

Electrochemical reduction of carbon dioxide by hexa-azamacrocyclic complexes

Juan Costamagna¹, Juan Canales¹, Juan Vargas² and Guillermo Ferraudi³.

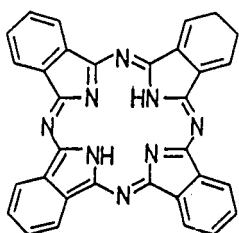
¹ Faculty of Chemistry and Biology, Universidad de Santiago, Santiago-2, Chile; ² Department of Chemistry, Universidad Metropolitana de Ciencias de la Educación, Santiago, Chile; ³ Radiation Laboratory, University of Notre Dame, Indiana, U.S.A.

ABSTRACT

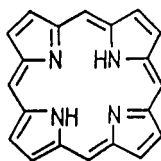
Diethenodipyrido-hexa-aza-tetradecine complexes act as a tetradentate ligand, and its complexes of Co(II), Ni(II) and Cu(II), are essentially planar. This work shows electrochemical, radiolytic and spectroscopic studies of electron transfer processes and solution equilibria. The presence of carbon dioxide notoriously change the optical properties in solution. Some pulse radiolysis studies for the reduction process of these complexes in carbon dioxide medium are also shown. In addition, electrochemical studies were performed in carbon dioxide atmosphere in order to obtain preliminary information about electrocatalytical reductions.

INTRODUCTION

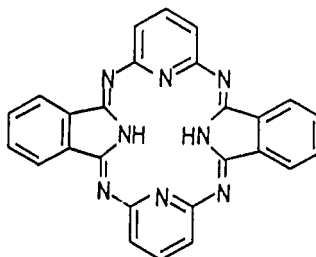
Studies on synthesis, characterization and applications of macrocyclic complexes have been published in the last years. Specific research on aza-type ligands is arising as one of the most abundant in the literature (1-7). The attention has been focused for a long time on phthalocyanines(1), porphyrines(2), hemiporphyrazines(3), and cyclic tetramines(4) and tetraamines(5), among others.



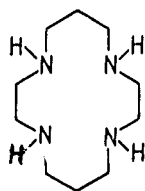
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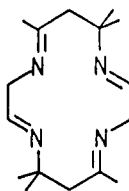
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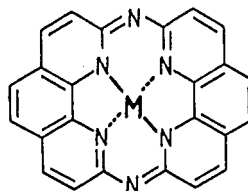
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However, little care has been taken on hexa-azamacrocycles derived from the condensation of phenanthrolines(6). This lack of information could be attributed to the low yield observed on the synthesis of these ligands (8-11). Nevertheless, recent publications have shown that rigorous elimination of humidity and use of chromatographic separations have lead to a significative increasing of yields. This improvement permitted to obtain additional information related to spectroscopic and electrochemical properties on these ligands and some complexes (12-13).

Lately, further theoretical studies based on the interpretation of electronic spectra for these complexes has been published (14). This kind of azamacrocyclic ligands have shown catalytic activity in electrochemically assisted reaction processes with several substrata (15,16). Carbon dioxide have been tested in some of these systems in order to lower its high reduction potential (17,18). In addition, some azamacrocyclic complexes have shown a marked catalytic effect in the electroreduction of carbon dioxide (19). Ligands favoring low oxidation states and efficient electron transfer processes were expected to behave more efficiently in these cases (16).

The aim of this work is focused in the study of electron transfer processes and thermodynamic properties for complexes shown in (6) [M(HAMC); M = Ni, Co, Cu]. These properties has been obtained through results provided by electrochemical, radiolytical and spectroscopic methods. Some electrochemical studies were performed in carbon dioxide atmosphere in order to obtain preliminary information about electrocatalytical behavior for these systems.

EXPERIMENTAL

Materials. The preparation and purity of copper and nickel hexa-azamacrocyclic complexes was informed previously (13). The cobalt complex was obtained by analogous methods. N,N-dimethylformamide p.a.(Merck) was used without further purification. Purum grade [C₂H₅₄N]ClO₄ >99% (Fluka), was used after carefully dried. Reagent grade anhydrous trifluormethanesulphonic acid (HTFMS), its potassium salt (KTFMS) and O₂, N₂O, CO₂ and N₂ gases were used without further purification.

