Electrochemical oxidative polymerization of binuclear 'anil' and 'salen'-type complexes and tetrahydro derivatives

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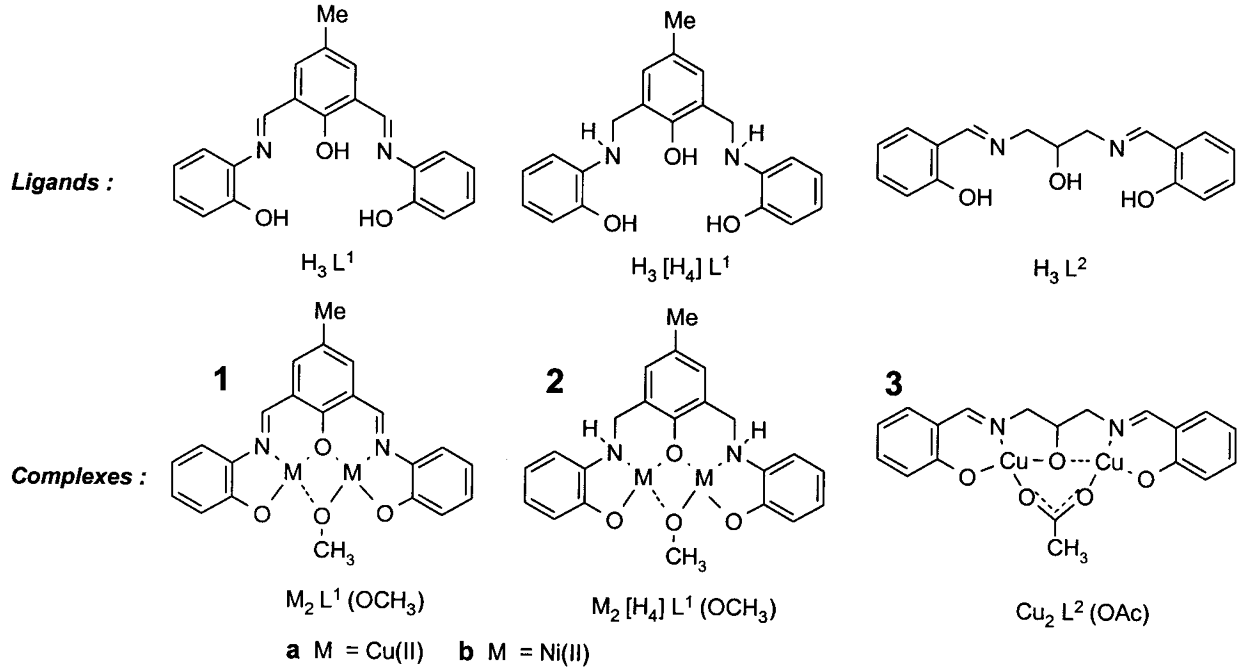
New kinds of modified electrodes have been prepared on the basis of electroactive polymers containing bimetallic 'anil' and 'salen'-type complexes. New tetrahydro 'anil' ligands and complexes have been synthesized, giving birth to a new family of electroactive polymers. The polymers have been prepared potentiostatically and exhibit electrochemical properties analogous to simple polysalens. In the case of binuclear complexes both imino- and amino-linked monomers polymerize, but the polymers exhibit quite different charge transfer dynamics.

Electropolymérisation anodique de complexes binucléaires de type 'anil' et 'salen' et de leur dérivés tetrahydrogénés. Un nouveau type d'électrodes modifiées a été élaboré sur la base de polymères électroactifs issus de complexes bimétalliques de type 'anil' et 'salen'. Nous avons synthétisé des ligands et complexes tetrahydro 'anil' originaux donnant accès à une nouvelle famille de polymères électroactifs. Les complexes binucléaires possédant des liaisons imine et amine polymérisent également, mais les polymères présentent des comportements très différents sur le plan du transfert électronique.

