[4] R.A. Michelin, S. Faglia and P. Uguagliati, Inorg. Chem., 1983, 22, 1831.

[5] W.E. Geiger, Progress Inorg. Chem., 1985, 33, 275.

[6] L. Chen, J.A. Davies and R. Staples, Inorg. Chim. Acta, 1989, 163, 1; Y.A. Davies, V. Uma and J.G. Mierzwiak, J. Electroanal. Chem., 1985, 196, 329, and refs. therein.

[7] L. Chen and J.A. Davies, Inorg. Chim. Acta, 1990, 175, 41; J.A. Davies, L. Chen, C.T. Eagle and R.L. Staples, in "Molecular Electrochemistry of Inorganic, Bioinorganic and Organometallic Compounds", A.J.L. Pombeiro and J. McCleverty (eds.), NATO ASI Series, Kluwer Academic Publ., Dordrecht, the Netherlands, in press.

Acknowledgements

This work has been partially supported by a fellowship (to E.M.P.R.P.B.) under the PEDIP programme, by JNICT and INIC (Portugal).

REDOX PROPERTIES OF SOME TRYPTAMINE-DERIVED SALICYLALDIMINES AND OF THEIR TETRA-COORDINATE COBALT(II), NICKEL(II) OR COPPER(II) COMPLEXES

YU-YING TONG, M. FÁTIMA C. GUEDES DA SILVA,
JOÃO J.R. FRAÚSTO DA SILVA and ARMANDO J.L. POMBEIRO

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

P. MARTIN-ZARGA, G. MARTIN and P. GILI

Departamento de Química Inorgânica,
Universidad de la Laguna, Tenerife,
Canary Islands, Spain

Summary

The redox properties of various Schiff bases (HL, derived from condensation of tryptamine with salicylaldehyde derivatives) and of some of their complexes [ML_2] (M = Co, Ni or Cu) have been studied by cyclic voltammetry and cathodic controlled potential electrolysis, in aprotic media. They present both anodic and cathodic processes which, in the case of the complexes, can be either ligand or metal centred, the redox potentials of the latter, for both the M(II/III) and M(I/II) redox pairs, following the order: Co < Ni < Cu.

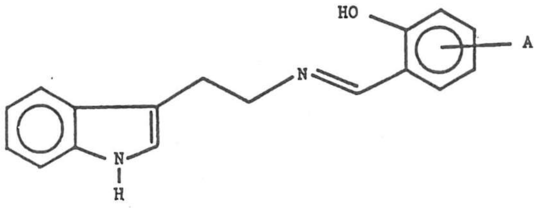
Introduction

Although complexes with Schiff bases presenting a bulky group can exhibit unusual properties, only a limited number of them have been reported [1] to contain an indole group in particular within a derivative of triptamine (a species with a recognized biological activity). Therefore, in pursuit of our interest on the redox properties of complexes with biological significance [2], we have embarked upon the investigation of the electrochemical behaviour of complexes with such a type of Schiff bases, and we now report the preliminary results we have obtained.

Portugaliæ Electrochimica Acta, 11 (1993) 87-92

Results and discussion

The following Schiff bases (HL), derived from condensation of tryptamine (TPA) with salicylaldehyde (SAL) derivatives [1], have been considered:



HL	SALTPA	3 MeO-SALTPA	3 EtO-SALTPA	5 Br-SALTPA
A	H	3-MeO	3-EtO	5-Br

Their redox properties, as well as of some of their tetra-coordinated cobalt(II), nickel(II) or copper(II) complexes $[ML_2]$ (M=Co, Ni or Cu; L = basic form of HL), have been studied by cyclic voltammetry (CV, at a Pt disc or hanging Hg drop electrode) and by cathodic controlled potential electrolysis (CPE, at a Hg-pool electrode), in 0.2 M $[Bu_4N][BF_4]$/NCMe.

The studies have been hindered by strong and fast electrode poisoning and inactivation, and have required some modifications of the common CV cell in particular by adapting easily removable disc working and counter electrodes, for ready cleaning purposes.

Nevertheless, we have recognized that, by CV, the free Schiff bases undergo two successive irreversible anodic waves, the first one at ca. 0.9-1.1 V and the second one at ca. 1.3 V vs. SCE, apart from an irreversible cathodic wave (involving ca. 0.7-0.8 electrons as measured by CPE) at ca. -1.7 to -1.9 V vs. SCE (see Fig. 1 for HL = 3MeO-SALTPA). Moreover, their complexes exhibit metal or ligand based redox processes which can be accounted for by considering the expected order of the redox potentials for the M(II/III) or M(I/II) redox pairs (Co < Ni < Cu).