Electronic Spectra and Conductance Measurements. Ultraviolet-Visible measurements in solution has been done in a Cary-17 model in the 210-600 nm range. The solvent was methanol which contained HTFMS and KTFMS to keep constant ionic strength. Conductance measurements has been done in a conventional apparatus using NaCl as cell calibrant.

Electrochemical Procedures. The experiments were carried out on a PAR 173 potentiostat/galvanostat instrument with a PAR 175 model universal programmer coupled to a PAR 179 digital coulometer. The voltammograms and the simultaneous current intensity-time plots for electrolysis were registered in a X-Y Houston-Ommigraphic 2000 recorder.

Cyclic voltammetry, and controlled potential electrolysis coulometry at room temperature (ca. 25 °C) under either inert (N₂) or saturated CO₂ atmosphere were performed at a specially designed air-tight electrochemical cell with double three-electrode system, to obtain cyclic voltammograms "in situ" for the electrolytically generated products. All electrodes were introduced into the cell body by means of a ST glass joint, and caps with Teflon faced-silicone septa were used for the needles that bubble and exit gases. Coulometric measurements were performed using a reticulated vitreous carbon (ERG)

and a saturated calomel as working and reference electrodes respectively. The last one was supplied by a vycor tip glass end. Platinum spiral wire counter electrode was separated by means of a salting bridge through sinterized glass. For cyclic voltammetry experiments a vitreous carbon polished button teflon coated was used as working electrode. The reference and counter electrode were the same as above.

Radiolytic Procedures. Radiolysis in methanol or in methanol/water mixtures using ionizing radiation has been previously informed (20-22). These studies have shown that pulse radiolysis can be used as a source of $e^-(\text{solv})$ or $\cdot\text{CH}_2\text{OH}$ radicals, which can be used as strong reducing agents. The large reduction potentials, -2.8 V vs NHE for solvated electron, $e^-(\text{solv})$, and -0.92 V vs NHE for $\cdot\text{CH}_2\text{OH}$, allow their use for the reduction of complexes and for the study of charge transfer reactions. Experimental details for reduction for these complexes in methanol by pulse radiolysis have been published recently (23,24,25).

RESULTS AND DISCUSSION

Equilibria in Solution. Hexa-azamacrocyclic complexes are sparingly soluble in methanol and water. However, the solubility in these solvents is increased by addition of acids. Electronic spectra has been obtained for several values of $[\text{AH}]:[\text{M}(\text{HAMC})]$ molar ratios in order to get information about soluble species formed upon acid aggregates. In these cases AH is HTFMS.

Some UV-visible results for these complexes dissolved in methanol at different $[\text{AH}]:[\text{M}(\text{HAMC})]$ molar ratios has been informed in a previous work (25). The most important conclusions obtained were the appearance of a band located at 280 nm for high HTFMS concentrations, changes in optical density observed at 220, 250, 280, 300 and 320 nm, that arise when $[\text{AH}]:[\text{M}(\text{HAMC})]$ ratios are less than unity for Cu(II) and Co(II) complexes, and the invariance of the spectra for $[\text{AH}]:[\text{M}(\text{HAMC})]$ ratio between 1.0 and 2.5. These results suggested that the main reaction would be a single protonation of one of the external nitrogen atoms of the macrocyclic complex (10,11). Also, values of the equilibrium constants informed for this protonation process were calculated and compared with those of analogous systems.

Figure 1 shows electronic spectra of Cu(HAMC) and Ni(HAMC) complexes in methanol at different $[\text{AH}]:[\text{M}(\text{HAMC})]$ ratios and in saturated carbon dioxide. The positions and intensities of some bands observed in Fig. 1(a), for Cu(HAMC), are different than those in Fig. 1(b), for Ni(HAMC). In addition, the spectra of Ni(HAMC) do show variations until $[\text{AH}]:[\text{M}(\text{HAMC})] = 2.5$. This spectral information is in agreement with the conclusion obtained previously about the existence of more than one equilibria for Ni(HAMC), i.e. a probable second protonation reaction in the range of concentrations studied (25).