The electrochemical behaviour of metal complexes is arousing more and more interest, especially when new polymers can be built and used for various applications,[1] including electrode modifiers,[2] electrocatalysis,[3–10] sensors[11,12] and nonlinear—and near-field—optics.[13] The behaviour of metal-salens and analogous square planar complexes is attractive, given the ease with which these compounds electropolymerize into conducting polymers,[14–20] exhibiting in some cases electrocatalytic properties.[21] Also thiophene-salen compounds have been recently electropolymerized and their electrochemical properties have been reported.[22]

We describe here the electrochemical behaviour of bimetallic copper(II) and nickel(II) complexes derived from pentadentate binucleating 'anil' and 'salen' Schiff base ligands. More precisely, these complexes are Robson's[23–25] 'anil' structures (Scheme 1, **1a** and **1b**) and Mazurek's[26,27] 'salen' series (structure **3**). These ligands are derived from reaction of 2-aminophenol with 3-formyl-5-methyl-salicylaldehyde ('anil')



Scheme 1

and from reaction of salicylaldehyde with 1,3-diaminopropan-2-ol ('salen'). Furthermore, we have synthesized and studied new binuclear complexes (Scheme 1, structures **2**) derived from saturated diamino ligands prepared by sodium borohydride reduction of the anil Schiff bases.

In these complexes, the electronic environment of the metals is square planar and mimics the classical salens; however, the metal ions are close enough so that they can interact and have their electron-exchange properties modified in comparison with the mononuclear complexes. Moreover, the *para* positions of the phenolates are free in each of the complexes, thus allowing oxidative polymerization (*e.g.*, electrochemical) when this is a feasible process (*e.g.*, when the oxidation potential is low enough). The monomeric substrates have been studied both in oxidation and reduction. Electropolymerization of the substrates has been performed for complexes **1a**, **1b**, **2a**, **2b** and **3**. The electrochemical behaviour of the polymers has been investigated both in oxidation and reduction, and is reminiscent of that of salen complexes.

Experimental

Syntheses of the monomer complexes

Precursor ligand 5-methylisophthalaldehyde di-2′-hydroxyanil (H_3L^1) has been prepared by reaction of *ortho*-aminophenol with 5-methylisophthalaldehyde in methanol and its derived metallic complexes **1a** (Cu_2L^1OMe) and **1b** (Ni_2L^1OMe) by subsequent reaction with a Cu^{II} or a Ni^{II} salt in basic medium according to Robson.[23,24] The previously unknown tetrahydro ligand $H_3[H_4]L^1$ is prepared from the H_3L^1 Schiff base by reduction of both C=N double bonds with sodium borohydride in methanol. The copper and nickel complexes **2a** and **2b** are obtained by reaction of $H_3[H_4]L^1$ with copper and nickel salts in basic medium.

1,3-Bis(salicylideneamino)propan-2-ol (H_3L^2)[26] and copper complex **3** (Cu_2L^2OAc)[27] have been prepared according to Mazurek's procedures from commercially available salicylaldehyde and 1,3-diaminopropan-2-ol.

$H_3[H_4]L^1$ ligand. The red H_3L^1 ligand (1.038 g, 3 mmol) is dissolved in 20 ml methanol and excess sodium borohydride (0.114 g, 3 mmol) is slowly added (10 min) with stirring at ambient temperature. The solution rapidly decolourizes; 30 min later, MeOH is distilled off under reduced pressure. The residue is first dissolved in 10% phosphoric acid (15 ml) and then 10% sodium hydroxide is added to establish pH 7. The colourless crystalline product, which begins to separate, is extracted with ethyl acetate (150 ml), dried over magnesium sulfate and filtered. It crystallizes after solvent evaporation, and is dried *in vacuo* (25 °C). Yield: 0.885 g (84%), mp 160 °C (decomp.) (diethyl oxide). Anal. calcd. % for $C_{21}H_{22}N_2O_3$: C, 71.98; H, 6.33; N, 7.99. Found C, 71.83; H, 6.36; N, 7.87. ^1H NMR (d_6-DMSO, δ): 2.13 (s, 3H, CH_3), 4.27 (s, 4H, 2 CH_2), 6.5–7.5 (m, 10H, arom.), 9.32 (s, 2H). ^{13}C NMR (d_6-DMSO, δ): 20.51, 43.11, 110.68, 113.54, 116.39, 119.71, 126.38, 127.57, 137.29, 144.49, 150.89.