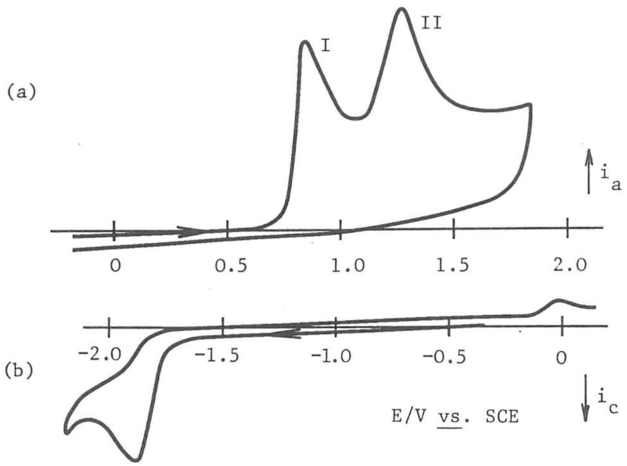


Fig. 1 - Cyclic voltammogram of 3MeO-SALTPA in 0.2 M $[Bu_4N][BF_4]$/NCMe at a Pt disc electrode. Anodic (a) and cathodic (b) scan (100 mV s^{-1}).

In fact, metal centered oxidations are clearly observed only for the Co(II) compounds (at ca. 0.5 V vs. SCE), as shown in Fig. 2a, for $[Co(5Br\text{-}SALTPA)_2]$ (wave I). The other two detected anodic waves occur at higher potentials (${}^{II}E_p^{ox}$ = 1.27 and ${}^{III}E_p^{ox}$ = 1.54 V vs. SCE) which are somewhat more anodic (by ca. 0.14 and 0.25 V, respectively) than those of the free ligand and are assigned to ligand based oxidation processes.

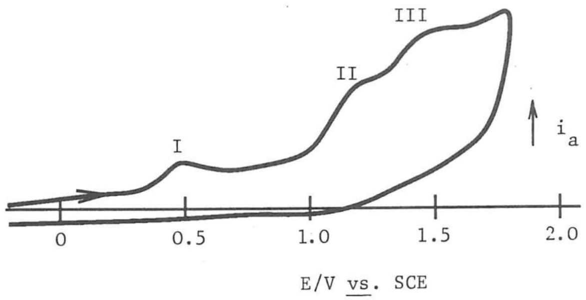


Fig.2 - Cyclic voltammogram (anodic scan, 100 mVs^{-1}) of $[Co(5Br\text{-}SALTPA)_2]$ in 0.2 M $[Bu_4N][BF_4]$/NCMe at a Pt disc electrode.

The Cu(II) complexes only exhibit, by CV, the two ligand centred anodic waves, whereas the Ni(II) compounds present a composite wave at ca. 0.8 - 1.0 V which appears to involve the oxidation of the metal and the first oxidation of the ligand, being followed, at a higher potential (ca. 1.0-1.3 V) by a second anodic wave possibly based on the ligand.

The cathodic behaviour of the complexes has also been investigated and, apart from the expected reduction of the ligand, metal based reductions have been detected, at higher potentials, in particular for the Cu(II) compounds (at ca. -0.8 to -1.0 V) and, possibly, for the Ni(II) species (at ca. -1.5 V).

This is shown in Fig. 3 for [Ni(3MeO-SALTPA)$_2$] which undergoes a single-electron reduction (as measured by CPE at a Hg-pool electrode) to Ni(I) species, with a considerable degree of reversibility (as recognized by CV).

Other reduction waves, at lower potentials (comprising the range for the cathodic processes of the free ligands), are also detected by CV, for all the complexes, being assigned to ligand centred reductions. The numbers of transferred electrons have been measured by CPE, and the obtained values (ca. 0.6-1.5 e/metal atom) suggest the reduction can occur, in some cases, at both ligands (compare with the abovementioned number of electrons, ca. 0.7-0.8, involved in the cathodic process for each free ligand). However, the numbers of electrons thus obtained should be taken cautiously, in view of adsorption and poisoning effects at the electrode (see above) which, moreover, have prevented such measurements for the anodic processes at Pt gauze electrodes.

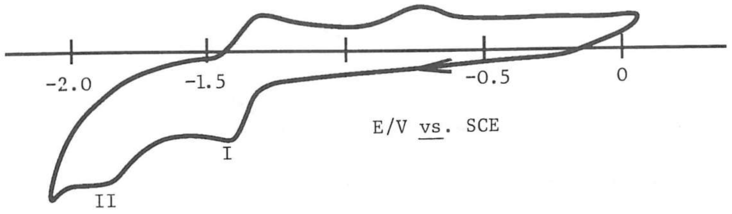


Fig. 3 - Cyclic voltammogram (cathodic scan, 100 mVs^{-1}) of [Ni(3MeO-SALTPA)$_2$] in 0.2 M [Bu$_4$N][BF$_4$]/NCMe at a Pt disc electrode.

Final comments

The main observations of this study can be summarized as follows.