The spectra of $\text{M}(\text{HAMC})$ ($\text{M} = \text{Cu}, \text{Ni}$) in CH_3OH with carbon dioxide instead of HFTMS are shown in Fig. 1³ in dotted lines. They are substantially different from the original complexes and show some similarities to the spectra taken in the presence of high amounts of HTFMS. The effect of the presence of carbon dioxide has been interpreted in terms of protonation (25). This effect was confirmed by solution conductivity data: for example, conductivity data for CH_3OH ; $\text{CH}_3\text{OH} + \text{CO}_2$; Cu(HAMC) in CH_3OH and Cu(HAMC) in $\text{CH}_3\text{OH} + \text{CO}_2$ are 1.15, 1.60, 2.3 and 9.65, $\mu\Omega^{-1}$, respectively (25). In addition, increasing amount of water to the system do not change these figures.

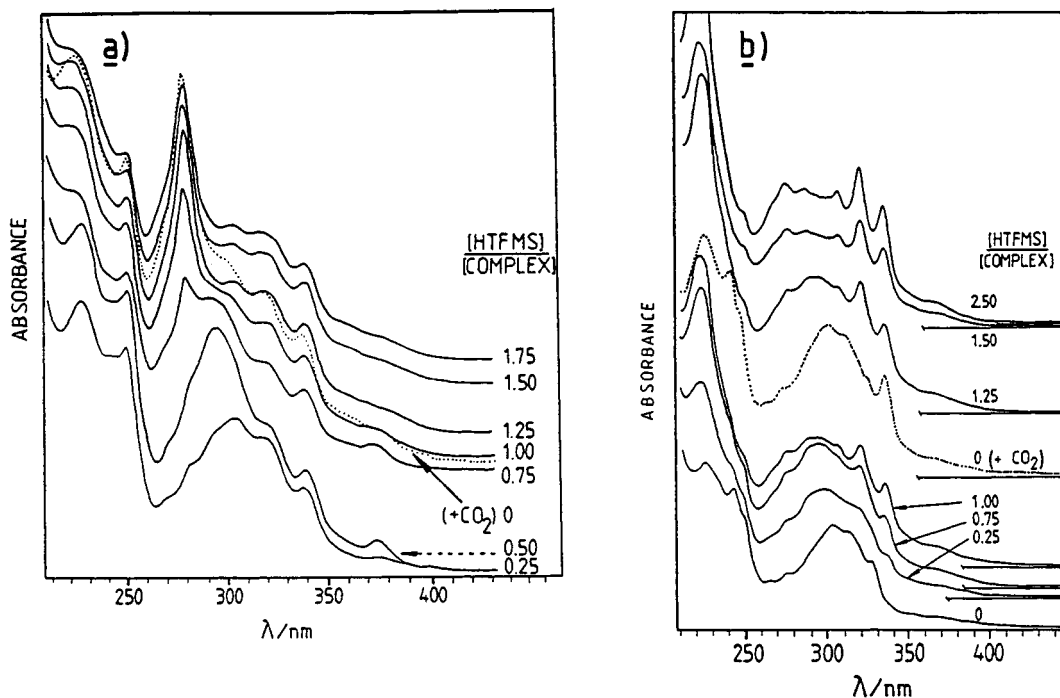


Fig. 1 Effect of trifluoromethane sulphonic acid (HTFMS) and carbon dioxide on the spectrum of $M(\text{HAMC})$ 2.25×10^{-3} M. in methanol for: (a), $M = \text{Cu}$; (b), $M = \text{Ni}$.

Quantum Chemical study on the geometry, electronic structure and spectra of these hexa-azamacrocyclic complexes has been carried out using the INDO method in its INDO/1 and INDO/2 parametrization. It has been confirmed that these planar and neutral complexes show a marked negative electronic density on the external nitrogen atoms (see 6). These results confirm the proposed protonation process (14).

Electron Transfer Process: Cyclic Voltammetry and Coulometry. In terms of potential applications to catalysis it is of particular interest to establish the nature of the redox processes by cyclic voltammetry and characterize the electron transfers involving either or both metal center and the ligand as in the case of phthalocyanines (26). Costamagna *et al.* have reported cyclic voltammetry results in the cathodic region for Ni(II) and Cu(II) hexa-azamacrocyclic complexes and suggested the stabilization of both Ni(I) and Cu(I) at -0.85 and -0.80 V vs SCE respectively. Coulometric measurements indicate that these reductions involve one-electron reduction.

