Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Synthesis and structural characterization of new 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene ligands. Study of their behavior as complexing agents for determination of nickel(II) by adsorptive stripping voltammetry

John Hurtado [a], Edgar Nagles [a], Verónica Arancibia [a], René Rojas [a], Mauricio Valderrama [a] & Roland Fröhlich [b]

[a] Facultad de Química, Departamento de Química Inorgánica, Pontificia Universidad Católica de Chile, Santiago, Chile

[b] Organisch-Chemisches Institut der Universität Münster, Münster, Germany

To cite this article: John Hurtado, Edgar Nagles, Verónica Arancibia, René Rojas, Mauricio Valderrama & Roland Fröhlich (2013) Synthesis and structural characterization of new 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene ligands. Study of their behavior as complexing agents for determination of nickel(II) by adsorptive stripping voltammetry, Journal of Coordination Chemistry, 66:4, 592-601, DOI: 10.1080/00958972.2013.764997

To link to this article: http://dx.doi.org/10.1080/00958972.2013.764997

Journal of Coordination Chemistry
Vol. 66, No. 4, 20 February 2013, 592–601

Synthesis and structural characterization of new 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene ligands. Study of their behavior as complexing agents for determination of nickel(II) by adsorptive stripping voltammetry

JOHN HURTADO†, EDGAR NAGLES†, VERÓNICA ARANCIBIA*†, RENÉ ROJAS†,
MAURICIO VALDERRAMA*† and ROLAND FRÖHLICH‡

†Facultad de Química, Departamento de Química Inorgánica, Pontificia Universidad
Católica de Chile, Santiago, Chile
‡Organisch-Chemisches Institut der Universität Münster, Münster, Germany

(*Received 16 August 2012; in final form 26 October 2012*)

Reaction of 2-bromo-1,3-bis(bromomethyl)benzene (**1**) with 1,2,3-triazole and benzotriazole yields 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene (**2**) and 2-bromo-1,3-bis(benzotriazol-1-ylmethyl)benzene (**3**), isolated as white solids, air stable at room temperature, and characterized by elemental analysis, mass spectra, IR, and NMR (^{1}H, ^{13}C) spectroscopy. The molecular structure of **3** was determined by single-crystal X-ray diffraction. These ligands were evaluated for determination of ultra-trace concentrations of nickel by adsorptive stripping voltammetry. The method is based on adsorptive accumulation of the Ni(II)-L complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using square wave modulation. However, only with **2** was a signal observed at -0.81 V. Under the best experimental conditions (pH 5.5; ligand concentration 0.30 μmol L^{-1}; adsorptive potential (E_{ads}) -0.70 V and adsorptive time (t_{ads}) 80 s), the peak current is proportional to the Ni(II) concentration to 15.0 μg L^{-1}, with a 3 detection limit of 0.2 μg L^{-1}. The proposed method was validated by determining Ni(II) in certified reference waste water (SPS–WW1) with satisfactory results.

Keywords: Nickel; Adsorptive stripping voltammetry; Bidentate ligands

1. Introduction

Multidentate ligands [(N–C–N)Br] have been developed to control the coordination sphere of metallic species [1–6]. The nature of the N donor and their substituents can control accessibility of the metal and the electron density around the metal center to potentiate their reactivity in the complexes. Van Koten *et al.* prepared the diamagnetic [BrNi(N–C–N)] compounds using 2-bromo-1,3-bis[(dimethylamino)methyl]benzene and [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) (scheme 1).

The square-planar nickel(II) compounds are very stable due to formation of two five-membered metallocycles that provide additional stabilization of the carbon–metal bond

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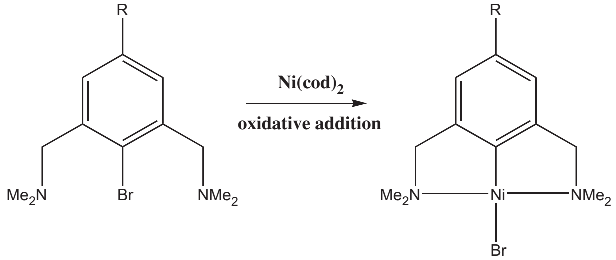
*Corresponding authors. Email: jmvalder@puc.cl (M. Valderrama); darancim@uc.cl (V. Arancibia)

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2013.764997



Scheme 1. R=H, NO_2, NH_2, MeO, Cl, MeC(O).

