

Synthesis and Cyclic Voltammetric Studies of some Complexes of Cobalt(II), Nickel(II), Manganese(II) and Copper(II) with 2,2'-Bi-4,5-dihydrothiazine (btz) and 2,2'-Bi-2-thiazoline (bt).

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Abstract-Four complexes of 2,2'-bi-4,5-dihydrothiazine (btz) with Co(II), Ni(II), Mn(II) and Cu(II), and two complexes of 2,2'-bi-thiazoline (bt) with Co(II) were synthesized and characterized, three of them, the Mn(II) complex and the two bt complexes, for the first time. These six complexes were studied using cyclic voltammetry in acetonitrile solution. All displayed reversible or quasi-reversible behaviour, and two waves were observed in the case of $[\text{Co}(\text{btz})_3] [\text{ClO}_4]_2$. All the results are described and discussed.

Keywords: heteroalicyclic ligands; bivalent transition metal complexes; cyclic voltammetry.

Some twenty years ago, Nelson *et al.* [1] reported the synthesis, characterization and physical properties of several metal complexes with the didentate, heteroalicyclic ligands 2,2'-bi-4,5-dihydrothiazine (btz), and 2,2'-bi-2-thiazoline (bt), as well as their 4,4'-dimethyl (btn) and 5,5'-dimethyl (bts) derivatives. The cyclic voltammetric behaviour of $[\text{Fe}(\text{btz})_3] [\text{ClO}_4]_2$, $[\text{Fe}(\text{bt})_3] [\text{ClO}_4]_2$, and $[\text{Fe}(\text{bts})_3] [\text{ClO}_4]_2$ was also reported. Seven years later, Nelson *et al.* [2] published a paper on the copper(I) complexes of btz and bt.

A literature survey revealed that, over the years, quite a number of papers were published on the so-called spin crossover of Fe(II) complexes with btz and, or, bt and related didentate ligands. In one of these papers [3], Fe(III) complexes, with only that type of ligands, were also considered. In other papers, mixed ligand complexes of Fe(II) with btz [4] or bt [5] and other anionic or molecular ligands were reported. Thus to the best of our knowledge only the redox properties of those three Fe(II) complexes of btz,

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bt, and bts were studied using cyclic voltammetry. The present paper describes the work carried out on the cyclic voltammetry of six complexes of other transition metal ions with btz and bt, three of which were prepared for the first time.

EXPERIMENTAL

The ligands were synthesized, purified, and characterized as described by Nelson *et al.* [1]. The following complexes $[\text{Co}(\text{btz})_3] [\text{ClO}_4]_2$, $[\text{Ni}(\text{btz})_3] [\text{ClO}_4]_2$, and $[\text{Cu}(\text{btz})_3] [\text{ClO}_4]_2$, were prepared and characterized as previously reported [1].

Preparation of $[\text{Mn}(\text{btz})_3] [\text{ClO}_4]_2$

On addition of a warm ethanolic solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to a stirred, warm ethanolic solution of a small excess of btz, a buff coloured solid was obtained. Found: C, 33.5; H, 5.0; N, 9.7%. Calc. for $[\text{Mn}(\text{btz})_3] [\text{ClO}_4]_2$: C, 33.7; H, 5.0; N, 9.8%.

Preparation of $[\text{Co}(\text{bt})_2 (\text{H}_2\text{O})_2] [\text{ClO}_4]_2$

From the reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with bt, using the procedure described above, a brownish yellow solid was obtained. Found: C, 22.6; H, 3.1; N, 8.6%. Calc. for $[\text{Co}(\text{bt})_2 (\text{H}_2\text{O})_2] [\text{ClO}_4]_2$: C, 22.6; H, 3.2; N, 8.8%.

Preparation of $[\text{Co}(\text{bt})_3] [\text{ClO}_4]_2$

A solution of the ligand was prepared by extraction from the solid compound with ethanol, in a Soxhlet, on refluxing for about one hour. A warm ethanolic solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added, and the mixture was refluxed for a further hour. On cooling, an orange yellow solid was precipitated out, which was filtered and dried. Found: C, 27.4; H, 3.1; N, 10.6%. Calc. for $[\text{Co}(\text{bt})_3] [\text{ClO}_4]_2$: C, 27.9; H, 3.1; N, 10.8%.