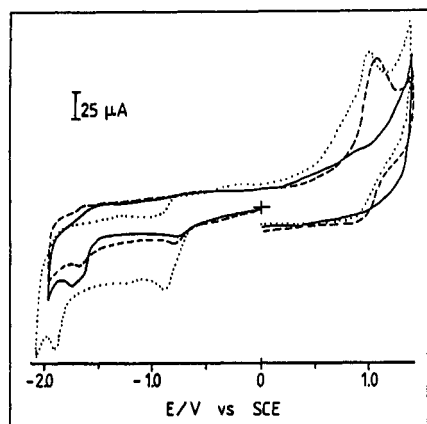


Fig. 2. Cyclic Voltammograms, in DMF, under N_2 for: $\text{Co}(\text{HAMC})$, (----); $\text{Ni}(\text{HAMC})$, (.....); $\text{Cu}(\text{HAMC})$, (—); ca. 0.1 mM; scan rate 0.2 V.s^{-1} .

Furthermore, the absence of significant redox process for the free ligand in the region in which reduction happens suggest that this process would probably occur on the metal center (13). On the other hand redox value of -0.81 V (vs SCE) has been obtained in this work for Co(HAMC) which is close to those previously observed for Cu(HAMC) and Ni(HAMC). Also, coulometric measurements indicate one electron reduction process (*vide infra*). Figure 2 summarizes significant cyclic voltammograms.

Electron Transfer Process: Pulse Radiolysis. Charge transfer processes were also studied by pulse radiolysis. Radicals coordinated to complexes with phthalocyanines and porphyrins (1,2) as ligands has been informed (27,28). The species formed are intermediates of photochemical or thermic reactions. Their short half lives as been determined by esr and electronic spectroscopy. However, there are some radicals coordinated to ruthenium(II) and rodium(III) complexes with phthalocyanine which show marked thermic and kinetic stability and they have been isolated (29-33).

Information available on radicals coordinated to complexes with ligands less insaturated than phthalocyanines and porphyrins is rather limited (33,34) and a similar behavior is predicted for complexes derived from (6); So, it is reasonable to foresee the coordination of radicals to complexes derived from this ligand. It is also expected that they would probably participate as intermediate in charge transfer reactions (25).