[7–9]. These complexes have been used as catalysts in the Kharasch addition reaction [10] and for synthesis of metallodendrimers [11]. Recently, our research focused on the synthesis of new ligands of the [(N–C–N)Br] type. In this context, we report the synthesis and characterization of nickel(II) bromide complexes bearing 2-bromo-1,3-bis(3,5-dimethylpirazol-1-ylmethyl)benzene (figure 1(A)) and 2-bromo-1,3-bis(indazol-2-ylmethyl)benzene (figure 1(B)) [12].

Nickel is a moderately toxic element compared with other transition metals, but different studies have shown chronic effects of nickel exposure, such as inhibition of growth and reproduction in invertebrates. Since the concentration of nickel in environmental and biological samples is low (pristine streams, rivers, and lakes are between 0.2 and $10\,\mu g\,L^{-1}$), development of adequate methods for determination of trace amounts is required [13]. In trace analysis of metal ions, anodic stripping voltammetry has been the most popular electroanalytical technique because of its speed, good selectivity and sensitivity, and low instrumentation cost compared to other techniques. Traditionally, the hanging mercury drop electrode (HMDE), due to its sensitivity, has been used most widely as the working electrode. However, nickel does not form amalgams with mercury. In these cases, adsorptive stripping voltammetry (AdSV) is the technique for their determination in a variety of matrices. Complexing agents such as dimethylglyoxime [14–19], 1-nitroso-2-naftol [20], pyridoxal salicyloylhydrazone [21], N-2-pyridyl-benzamidine [22], eriochrome black T [23], and others have been used.

The purpose of the present study was to report the synthesis and structural characterization of new 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene ligands and posterior application as complexing agents for determination of Ni(II) by AdSV. To our knowledge, similar results have not yet been reported.

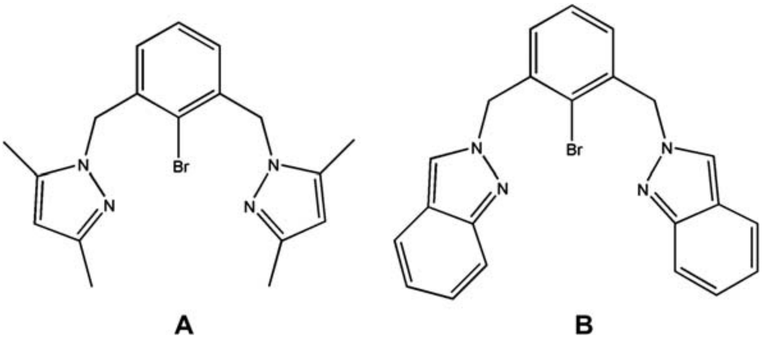


Figure 1. Schematic structure of bis(diazolate) ligands.

2. Experimental

2.1. *General procedures*

The reactions were carried out under an atmosphere of purified nitrogen. All reagent-grade solvents were dried, distilled, and stored under nitrogen. The starting compound 2-bromo-1,3-bis(bromomethyl)benzene (**1**) was synthesized according to literature procedures [24]. Other reagents were purchased from commercial sources and used without purification. Elemental analyses (C, H, N) were made on a Fisons EA 1108 CHNS-O microanalyzer. FTIR spectra were recorded throughout the 4000–250 cm^{-1} region, with samples prepared as KBr disks on a Bruker Vector-22 spectrophotometer. NMR spectra were recorded on Bruker AC-200P and Avance-400 spectrometers and chemical shifts are reported in ppm relative to $SiMe_4$ (^1H, ^{13}C). Mass spectra were obtained on a Micromass Quattro LC-Z electrospray mass spectrometer. Melting points were determined using an electrothermal melting point apparatus in open capillary tubes and are uncorrected.