Copper complex ($Cu_2[H_4]L^1OMe$) 2a. $H_3[H_4]L^1$ ligand (0.350 g, 1 mmol) is dissolved in hot methanol (15 ml) and treated with $Cu(OAc)_2 \cdot H_2O$ (0.400 g, 2 mmol) in 20 ml hot methanol. The solution is stirred for 2 h. A green solid separates, which is dried to a constant weight *in vacuo* (25 °C). Yield: 0.394 g (78%). Anal. calcd. % for $C_{22}H_{22}N_2O_4Cu_2$: C, 52.27; H, 4.38; N, 5.54; Cu, 25.14. Found C, 52.15; H, 4.42; N, 5.52; Cu, 25.12.

Nickel complex ($Ni_2[H_4]L^1OMe$) 2b. $H_3[H_4]L^1$ ligand (0.350 g, 1 mmol) is dissolved in methanol (20 ml) and 0.8 ml of 5 M sodium methoxide in methanol (4 mmol) is added. Then, 0.498 g $Ni(OAc)_2 \cdot 4H_2O$ (2 mmol) dissolved in 10 ml methanol is added under stirring at room temperature. Methanol is distilled under reduced pressure. The residue is dissolved in chloroform (150 ml), filtered and the solvent distilled under reduced pressure. An orange-brown complex is isolated, which is dried to a constant weight *in vacuo* (25 °C). Yield: 0.396 g (80%). Anal. calcd. % for $C_{22}H_{22}N_2O_4Ni_2$: C, 53.29; H, 4.47; N, 5.65; Ni, 23.67. Found C, 53.21; H, 4.50; N, 5.61; Ni, 23.60.

Electrochemical setup

Polymer electrosyntheses and analytical experiments were performed in a three-compartment cell fitted with a saturated calomel reference (SCE), a glassy carbon electrode (diameter 1.2 mm) or a platinum electrode (diameter 1 mm) and a platinum counter electrode. The electrochemical apparatus was a home-made potentiostat[28] (equipped with an Ohmic drop compensation system) fitted with a PAR 173 Universal programmer, a Nicolet digital oscilloscope and a Sefram 164 plotter. The solvent was spectroscopic grade acetonitrile (distilled over CaH_2 and stored on 3 Å molecular sieves) with 0.1 M tetraethylammonium perchlorate (Fluka puriss. recrystallized once in acetonitrile–diethyl oxide) as the supporting electrolyte. Concentration of the monomeric substrates was usually 2×10^{-3} M and the cells were flushed with argon throughout the experiments. Ohmic compensation was used when necessary (*i.e.* when scan rates were over 1 V s^{-1}).

For film studies, two cells were used in series, one containing a saturated monomer solution for the film synthesis, another containing a clean electrolyte solution, into which the films were transferred for electrochemical studies. The electrode was carefully cleaned between each experiment. The films were prepared potentiostatically at various potentials ranging between 1.2 and 1.6 V as stated in the discussion.

When a precise potential determination was desired, ferrocene was used as an internal standard; its potential was assumed to be $+405 \pm 5$ mV *vs.* SCE; the ferrocene potential was checked after each set of experiments, but values in tables are given against SCE.

For the diffusion coefficient determination, the classical Cottrell law has been used $[i = nFAc^\circ D^{1/2}/(\pi t)^{1/2}]$, assuming $n = 1$ per monomer unit in the film and a volumic mass of $\mu = 1.5$ g cm^{-3} as usually assumed for most conducting polymers; therefore the concentration c° of electroactive moieties inside the films is expressed as $c^\circ = \mu/M$, where M represents the molar mass of the monomer unit (taking into account one counter ion per moiety in the oxidized polymer).

