cu(II)} \rightarrow \text{Cu(I)}$ , at  $\text{CuCl}_2$  ( $E_{1/2}^{\text{red}} = 0.70 \text{ V}$ ), respectively, in agreement with electron transfer processes essentially centred at the metal site.

Table 3 Cyclic voltammetric data<sup>a</sup> for  $[\text{FeCl}_2\text{L}_2][\text{FeCl}_4]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{NMe}_2$ , OH, OMe;  $\text{L}=\text{B}$ ,  $\text{NMe}_2$ , and  $[\{\text{CuCl}_2\text{L}\}_2]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{OH}$ , OMe).

| $[\text{FeCl}_2\text{L}_2][\text{FeCl}_4]$ |                                     | $[\{\text{CuCl}_2\text{L}\}_2]$ |                                     |                                  |                                |
|--|-------------------------------------|---------------------------------|-------------------------------------|----------------------------------|--------------------------------|
| (ligand type) / R group                    | $E_{1/2}^{\text{red}}$ <sup>b</sup> | (ligand type) / R group         | $E_{1/2}^{\text{red}}$ <sup>I</sup> | $E_p^{\text{red}}$ <sup>II</sup> | $E_p^{\text{ox}}$ <sup>b</sup> |
| (A) / $\text{NMe}_2$                       | 0.08<br>(—)                         | (A) / OH <sup>c</sup>           | 0.70                                | -2.11<br>(-1.68)                 | —<br>(1.54)                    |
| (A) / OH                                   | 0.08<br>(-1.68)                     | (A) / OMe <sup>c</sup>          | 0.70                                | -1.91<br>(-2.02)                 | 1.11<br>(1.86)                 |
| (A) / OMe                                  | 0.08<br>(-2.02)                     |                                 |                                     |                                  |                                |
| (B) / $\text{NMe}_2$                       | 0.10<br>(-1.42)                     |                                 |                                     |                                  |                                |

<sup>a</sup> Values in V  $\pm 20$  mV vs. SCE measured (at  $200 \text{ mV s}^{-1}$ ) at a Pt wire electrode, in 0.2 M  $[\text{NBu}_4][\text{BF}_4] / \text{CH}_2\text{Cl}_2$ , using  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$  ( $E_{1/2}^{\text{ox}} = 0.54 \text{ V}$ ) as internal reference. <sup>b</sup> In brackets are given the potential values measured for corresponding processes on the free ligands. <sup>c</sup> In THF.

By controlled potential electrolysis performed at  $[\text{FeCl}_2\text{L}_2][\text{FeCl}_4]$  complexes, we confirmed that one electron *per* iron atom is transferred at the cathodic process. Moreover, by exhaustive controlled potential electrolysis of  $[\text{FeCl}_2\text{L}_2][\text{FeCl}_4]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{OH}$ ) the new species  $[\text{FeCl}_2\text{L}_2]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{OH}$ ) was obtained, which was isolated and characterized by I.R. and  $^1\text{H}$  NMR spectroscopies and elemental microanalysis.

Cathodic controlled potential electrolyses performed on  $[\{\text{CuCl}_2\text{L}\}_2]$  ( $\text{L}=\text{A}$ ,  $\text{R}=\text{OH}$  or OMe) at 0.70 V show that one electron *per* molecule is transferred, in agreement with the formation of a mixed valence Cu(I)-Cu(II) species, which was not possible to isolate from the electrolysed solution. This behaviour was previously

detected<sup>(4)</sup> in copper complexes derived from the related ligand



A considerably different redox behaviour is detected for the first row (Fe and Cu) compared to second (Pd) and third row (Pt) complexes, since on iron and copper complexes the reduction processes have a metal centred character. However, the two types of ligands seem to have different behaviours when they bind metals such as palladium or platinum. In fact, the redox processes observed at complexes derived from type (B) ligands seem to display considerable ligand character, in contrast with complexes derived from type (A) ligands for which the cathodic processes appear to have usually a considerable metal character, possibly as a consequence of different participation of these ligands on the LUMO and on the HOMO of the complexes.