2.2. *Electroanalytical studies*

2.2.1. Reagents. Water used for sample preparation, dilution of the reagents, and rinsing purposes was obtained in a Milli-Q system (18.2 M. Millipore, USA). All chemicals (nitric acid, acetic acid, sodium hydroxide, etc.) were analytical grade from Merck (Darmstadt, Germany). Standard Ni(II) solutions were prepared by diluting commercial standard containing 1000 $mg\,L^{-1}$, Merck (Darmstadt, Germany). Ligand solutions were prepared by dissolving appropriate amounts in methanol. Britton Robinson (BR) buffer solutions were used to investigate pH from 4.0 to 10.0. These buffers (0.4 $mol\,L^{-1}$) were prepared by mixing equal volumes of orthophosphoric acid, acetic acid, and boric acid, adjusting to the required pH with 2.0 $mol\,L^{-1}$ NaOH solution. Certified reference waste water (SPS–WW1) containing Al 2.00, As 0.1, Cd 0.02, Co 0.06, Cr 0.20, Cu 0.40, Fe 1.00, Mn 0.4, Ni 1.0, P 1.00, Pb 0.1, V 0.1, and Zn 5.00 $mg\,L^{-1}$ was used for validation studies. Dissolved oxygen was removed from the studied solutions by purging with water-saturated nitrogen (99.99%).

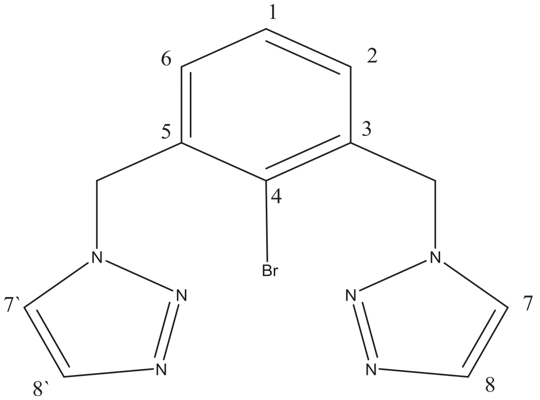
2.2.2. Instrumentation. Voltammograms were obtained on a Metrohm model 797 VA Computrace in a three-electrode configuration. The HMDE was used as working electrodes with a Ag/AgCl/KCl 3 $mol\,L^{-1}$ reference electrode, and a platinum wire auxiliary electrode. The pH measurements were carried out with Orion-430 digital pH/mV meters equipped with combined pH glass electrode.

2.2.3. Voltamperometric procedure. Ten milliliter of deionized water (or 50 μL of certified waste water), 0.1 mL of BR buffer solution (0.4 $mol\,L^{-1}$), 10–40 μL of ligand (0.15 $mmol\,L^{-1}$), and aliquots of Ni(II) solution (0.5 $mg\,L^{-1}$) were pipetted into the voltammetric cell. The solution was purged with nitrogen (saturated with water vapor) for 5 min in the first cycle and for 60 s for each successive cycle. The standard measuring procedure was performed using square wave stripping voltammetry. A mercury drop was formed and accumulation of the Ni(II)-L complex was carried out at -0.7 V for 80 s from stirred solution. At the end of the accumulation time, the stirrer was switched off, and after the equilibration time of 5 s, a square wave voltammogram was recorded, while the potential was scanned from -0.1 to -1.3 V with 0.01 V step amplitude, 0.04 V pulse amplitude, and a frequency of 25 Hz. Each voltammogram was repeated three times. The standard additions method was used to determine Ni(II) in the certified water and to check linearity of response. All experiments were carried out at room temperature.