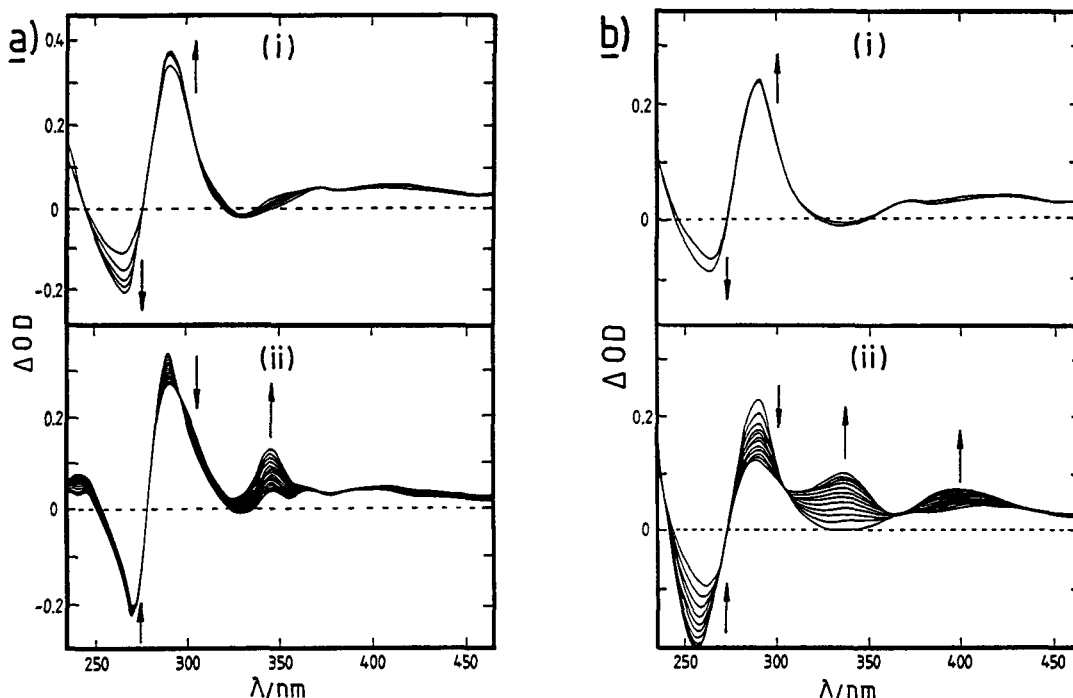


Fig. 3. Transient different spectra for reactions between $\cdot CH_2OH$ and 1.8×10^{-5} M Co(HAMC) equilibrated under 0.33 Atm. of CO_2 and 0.67 Atm. of N_2O gas mixture. The arrows give the sense of increasing sampling intervals.

(a) in CH_3OH , (i) spectra were recorded $0.6 \mu s$ after the pulse radiation at $0.6 \mu s$ intervals, (ii) spectra were recorder $36 \mu s$ after the pulse at $6 \mu s$ intervals.

(b) in $CH_3OH:H_2O$ 1:1, (i) spectra were recorded $0.6 \mu s$ after pulse at $0.6 \mu s$ intervals, (ii) spectra were recorded $18 \mu s$ after pulse radiation at $6 \mu s$ intervals.

Some results of transient difference electronic spectra from pulse radiolysis for these complexes in methanol were obtained recently (25). Different [AH]:[M(HAMC)] ratios has been employed in those studies. The most important results were the detection and the kinetic and spectroscopic characterization of reduction products, such as $M(\text{HAMC})^\cdot$ ($M = \text{Co}, \text{Cu}$). The decay process for these radicals has also been studied and their products were widely characterized (25).

The radiolytic behavior of these complexes dissolved in methanol in a mixture of $\text{N}_2\text{O}:\text{CO}_2 = 3:1$ were also studied in absence of HTFMS. A typical transient difference electronic spectra is shown in Fig. 3(a) for $\text{Co}(\text{HAMC})$. These spectra show the formation of about 25% of CO_2^\cdot which did not interfere with the reactions of the $\cdot\text{CH}_2\text{OH}$ radical. Moreover, they were similar to those observed previously which led to the formation of $M(\text{HAMCH})^\cdot$, where H denotes the protonated species of (6) (25). After radical formation a new band is observed at 340 nm for copper and cobalt complexes upon decay (see Fig. 3). Their lifetimes have been previously measured (25). These spectra were similar and independent of the metals and they only could be observed in the presence of carbon dioxide. So, these decay products could be assigned to probable adducts between CO_2^\cdot and the radicals which would act as an intermediate in the activation of CO_2 .

In addition, these complexes studied in water-methanol mixtures showed an analogous behavior but the yield were lower. Figure 3(b) shows a decrease of the intensity of the characteristic band of the radical $\text{Co}(\text{HAMCH})^\cdot$, observed at 290 nm. These results were interpreted in terms of a probable hydrolysis of the radicals formed or to a possible demetalation (25). In addition, these spectra shown the absence of CO_2^\cdot radical and the decay product shows a new band at 400 nm which could be assigned to stable hydrolysis products.

Electrochemical Reduction of Carbon Dioxide in the Presence of Hexa-azamacrocyclic Complexes. Figure 4 shows the electrochemical behavior for $\text{Ni}(\text{II})$ complex in absence and presence of carbon dioxide. It is possible to see a clear modification of the cyclic voltammogram. The intensity of the cathodic peak is increased 4.8 times when nitrogen is changed to carbon dioxide as media. Similar values have been calculated for fluorinated $\text{Ni}(\text{Cyclam})^{2+}$ complexes (35). The observed reduction potentials in presence of carbon dioxide would indicate charge transfer processes thermodynamically favored. The TABLE summarizes the data for the other complexes.

TABLE. Cyclic Voltammograms for $M(\text{HAMC})$ ($M = \text{Cu}, \text{Co}, \text{Ni}$) in N_2 and CO_2 media^(a).

Complexes	$E_{\text{PC}}(\text{N}_2)$	$E_{\text{PC}}(\text{CO}_2)$	$R^{(b)}$
Ni(HAMC)	-0.87	-1.85	4.8
Cu(HAMC)	-0.82	-1.75	5.9
Co(HAMC)	-0.81	-1.68	4.6

(a): Solvent, $\text{N,N}'$ -dimethylformamide; concentrations, ca. 10^{-4} M; Potentials vs SCE;

(b): $R = I_{\text{PC}}(\text{CO}_2)/I_{\text{PC}}(\text{N}_2)$ for the first reduction peak.