Results and discussion

Behaviour of monomer complexes

All complexes were studied by means of cyclic voltammetry prior to polymer synthesis, both in oxidation and reduction. The behaviour in reduction of these complexes is much less complicated than that of classical salens. Nickel-containing compounds exhibit a large, multielectronic, irreversible reduction peak around −1.8 V, whereas copper-containing compounds exhibit a monoelectronic reversible wave around −1.1 V with a slow charge transfer as attested by the peak separation of about 200 mV, attributable to the Cu^{II}/Cu^{I} reduction for one ion per cage (The number of electrons has been estimated by comparison to a ferrocene standard). The electrochemical reduction has been performed both in acetonitrile, a solvent able to complex the metals, and in dichloromethane, a non-complexing solvent, but the behaviours are quite similar. The voltammograms in Fig. 1 display the electrochemical responses of some complexes.

Upon electrochemical oxidation at a potential in the 1.1–1.4 V range, all complexes (**1**, **2** and **3**) exhibit an irreversible two-

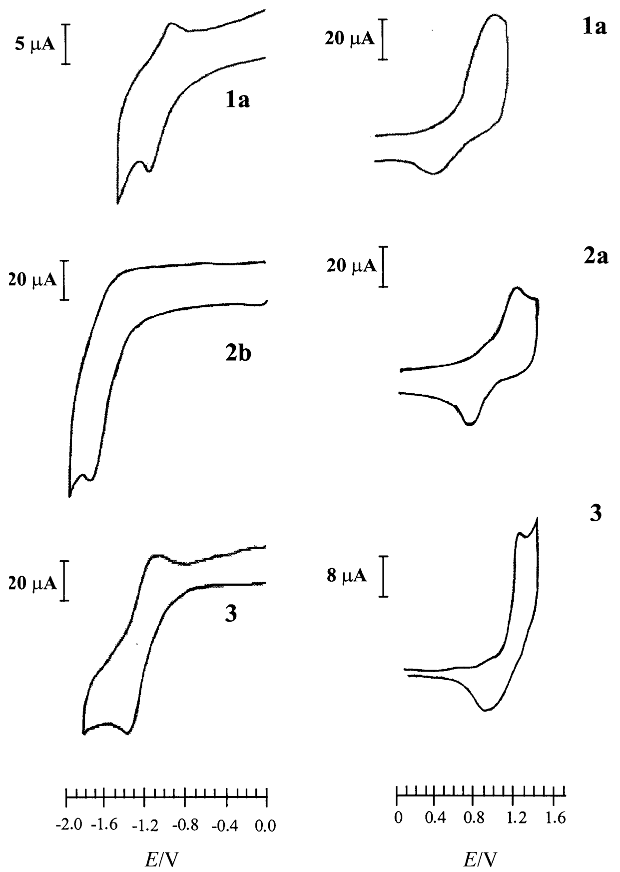


Fig. 1 Electrochemical reduction (left) and oxidation (right) of complexes **1** ($v = 1.2$ V s^{-1}), **2** ($v = 2$ V s^{-1}) and **3** ($v = 1.2$ V s^{-1}) in CH_3CN, TEAP (0.1 M) performed on a 1.2 mm diameter carbon electrode.