2.3. *Synthesis of ligands*

2.3.1. Synthesis of 2-bromo-1,3-bis(triazol-1-ylmethyl)benzene (2). Triazole (332 mg, 4.66 mmol), 2-bromo(1,3-bis(bromomethyl)benzene (800 mg, 2.33 mmol), Et_3N (2 mL), and toluene (40 mL) were placed in a Schlenk flask provided with a reflux condenser and the mixture was refluxed for 48 h. The resulting mixture was treated with water and extracted with $CHCl_3$. The organic layer was separated and dried with magnesium sulfate. The solution was evaporated to dryness to give a white solid that was crystallized from chloroform–diethyl ether. Yield 302 mg (41%). m.p.: 139–141 °C. Anal. Calcd for $C_{12}H_{11}N_6Br$: C, 45.2; N, 26.3; H, 3.5%. Found: C, 45.0; N, 25.9; H, 3.9%. MS–ESI (*m/z*, ES^+): 319.16 $[M]^+$, 342.15 $[M+Na]^+$. IR (KBr, cm^{-1}): ν 1417s, 1290s, 1216s, 1092s, 1066s, 805s, 768s, 3091m, 1464m, 1365m, 1119m, 1111m, 1026m.

Atom numbering for ligand **2** is as follows:

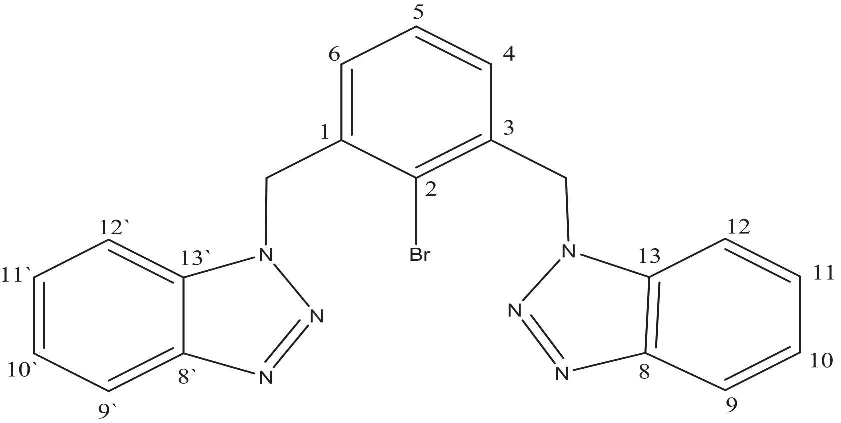


NMR ($CDCl_3$, 295 K): ^1H, δ 5.7 (s, 4H, CH_2), 6.8 (d, $2H_{2,6}$, J(HH) = 7.6 Hz), 7.2 (*t*, $1H_1$, J(HH) = 7.6 Hz), 7.6 (d, $2H_{7,7}$, J(HH) = 8.0 Hz) and 7.7 (d, $2H_{8,8}$, J(HH) = 8.0 Hz) ppm. $^{13}C\{^1H\}$, δ 54 (CH_2), 124 (C7, 7′), 124 (C4), 129 (C1), 130 (C2, C6), 134 (C8, 8′) and 137 (C3, C5) ppm.

2.3.2. Synthesis of 2-bromo-1,3-bis(benzotriazol-1-ylmethyl)benzene (3). Benzotriazole (414 mg, 3.48 mmol), 2-bromo(1,3-bis(bromomethyl)benzene (610 mg, 1.74 mmol), and toluene (25 mL) were placed in a Schlenk flask provided with a reflux condenser and the mixture was refluxed for 48 h. The resulting mixture was filtered and the toluene solution was cooled to yield a white solid. The solid was chromatographed on silica gel, eluting with $CHCl_3$: ethyl acetate 2 : 1 to give a pure compound. Yield: 270 mg (66%). m.

p.: 144–145 °C. Anal. Calcd for $C_{20}H_{15}N_6Br$: C, 57.3; N, 20.0; H, 3.6%. Found: C, 57.2; N, 20.0; H, 3.9%. MS–ESI (*m/z*, ES^+): 418.05 $[M]^+$, 441.04 $[M+Na]^+$. IR (KBr, cm^{-1}): ν 1229s, 1089s, 748s, 1455m, 1424m, 1265m, 1163m, 1028m, 944m.