Measurements

Elemental analyses were carried out on a Carlo Erba EA 1106/R elemental analyzer.

Infrared spectra were recorded in the range 450-4000 cm^{-1} as KBr pellets using a Mattson 5000 spectrometer.

A Shimadzu UV-3101 PC, UV-VIS-NIR, scanning spectrophotometer, was used in measurements of the electronic spectra.

Cyclic voltammograms were obtained using the techniques and instruments described previously [6], at 25.0 ± 0.1 °C, in dry MeCN under O_2 -free conditions. The supporting electrolyte was a 0.1 M solution of TEAP (tetraethylammonium perchlorate) in acetonitrile.

After several preliminary experiments, two working electrodes were selected: a glassy carbon disk (Metrohm 6.0805.020, *ca.* 3mm in diameter) for the btz complexes; a gold disk (Metrohm 6.1204.020, also *ca.* 3mm in diameter) for the bt complexes.

Potentials are quoted versus SCE and are uncorrected for liquid junction potentials and iR drop; peak currents were corrected for background currents, if relevant.

Under these experimental conditions, the Fc^+/Fc couple gave reversible voltammograms with $E_{1/2} = +350$ mV ($\Delta E = 70$ mV).

RESULTS AND DISCUSSION

Of the three new complexes that were prepared, only the unexpected syntheses of two Co(II) bt complexes require some comments. These complexes, prepared using slightly different methods, were characterized by analysis, infrared and electronic spectra. The features of the infrared spectra were similar to those found by Nelson *et al.* [1], with one exception: only in the infrared spectra of $[\text{Co}(\text{bt})_2 (\text{H}_2\text{O})_2] [\text{ClO}_4]_2$ a very strong band appeared at *ca.* 3400 cm^{-1} , thus confirming the presence of coordinated water molecules, as has been inferred from the results of analysis.

How the differences in the preparation of the Co(II) bt complexes resulted in different complexes, one with three bt molecules and the other with only two and two water molecules, may simply be a consequence of a dehydrating effect of ethanol, enhanced by the prolonged reflux.

The experimental cyclovoltammetric results are summarized in Table 1, for the btz complexes, and in Table 2, for the bt complexes. Typical voltammograms of the Co(II) and Ni(II) complexes are shown in Fig.1.

Table 1

Electrochemical data for the btz complexes in MeCN solution^a, 0.1M in TEAP^b

Compound	Scan Rate (mV.s ⁻¹)	E _{p,c} (mV)	E _{p,a} (mV)	ΔE _p (mV)	E _{l/2} (mV)
[Co(btz) ₃] (ClO ₄) ₂	20	+130	+195	65	+162.5 ^c
I	50	+130	+200	70	+165 ^c
	100	+130	+210	80	+170 ^c
	200	+120	+210	90	+165 ^c
	200	+120	+210	90	+165 ^c
II	20	-965	-890	75	-927.5
	50	-970	-890	80	-930
	100	-975	-885	90	-930
	200	-985	-880	105	-932.5
[Ni(btz) ₃] (ClO ₄) ₂	20	+1460	+1530	70	+1495 ^c
	50	+1450	+1520	70	+1485 ^c
	100	+1450	+1520	70	+1485 ^c
	200	+1450	+1540	90	+1495 ^c
[Mn(btz) ₃] (ClO ₄) ₂	20	+925	+1060	135	+992.5
	50	+925	+1060	135	+992.5
	100	+925	+1100	195	+1002.5
	200	+885	+1130	245	+1007.5
[Cu(btz) ₃] (ClO ₄) ₂	20	+90	+210 ^d	120	+150
	50	+90	+210 ^d	120	+150
	100	+90	+210 ^d	120	+150
	200	+90	+230 ^d	140	+160

^a Solutions ca. 1 mM in complex. ^b Potentials vs. SCE. Uncertainty ± 5 mV.
^c i_{p,a}/i_{p,c} ≅ 1. ^dVery broad.