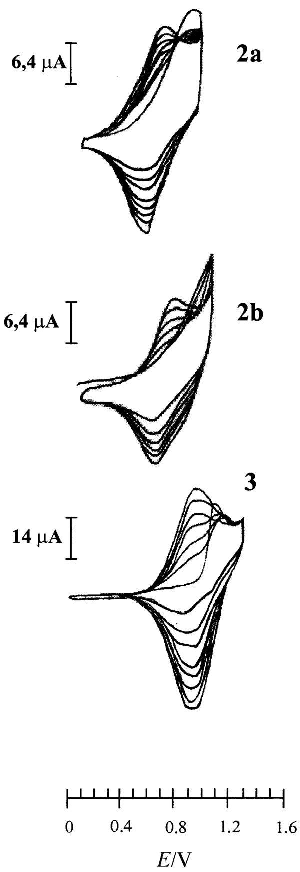
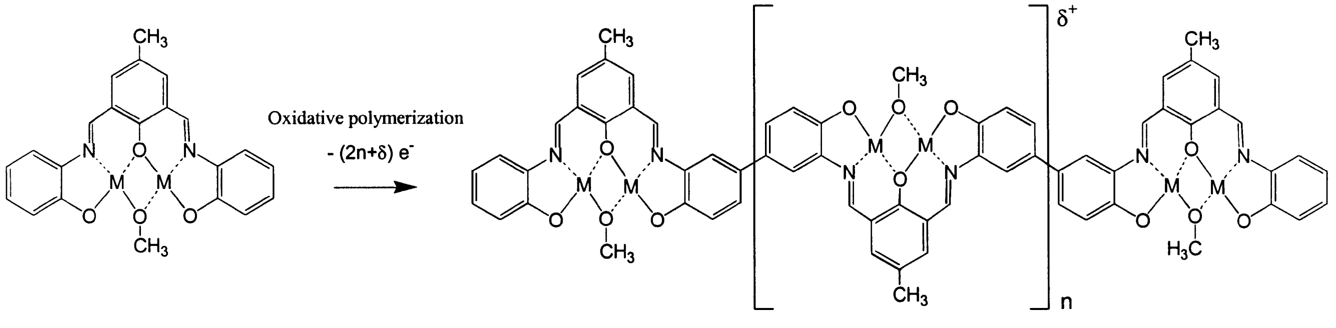


Fig. 2 Accumulative synthesis *via* electrochemical oxidation of complexes **2a** ($v = 700$ mV s^{-1}), **2b** ($v = 250$ mV s^{-1}) and **3** ($v = 280$ mV s^{-1}) in CH_3CN, TEAP (0.1 M) performed on a 2 mm diameter Pt electrode.

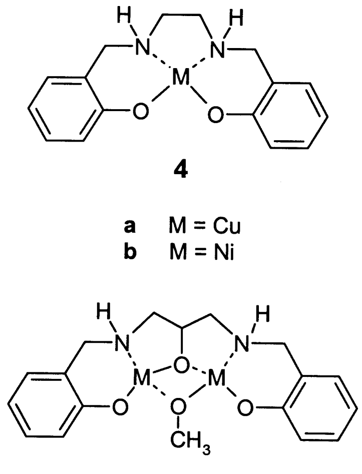
electron oxidation that leads to polymer formation on the electrodes (Fig. 2). As in several cases examined previously,[17] the coupling between two entities occurs probably *via* a CR–CR (cation-radical–cation-radical) coupling mechanism at the *para* position of the phenolate as shown in Scheme 2. The synthesis of the polymer films may occur either at a controlled potential, or upon repetitive cycling in the solution. However, although the oxidation begins slightly before 1.0 V, a potential between 1.3 and 1.6 V is required to obtain clean films. Usually, optimum polymerization is obtained at potential values quite above that required for the formation of classical polysalens. The potential range where efficient polymerization takes place is also wider than in the case of the polymerization of simple salens or functionalized conducting polymers in general (*e.g.*, polypyrrole).

We have observed that mononuclear complexes **4a**,**b** (Scheme 3) prepared according to the literature[29] and dinuclear **5a**,**b** tetrahydrosalen complexes prepared from the $H_3[H_4]L^2$ ligand[30] cannot be transformed into electroactive polymers under the same experimental conditions as their unsaturated analogous complexes.

The peculiar behaviour of the ‘tetrahydroanil’ series in particular should be outlined since the binuclear amine complexes **2a** and **2b** readily polymerize, like their Schiff-base analogues **1a** and **1b**. To our knowledge this is the first example of the polymerization of a copper or nickel amine complex. This made us wonder about the possibility first to oxidize (dehydrogenate) the amino complexes **2a** and **2b** into the imino compounds **1a** and **1b** (*via* intermediate Cu^{III} and Ni^{III} oxidation states), which would then be easily polymerized. Such a metal-catalyzed dehydrogenation of the HC—NH bond has been previously observed in some copper, nickel and cobalt *para*-substituted tetrahydrosalen complexes[31] that are transformed into half-salen (dihydro) derivatives. But this hypothesis is ruled out because poly-**2a** and poly-**2b** exhibit very different electrochemical properties compared with their poly-**1a** and poly-**1b** analogues (see Discussion below), sug-



Scheme 2



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a M = Cu
b M = Ni

5

Scheme 3

gesting that the monomer structure (imine or amine bonds) is indeed retained in the subsequent final polymer.