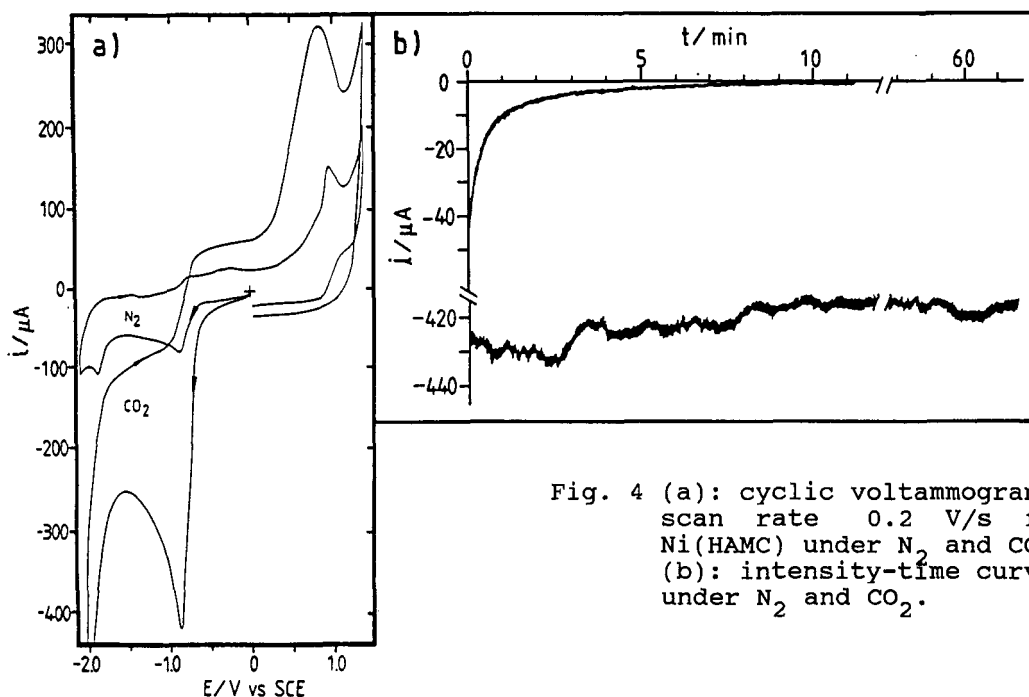


Fig. 4 (a): cyclic voltammograms, scan rate 0.2 V/s for Ni(HAMC) under N_2 and CO_2 ; (b): intensity-time curves under N_2 and CO_2 .

In addition, Fig. 4 shows that coulometry by controlled potential electrolysis at -0.87 V in CO_2 medium is having constant intensity for a long period of time, while the behavior in nitrogen atmosphere is normal and shows one electron reduction process. The observed results suggest electrocatalytic activity for the complexes on reduction of carbon dioxide. These phenomena²⁺ has been previously observed in similar systems such as $Ni(Cyclam)_2^{2+}$ complexes (16,36). The reduction of carbon dioxide might produce formic acid, -0.61 V; carbon monoxide, -0.52 V; formaldehyde, -0.48 V; methanol, -0.38 V or methane, -0.24 V (vs NHE), in multielectron transfer reactions (37). A comparison of these electron transfers with the one electron reduction of carbon dioxide to CO_2^- , -1.2 V; or to CO_2H^+ , -0.60 V (vs NHE), shows that the thermochemical advantage is balanced by the kinetic constrains that are imposed by the requirement of multi-electron transfers. According to the values of the relationships for the intensity of the cathodic peaks in nitrogen and carbon dioxide media (see TABLE) some of the products indicated formerly can be formed. Related to mechanisms for these reductions it is probable the presence of adducts of CO_2 as it has been found in radiolytic studies shown above.

A quantitative evaluation of electrocatalytic properties such as turnover cycles, percentage of average current efficiency, selectivity and chromatographic separations are currently being developed and will be published afterwards.

ACKNOWLEDGEMENTS

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