Atom numbering for ligand **3** is as follows:



NMR ($CDCl_3$, 295 K): ^1H, δ 5.9 (s, 4H, CH_2), 6.7 (d, $2H_{4,6}$, *J*(HH) = 7.8 Hz), 7.0 (*t*, H_5, *J*(HH) = 7.8 Hz), 7.3 (m, 6H, $H_{10,11,12}$) and 8.0 (d, $2H_{9,9}$, *J*(HH) = 8.0 Hz) ppm. $^{13}C\{^1H\}$, δ 58 (CH_2), 110 (C11,11′), 120 (C9,9′), 123 (C2), 124 (C10,10′), 128 (C12,12′), 128 (C5), 129 (C4, C6), 133 (C13,13′), 135 (C1, C3) and 146 (C8, 8′) ppm.

2.4. *Crystal structure determination of ligand 3*

Crystals of **3** were grown by slow diffusion of diethyl ether into a dichloromethane solution. Intensity data were collected with a Nonius Kappa CCD diffractometer. The structure was solved using SHELXS-97 [25](a) and refinement using SHELXL [25](b). $C_{20}H_{15}BrClN_6\cdot 0.5\ CH_2Cl_2$, MW = 461.75, colorless crystal 0.25 × 0.20 × 0.10 mm in size, monoclinic, space group P2(1)/c, $a = 10.5782(5)$, $b = 8.4977(4)$, $c = 21.9778(10)$ Å, $\beta = 95.977(3)°$, $V = 1964.9(2)$ Å^3, $Z = 4$, Dc = 1.561 Mg m^{-3}, μ(Cu Kα) = 4.261 mm^{-1}, F (0 0 0) = 932. Limiting indices $-12 <= h <= 12$, $-9 <= k <= 10$, $-25 <= l <= 25$. Reflections collected/unique 15,108/3442 [R(int) = 0.039]. Semi-empirical absorption correction is from equivalents. Refinement method: full-matrix least squares on F^2. Final *R* indices [$I > 2(I)$] (*I*) $R1 = 0.0375$, $wR^2 = 0.0961$. *R* indices (all data) $R1 = 0.0407$, $wR^2 = 0.0984$. Solvent CH_2Cl_2 is disordered, refined with restraints, and hydrogens are calculated and refined as riding atoms.

3. Results and discussion

3.1. *Synthesis of ligands*

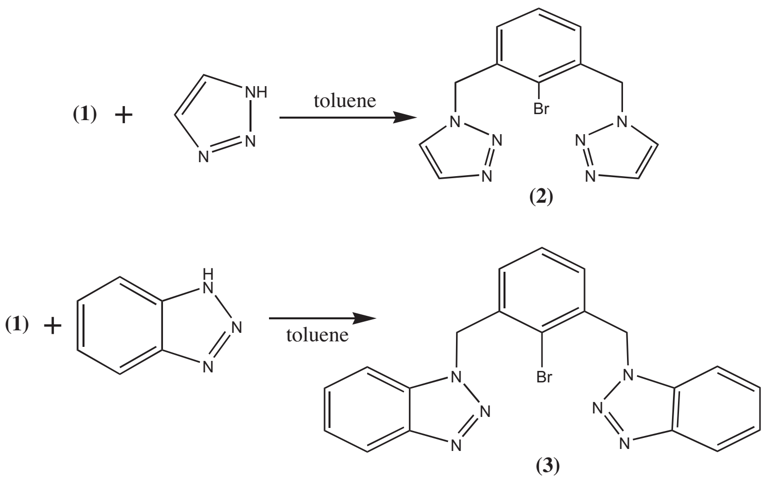
2-Bromo-1,3-bis(triazol-1-ylmethyl)benzene (**2**) was synthesized by reaction of 2-bromo-1,3-bis(bromomethyl)benzene with two equivalents of 1,2,3-triazole in toluene under reflux. The compound was isolated as air stable white solid at room temperature, soluble in dichloromethane and chloroform, and characterized by elemental analysis, mass spectra, IR, and NMR spectroscopy. The electron spray mass spectra showed the molecular ion, with the highest ion at 342.15 *m/z* with isotopic distributions that matched with those calculated for $[C_{12}H_{11}N_6Br]Na^+$.