Camphor imine species are versatile ligands under the coordinative point of view, which bind the different metal sites through one of the available imine nitrogen atoms, adapting themselves to the characteristics of the transition metal. Moreover, at the iron and copper centres they possibly act as chelating ligands such as observed before<sup>(4)</sup> on copper complexes, in contrast with the monodentate coordination observed on metal sites of the second and third rows.

They also display high electronic versatility, stabilizing metal centres with considerably different redox properties.

#### Acknowledgements

This work was partially supported by Junta Nacional de Investigação Científica e Tecnológica (JNICT) and Deutscher Akademischer Austauschdienst (DAAD).

#### References

- (1)-M.F.N.N. Carvalho, L.M.G.Costa, A.J.L. Pombeiro, A. Schier, W. Scherer, S.K. Harbi, U. Verfürth and R. Herrmann, *Inorg. Chem.* 33 (1994) 6270.
- (2)-A.S.Viana, M.F.N.N.Carvalho, R.Herrmann, A.J.L.Pombeiro, *Inorg. Chim. Acta.* (1996) in press.
- (3)-A.S. Viana, M. F.N.N.Carvalho, R. Herrmann and A. J.L.Pombeiro, *Portugaliae Electrochimica Acta*, 13 (1995) 309.
- (4)- M.F.N.N. Carvalho, A.C.Consiglieri, M.T. Duarte, A.M. Galvão, A.J.L.Pombeiro, R.Herrmann, *Inorg.Chem.*, 32 (1993) 5160.

## Electrochemical behaviour of adducts of *trans*-[Mo(NCN)<sub>2</sub>(dppe)<sub>2</sub>] with some transition metal Lewis acids

Sónia M. P. R. M. Cunha, M. Fátima C. Guedes da Silva and Armando J. L. Pombeiro

*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex*

#### Abstract

The electrochemical behaviours of the bis(cyanoimide) complex *trans*-[Mo(NCN)<sub>2</sub>(dppe)<sub>2</sub>] (dppe=Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) and of the derived adducts with some transition metal [Pt(II), Re(I) or V(III)] Lewis acids have been investigated by cyclic voltammetry (CV) and, in some cases, by controlled-potential electrolysis (CPE), in aprotic media, at a Pt electrode. In general, anodic and cathodic processes are detected, by CV, being centred either at the Mo or at the other transition metal site, and the effect of the formation of the adduct on the redox potential is discussed, as well as the dependence of its stability on the electron-transfer process.

#### Introduction

The synthesis and study of the reactivity of compounds exhibiting enzyme-like activity is a major challenge in Chemistry. In pursuit of our interest in the activation by transition metal centres of alternative substrates of nitrogenase, we have been investigating the activation of cyanamide, a recently discovered substrate of this enzyme, by dinitrogen binding sites, and, e.g., we obtained the bis(cyanoimide) complex *trans*-[Mo(NCN)<sub>2</sub>(dppe)<sub>2</sub>] (dppe=Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) from the reaction of cyanamide with the parent dinitrogen complex, *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>].

In the cyanoimido-complex, one of the NCN ligands (or, in one of the cases, both of them - see below) undergoes electrophilic attack by a transition metal Lewis acid (ML<sub>n</sub>), e.g., derived from [Pt<sub>2</sub>Cl<sub>4</sub>(PEt<sub>3</sub>)<sub>2</sub>], [ReCl(N<sub>2</sub>)(PMePh<sub>2</sub>)<sub>4</sub>] or [VCl<sub>3</sub>(THF)<sub>3</sub>], to form the corresponding dinuclear adduct of the type *trans*-[Mo(NCN→ML<sub>n-1</sub>)(NCN)(dppe)<sub>2</sub>] (or the trinuclear product if both the NCN ligands bind to ML<sub>n-1</sub> centres).

We now report the results of an electrochemical study of both the bis(cyanoimide) complex and the corresponding adducts, by CV and, in some cases, by CPE.