Behaviour of polymers

All polymers derived from compounds **1**, **2** and **3** behave similarly to the polysalens upon electrochemical oxidation, with in many cases a better definition of the oxidation process, as evidenced by the voltammograms shown in Fig. 3. The potentials and the doping levels are listed in Table 1.

Table 1 Electrochemical data of complexes **1**, **2** and **3** and their associated polymers

Complex	Potential/mV *vs.* SCE Monomer/(E_{pic})[a]	Polymer/($E°$)	δ[b]	D/cm^2 s^{-1}
1a	−1105/955	805	0.88	8.1×10^{-10}
1b	−1690/890	775	0.67	1.3×10^{-9}
2a	−1150/1020	1035	0.87	4.5×10^{-11}
2b	−1730/990	990	0.92	1.93×10^{-12}
3	−1140/1090	950	0.56	1.52×10^{-10}

[a] Reduction/oxidation.
[b] Calculated from eqn. (1).

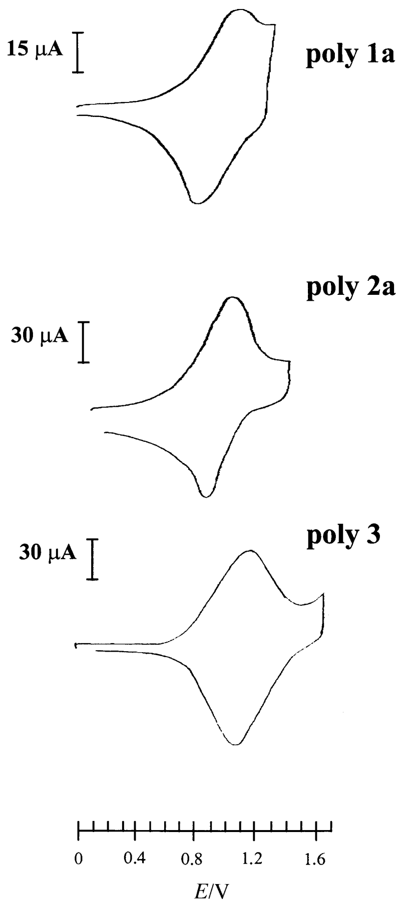

Fig. 3 Cyclic voltammograms of several polymers derived from complexes **1a** ($v = 1.0$ V s^{-1}), **2a** ($v = 1.0$ V s^{-1}) and **3** ($v = 1.5$ V s^{-1}). Polymerization charge $Q_{\text{polymerization}} = 6.4$ mC cm^{-2}.

As with the monomers, the peak potentials are more positive than in the case of simple salens. The peaks are better defined and the capacitive tailing is less important. The doping levels δ have been calculated from the following classical equation:[32]

$$\delta = \frac{2Q_{\text{redox}}}{Q_{\text{total}} - Q_{\text{redox}}} \quad (1)$$

where Q_{total} is the total charge during electropolymerization: $Q_{\text{polymerization}} + Q_{\text{redox}}$. Q_{total} is given by coulometric integration during electrosyntheses. Q_{redox} is calculated by integration of the cyclic voltammograms as $(Q_{\text{anodic}} + Q_{\text{cathodic}})/2$ to avoid problems linked to the basis line in the voltammograms. The polymerization charge $Q_{\text{polymerization}}$, the redox charge Q_{redox} and therefore the total charge are defined by the Faradaic law as:

$$n_{\text{monomer}} = \frac{m_{\text{polymer}}}{M_{\text{monomer}}} = \frac{Q_{\text{polymerization}}}{2F} = \frac{Q_{\text{redox}}}{\delta F} = \frac{Q_{\text{total}}}{(2 + \delta)F} \quad (2)$$