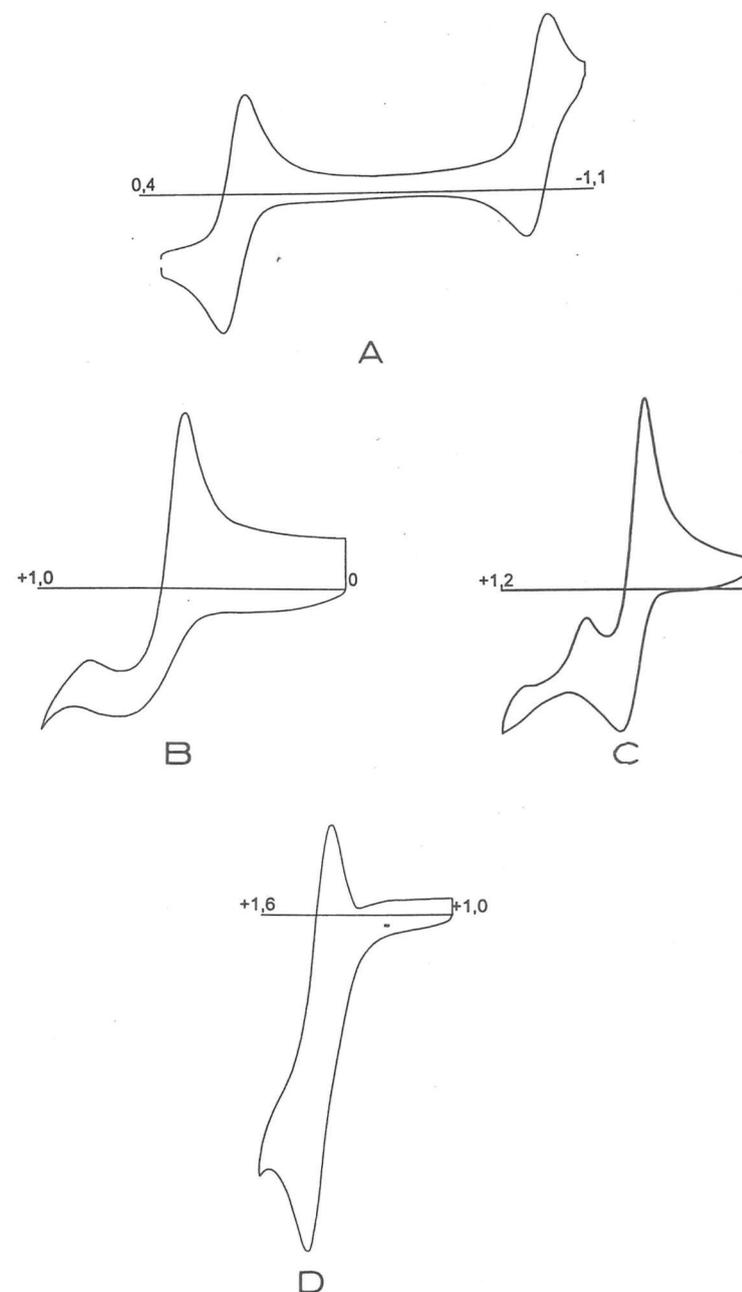


Fig. 1- Cyclic Voltammograms, at 100 mV s⁻¹ of:
 (A) [Co(btz)₃] [ClO₄]₂; (B) [Co(bt)₂(H₂O)₂] [ClO₄]₂
 (C) [Co(bt)₃] [ClO₄]₂; (D) [Ni(btz)₃] [ClO₄]₂

Table 2

Electrochemical data for the bt complexes in MeCN solution^a, 0.1M in TEAP^b

Compound	Scan Rate (mV s ⁻¹)	E _{p,c} (mV)	E _{p,a} (mV)	ΔE _p (mV)	E _{1/2} (mV)
[Co(bt) ₂ (H ₂ O) ₂] [ClO ₄] ₂	50	+540	+630	90	585
		+790 ^c			
	100	+530	+640	110	585
		+780 ^c			
	200	+530	+630	100	580
		+780 ^c			
[Co(bt) ₃] [ClO ₄] ₂	50	+540	+630	90	585
		+705 ^c			
	100	+530	+640	110	585
		+705 ^c			
	200	+520	+650	130	585
		+705 ^c			