The ^1H and ^{13}C NMR spectra are consistent with formation of a single isomer. The formulation was established on the basis of ^1H and ^{13}C NMR data and elemental analyses. The ^1H and ^{13}C chemical shifts were assigned with the aid of ^1H–$^1H^1$ (COSY), DEPT, ^1H-^{13}C (HMQC), HMBC, and NOESY experiments. Diagnostic peaks include (in ppm): δ 5.7 (s, 4 H, CH_2) and 7.7 (s, 2H, H8,8'-triazolyl). As shown in scheme 2, the triazolyl groups are connected to methylene spacers through N1.

The reaction of 3,5-bis(bromomethyl)toluene with two equivalents of benzotriazole in refluxing toluene gives 2-bromo-1,3-bis(benzotriazol-1-ylmethyl)benzene (**3**) in 66% yield. The compound was isolated as white solid, air stable at room temperature, and fully characterized by microanalysis, mass spectra, FTIR, and NMR spectroscopy. The electron spray mass spectra showed the molecular ion, with the highest ion at 441.04 *m/z* with isotopic distributions that matched with those calculated for $[C_{20}H_{15}N_6Br]Na^+$. NMR spectra of this complex are consistent with the proposed formulation. As shown in scheme 2, the triazolyl groups are connected to methylene spacers through N1. The ^1H and ^{13}C chemical shifts were assigned with the aid of ^1H–^1H (COSY), DEPT, ^1H–^{13}C (HMQC), HMBC, and NOESY experiments. In order to determine the molecular structure of **3**, an X-ray diffraction study was undertaken. Suitable crystals for structural determination were grown by slow diffusion of diethyl ether into a dichloromethane solution of **3**. A perspective view of the molecule is shown in figure 2.

As can be seen, in the solid-state, the phenyl and benzotriazole rings are planar and the benzotriazole and methylene groups are placed on the same side of the phenyl plane. All bond distances and angles fall within the expected ranges.

Ligands **2** and **3** rapidly react with Ni(II) salts in methanol solution to give green solutions. Unfortunately, all attempts to isolate the formed complexes as pure samples were unsuccessful. However, we use their coordination properties in determination of Ni(II) at low concentrations.



Scheme 2. Schematic structure of bis(triazolate) ligands **(2,3)**.