Except for poly-**3**, δ values are close to 1, which strongly suggests the exchange of one electron per monomer unit in the film; the difference between the supposed theoretical doping level of 1 and the calculated experimental one is attributable to synthesis yields slightly lower than 100% for the polymer films. Even in the remaining case of poly-**3**, this explication is probably still valid.[33] Therefore, even in polymerized binuclear complexes, it does not appear possible to oxidize each site more than once, despite the presence of two metal ions and the larger size of the cage. There is no significant change in the doping levels when passing from copper to nickel central ions, in contrast with classical polysalens.

The kinetics of electron transport in the polymers have been estimated on the basis of chronoamperometry experiments. As expected, there is no influence of the film thickness on the measurements. In fact, the electrochemical response of the film

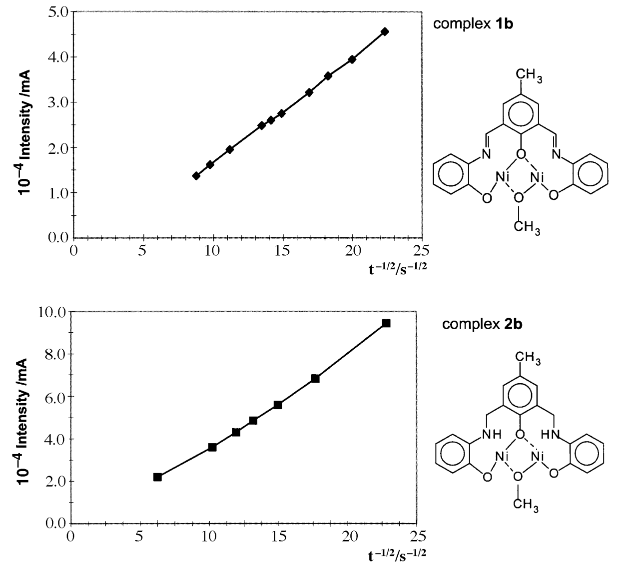

Fig. 4 Cottrell plot of poly-**1b** (top) and poly-**2b** (bottom) coated on a Pt electrode. The polymerization charge is 2.5 mC cm^{-2}.

exhibits a less important capacitive current and better defined peaks, the Cottrell plots (Fig. 4) display a behaviour closer to ideality, and the kinetics of charge transport are easily determinable from the experimental data. The diffusion coefficients for the charge transfer are slightly below that measured in the polysalen case. It is striking that, with the exception of poly-**3**, which has a different structure, the polymers with amine links **2a** and **2b** exhibit a much slower (see Table 1) charge transport than the polymers with imine links (**1a** and **1b**). Therefore, it is clear that some delocalization occurs through the imine bond in poly-**1a** and poly-**1b**, whereas poly-**2a** and poly-**2b** behave more like classical pendant-group polymers with a non-conducting backbone. In addition, while polysalens easily undergo degradation, the binuclear compounds appear resistant to high potential cycling (up to 1.7 V), without appreciable loss of electroactivity even after several hundreds of cycles.

The polymers are reducible at relatively low potentials. However, only in the case of poly-**2a** is the reduction reversible, featuring the reduction of one copper ion per unit in the film according to the integration of the voltammograms. Since the + 1 oxidation state of nickel is not stable, the Ni-containing films are reduced with two electrons per monomer unit. Poly-**2b** is not reducible, probably because the polymer is not conducting enough in this potential range.

Conclusion

In this paper we have describe the first oxidative electrochemical polymerization of binuclear copper and nickel complexes. Polymerization of amine-ligated copper and nickel (**2a** , **2b**) complexes is also an unprecedented transformation. The results for these new binuclear monomers and polymers show that, although the general trends are comparable to polysalens, noticeable differences are clearly discernible, especially an electrochemical behaviour closer to ideality and an improved stability towards high potentials.

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