^aSolutions ca. 1 mM in complex. ^bPotentials vs. SCE, uncertainty ± 5 mV. ^cNo anodic counterpart

Cyclic voltammetry of the Co(II) complexes

It can easily be seen that the electrochemical behaviour of [Co(bt)₃] [ClO₄]₂ is completely different from those of [Co(bt)₃] [ClO₄]₂ and [Co(bt)₂(H₂O)₂] [ClO₄]₂, these two being rather similar. This different behaviour does not seem to be ascribable to the difference in working electrodes.

Under the present experimental conditions, the voltammograms of [Co(bt)₃] [ClO₄]₂ display two well-defined, one-electron redox processes (Table 1 and Figure 1). This is not a common occurrence, which has only been observed in some cases [10], but with different ligands. By comparison with values reported in the literature [10(a), *e.g.*], wave I, with E_{1/2}=+0.17 V, is assigned to the Co(III)/Co(II) process, and wave II, with E_{1/2}=-0.93V, to the Co(II)/Co(I).

Experimental data (ΔE_p; i_{p,a}/i_{p,c}; linear dependence of i_{p,a} and i_{p,c} on v^{1/2}, Fig. 2) show that the process Co(III)/Co(II) is essentially reversible, particularly at low scan rates, in spite of the differences in bond lengths resulting from the different sizes of Co(III) and Co(II). The slight departure from reversibility at higher scan rates may even be a consequence of this difference and the concomitant time required for the rearrangement of the molecular structures.

On the other hand, the process Co(II)/Co(I) can at most be considered quasi-reversible. Although both i_{p,a} and i_{p,c} vary linearly with v^{1/2} (Figure 2), curiously enough, i_{p,a} is almost independent of v^{1/2}. Both i_{p,a} and i_{p,c} decrease on successive scan rates at the same rate, as well as successive scans at different rates, but E_{p,a} and E_{p,c} remain fairly unaltered. Taking all these facts into account, since Co(II) and Co(I) do not generally have the same coordination requirements and stabilities, it is suspected that, after the reduction of the Co(II) complex to the Co(I), this complex undergoes a fast, partial decomposition and the remaining Co(I) complex is reoxidized to the Co(II) complex on the reverse scan.

In the voltammograms of [Co(bt)₂(H₂O)₂] [ClO₄]₂ and of [Co(bt)₃] [ClO₄]₂ (Table 2, Figure 1) two redox processes were observed: one quasi-reversible (E_{1/2} = +0.59 V), assignable to a Co(III)/Co(II) couple, and the other, irreversible, at more positive potentials.

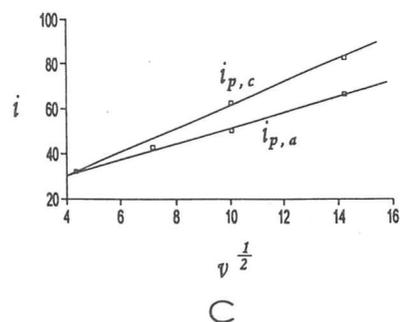
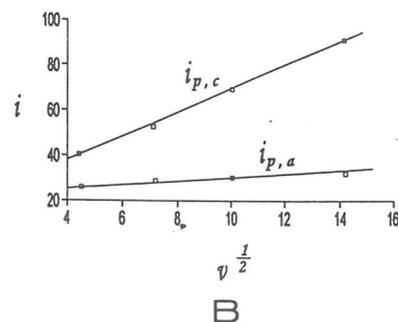
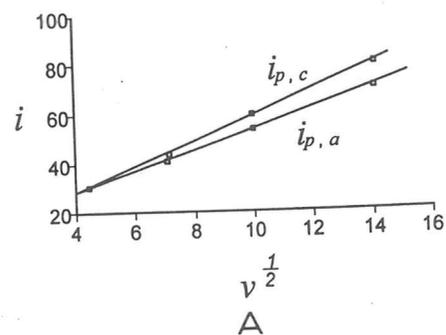