The cobalt(II) complexes undergo a first oxidation at lower potentials than the corresponding nickel(II) ones which, in turn, present lower first oxidation potentials than the corresponding copper(II) species, thus following the known order of the ionization potentials for the corresponding gaseous metal ions ($M^{2+} \rightarrow M^{3+}$), as observed [3] to occur for some tetraaza macrocyclic complexes with these metals. The first anodic wave of the Co(II) complexes is centred at the metal, whereas for the Ni(II) and, mainly, the Cu(II) compounds, it involves the oxidation of the ligand(s).

Moreover, the copper(II) complexes are reduced (first reduction wave) at higher potentials than the corresponding nickel(II) species which, in turn, present less cathodic reduction potentials than the cobalt(II) analogues. This follows the trend observed for the corresponding ionization potentials for the gaseous metal ions ($M^{1+} \rightarrow M^{2+}$). The first cathodic process appears to occur at the metal for the copper(II) and nickel(II) complexes, whereas, for the cobalt(II) compounds, it involves the reduction of the ligand(s).

References

[1] - P. Gili, P. Martin-Zarza, P. Nunez, A. Medina, M.C. Diáz, M.G. Martin, J.M. Arrieta, M. Vlassi, G. Germain, M. Vermeire and L. Dupont, J. Coord. Chem., 1989, 20, 273; P. Gili, P. Martin-Zarza, M.S. Palacios, M.L. Rodriguez, C. Ruiz-Perez and F.V. Rodriguez--Romero, Inorg. Chim. Acta, 1990, 176, 261; P. Martin-Zarza, P. Gili, A. Mederos, A. Medina, C. Valenzuela and A. Bernalte, Thermoch. Acta, 1989, 156, 231.

[2] - S.S.P.R. Almeida, J.J.R. Fraústo da Silva, R. Herrmann and A.J.L. Pombeiro, Portugaliae Electrochim. Acta, 1988, 6, 135; J.J.R. Fraústo da Silva, M.F.C. Guedes da Silva, J.A.L. Silva and A.J.L. Pombeiro, in "Molecular Electrochemistry of Inorganic,

Bioinorganic and Organometallic Compounds", A.J.L. Pombeiro and J. McCleverty (eds.), NATO ASI Series, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1993, 411.

[3] - J. Vasilevskis and D.C. Olson, Inorg. Chem., 1971, 10, 1228.

Acnowledgements

This work has been partially supported by the PEDIP programme (Y.Y.T.), INIC and JNICT (Portugal).

ANODICALLY INDUCED *cis* to *trans* ISOMERIZATION of the NITRILE COMPLEXES $[ReCl(NCR)(dppe)_2]$

M.FÁTIMA C. GUEDES da SILVA, JOÃO J.R. FRAÚSTO da SILVA and ARMANDO J.L. POMBEIRO

Centro de Química Estrutural, Complexo I, I.S.T.
Av. Rovisco Pais, 1096 Lisboa codex, Portugal

ABSTRACT

Reaction of *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe=$Ph_2PCH_2CH_2PPh_2$) with NCR (R=aryl) in toluene and under sunlight gives the corresponding *cis*-$[ReCl(NCR)(dppe)_2]$ compounds. The electrochemistry of these complexes in 0.2M $[Bu_4N][BF_4]$/THF is studied by cyclic voltammetry and controlled potential electrolysis, at Pt electrodes, which indicate the occurrence of an electroinduced *cis*-to-*trans* isomerization.

In pursuit of our studies on the coordination chemistry of small molecules, particularly C-N and C-C unsaturated species, at dinitrogen-binding metal sites [1], we have succeeded in preparing a series of *cis* and *trans* rhenium(I)-nitrile complexes involving the $\{Re(dppe)_2\}^+$ metal centre.

Extended Hückel MO calculations [2] indicate that for octahedral type phosphine complexes, namely of group 6 transition metals with CO and N_2 ligands, the relative stability of the *cis* and *trans* isomer depends on the oxidation state of the metal, with preference of the *cis* geometry for the 18-electron compounds,and the *trans* geometry for the 17-electron species. However, for related 18-electron Re(I) and Tc(I) complexes, such as $[MLL'(dppe)_2]^+$ or $[MXL(dppe)_2]$ (M=Re [3] or Tc [4]; X=Cl or H; L,L'=CO, N_2, CNR, etc.), the *trans* geometry of the phosphine appears to be favoured, though some exceptions have already been reported by us [5].

We have now succeeded in the synthesis of *cis*-$[ReCl(NCR)(dppe)_2]$ by reacting the parent *trans*-$[ReCl(N_2)(dppe)_2]$ with the apropriate nitrile in toluene and under sunlight (eq.1). The *trans* isomers can be prepared in the oxidized form by chemical or electrochemical oxidation of the *cis* or derived hydride species, whereas the neutral *trans* form is obtained by deprotonation or cathodic reduction of methyleneamido or hydride complexes, respectively.

$$\textit{trans}\text{-}[ReCl(N_2)(dppe)_2] + NCR \rightarrow \textit{cis}\text{-}[ReCl(NCR)(dppe)_2] + N_2 \tag{1}$$

Portugaliæ Electrochimica Acta, 11 (1993) 93-97