Fig.- 2 Plots of peak currents (arbitrary units, corrected peak heights in mm) vs. $v^{1/2}$ for: (A) wave I of $[\text{Co}(\text{btz})_3][\text{ClO}_4]_2$; (B) wave II of $[\text{Co}(\text{btz})_3][\text{ClO}_4]_2$; (C) $[\text{Ni}(\text{btz})_3][\text{ClO}_4]_2$

Comparing the peak potentials of the quasi-reversible wave, one can surmise that both complexes give rise to the same electroactive species in solution, which implies a certain degree of decomposition. A product of this decomposition may even be the species responsible for the irreversible process.

In bt, the two pentagonal rings are slightly puckered [2] and not quite coplanar with each other [5(a)]. Thus, the lone pairs of the N-donor atoms do not point in the most favourable direction to the formation of 5-membered chelate rings and the structure will be somewhat strained in the solid compounds. This strain might be relieved, at least partially, by solvation, thus giving rise to the same electroactive species from both complexes. The irreversible process may result from a by-product of the assumed decomposition by solvation.

Cyclic voltammetry of the Ni(II), Mn(II), and Cu(II) complexes

The cyclic voltammograms of $[\text{Ni}(\text{btz})_3][\text{ClO}_4]_2$ show a well-defined one-electron redox process (Table 1 and Figure 1), with $E_{1/2} = +1.45$ V, which can be assigned to the Ni(III)/Ni(II) couple. The estimated values, in mV, of ΔE_p (70-90 mV) and of the ratio $i_{p,a}/i_{p,c}$ ($\cong 1$), as well as the linear dependence of $i_{p,a}$ and $i_{p,c}$ on $v^{1/2}$ (Figure 2), show a practically reversible electrochemical process, more pronounced at the lower scan rates. Thus, any conformation rearrangement on changing the oxidation state of the metal ion will be fairly fast.

The manganese complex, $[\text{Mn}(\text{btz})_3][\text{ClO}_4]_2$, gives only a quasi-reversible, one-electron wave, better defined at relatively low scan rates (20 and 50 mV s^{-1}). From the $E_{1/2}$ values it seems reasonable to assume that the Mn(III)/Mn(II) couple is involved.

In the voltammograms of $[\text{Cu}(\text{btz})_3][\text{ClO}_4]_2$ a very sharp cathodic peak (+90 mV) and a very broad anodic band (at 210 mV to 230 mV) were observed. The value of $E_{1/2}$ (+0.15 V) hints at a reduction of Cu(II) to Cu(I), with a subsequent partial decomposition of the Cu(I) complex, followed by the reoxidation of the Cu(I) species to the primitive Cu(II) complex at potentials very close to one another.

CONCLUSIONS

One obvious conclusion from the results reported herein is that these heteroalicyclic ligands have little or no tendency to stabilize low oxidation states of the metal ions, in contrast with similar heteroaromatic ligands of the 2,2'-bipyridine type [10 (a), and references therein].

All the six complexes reported had the metal in the +2 oxidation state, but only in the case of $[\text{Co}(\text{btz})_3][\text{ClO}_4]_2$ was a +1 state detected, although not very stable. Thus, only this may show some promise of catalytic activity.

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REFERENCES

1. Nelson, J.; Nelson, S.M.; Perry, W.D. *J. Chem. Soc. Dalton Trans.* **1976**, 1282
2. Drew, M.G.B.; Pearson, T.R.; Murphy, B.P.; Nelson, S.M. *Polyhedron*, **1983**, *2*, 269.
3. Burnett, M.G.; Mckee, V.; Nelson, S.M. *J. Chem. Soc. Dalton Trans.*, **1981**, 1492.
4. Real, J.-A.; Gallois, B.; Granier, T.; Suez-Panamá, F.; Zarembowitch, *J. Inorg. Chem.*, **1992**, *31*, 4972.
5. (a) Ozarowsky, A.; McGarvey, B.R.; Sarkar, A.B.; Drake, J.E. *Inorg. Chem.*, **1988**, *27*, 628.
 (b) Figg, D.C.; Herber, R.H. *Inorg. Chem.*, **1990**, *29*, 2170.
 (c) Real, J.-A.; Bolvin, H.; Boussekson, A.; Dworkin, A.; Kahn, O.; Varret, F.; Zarembowitch, J. *J. Am. Chem. Soc.*, **1992**, *114*, 4650.
 (d) Kulshreshtha, S.K.; Iyer, R.M.; Konig, E. *J. Phys. Chem. Solids*, **1992**, *53*, 39.
 (e) Real, J.-A.; Castro, I.; Boussekson, A.; Verdaguer, M.; Burriel, R.; Castro, M.; Linares, J.; Varret, F. *Inorg. Chem.*, **1997**, *36*, 455.
6. Cabral, M.F.; Cabral, J.O.; Van Rijn, J.; Reedijk, J. *Inorg. Chem. Acta*, **1984**, *87*, 87.
7. Cabral, M.F.; Cabral, J.O.; Bowman, E.; Driessen, W.L.; Reedijk, J. *Inorg. Chim. Acta*, **1990**, *167*, 205.
8. Haanstra, W.G.; Cabral, M.F.; Cabral, J.O.; Driessen, W.L.; Reedijk, J. *Inorg. Chem.*, **1992**, *31*, 3150.
9. Cabral, M.F.; Cabral, J.O. *Port. Electrochim. Acta*, **1994**, *12*, 5.
10. (a) Guadalupe, A.R.; Usifer, D.A.; Potts, K.T.; Hurrell, H.C.; Mogstad, A.-E.; Abruña, H.D. *J. Am. Chem. Soc.*, **1988**, *110*, 3462.
 (b) Blake, A.J.; Reid, G.; Schroder, M. *J. Chem. Soc. Dalton Trans.* **1994**, 3291
 (c) Downard, A.J.; Bond, A.M.; Hanton, L.R.; Heath, G.A. *Inorg. Chem.* **1995**, *34*, 6395.
 (d) Goodman, D.C.; Reibenspiers, J.H.; Goswami, N.; Jurisson S.; Darensbourg M. Y. *J. Am. Chem. Soc.*, **1997**, *119*, 4955.

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STUDY OF OXIDE FILMS FORMED ON IRIIDIUM IMPLANTED Ti-6Al-4V ALLOY

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Abstract

The oxide films formed by potential cycling on commercial Ti6Al4V alloy, that has been surface implanted with iridium, are studied by capacitance measurements and Auger analysis. It is observed that these films become enriched in iridium when etched in sulphuric acid solution prior to their formation, simultaneously with a change in the type of semiconductivity (n-type to p-type).

Keywords

Iridium Oxide, Ion Implantation, Auger, Capacitance Measurements, Semiconductive Films

Introduction

The development of electronic devices for biomedical applications has been, in recent years, a very active area. Among these devices are the neural stimulating electrodes, which interface directly to the nervous system and are used to replace or supplementing function in the neurological handicapped [1-3].

Artificial stimulation of the nervous system requires the transfer of a certain amount of charge (typically $10\text{mC}/\text{cm}^2$ in the case of auditory prostheses [4]) from the electrode to the nerve cells, which can be accomplished by electrochemical processes occurring at the electrode/solution interface. Irreversible faradaic reactions, such as metallic corrosion or gas evolution, leading to the introduction of new species in the physiological medium, should be avoided as these new species can be potentially harmful to the neighbour tissues [5].

Safe stimulation of the nervous system requires therefore a reversible charge transfer process. Capacitive electrodes, in which charge is stored across a dielectric film, is one possible way to provide nerve stimulation. However, only a limited amount of charge, generally $20\text{-}30\ \mu\text{C}/\text{cm}^2$, is passed while the double layer is charging [3,6]. For that reason as an alternative, charge transfer based on reversible faradaic reactions has been investigated. These electrodes allow improved charge storage capacity through a fast and reversible redox reaction involving species that remain bound to the surface [5]. Iridium oxide is one of the most promising materials to be used in these