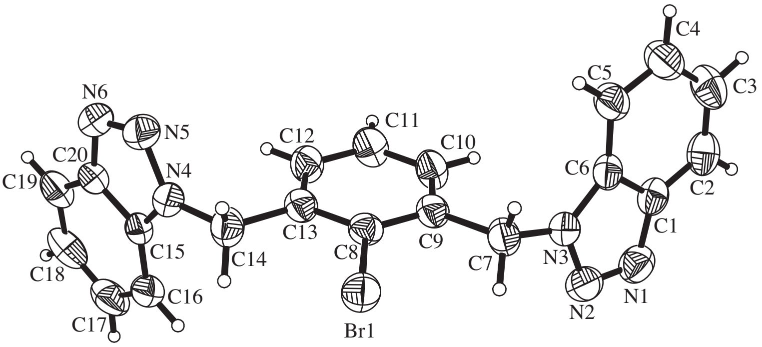


Figure 2. ORTEP-style plot of **3**. Thermal ellipsoids are shown at the 50% probability level. The numbering is arbitrary and different from that used in the ^{13}C NMR spectrum. Selected bond distances (Å) and angles (°): N(4)–N(5), 1.358 (3); N(5)–N(6), 1.299(3); N(6)–C(20), 1.376(4); N(4)–C(15), 1.358(3); N(4)–C(14), 1.452(4); C(15)–C(20), 1.392(4); C(8)–Br(1), 1.905(3); C(9)–C(10), 1.391(4); C(10)–C(11), 1.380(4); C(12)–C(13), 1.381(4); C(19)–C(20), 1.401(4); C(17)–C(18), 1.399(5); N(2)–N(1)–C(1), 108.5(2); C(7)–N(3)–C(6), 129.7(2); N(5)–N(4)–C(14), 120.0(2); N(4)–N(5)–N(6), 108.7(2); Br(1)–C(8)–C(9), 119.2(2); Br(1)–C(8)–C(13), 118.1(2); N(5)–N(6)–C(20), 108.4(2); C(8)–C(13)–C(14), 119.7(2); N(4)–C(14)–C(13), 113.0(2).

3.2. *Determination of Ni(II) in the presence of the new ligands [(N–C–N)Br]*

Because of the existence of reduction signals for the ligands, not only their complexing capacity with nickel needed to be taken into account, but also the possibility of overlapping peaks between the free ligand and the Ni-L complex peaks. Charge of the complex at different pH values is important due to changes in adsorption properties. The two ligands form complexes with Ni(II), however only with **2**, a sensitivity peak of Ni(II)-L complex appeared at about −0.81 V, while three peaks corresponding to a reduction process of free ligand were observed to −0.30, −0.40, and −1.20 V, respectively (figure 3).

To determine the M : L stoichiometry, cyclic voltammograms were recorded with 3.0 mmol L^{-1} of **2** in the presence of Ni(II) 1.0, 1.5, and 3.0 mmol L^{-1} obtaining the highest current with the Ni(II) : **2** ratio of 1 : 1. In order to find the optimum conditions with highest sensitivity for determination of Ni(II) with HMDE, influence of various parameters such as pH, $C_{L(\mathbf{2})}$, t_{ads}, E_{ads} on peak current were studied; pH of 4.0–10.0 was investigated.

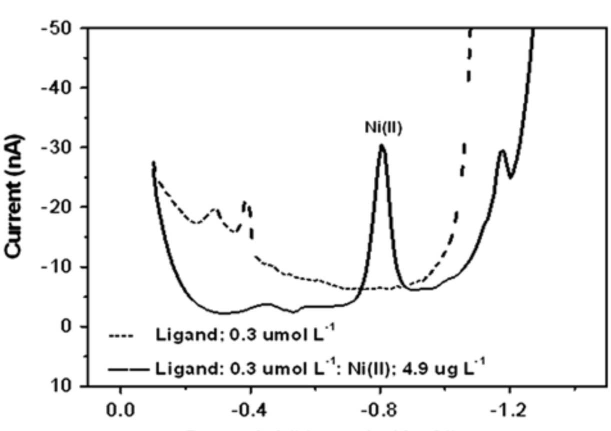


Figure 3. Adsorptive voltammograms corresponding to free **2** (- - -) and metal complex with Ni(II) (——). Conditions: pH = 5.5; Ni(II) = 4.9 μg L^{-1}; $C_{L(\mathbf{2})}$ = 0.30 μmol L^{-1}; E_{ads} = −0.10 V; t_{ads} = 80 s.

The peak potentials of both nickel and the nearest ligand peak shifted more negative with increasing pH, but higher peak resolution was obtained between pH 4.0 and 7.0 with maximum peak current at pH 5.5. For study of ligand concentration, the concentration of **2** in solution ranged from 0.15 to 0.80 µmol L^{-1}. As the nickel peak increases, the free ligand peak decreases. For low Ni(II) concentration (1.0 µg L^{-1}), a 0.15 µmol L^{-1} **2** concentration is adequate to obtain good sensitivity, however, if Ni(II) concentration is higher or the sample contains other metal ions, concentration of **2** of 0.60 or 0.8 µmol L^{-1} is needed.

Dependence of the nickel peak current on accumulation potential was examined from −0.1 to −1.3 V, and peak height was almost constant between −0.3 and −0.7 V, with −0.7 V providing the maximum peak height and was selected for measurements. Variation of the accumulation time showed that peak current increased linearly with accumulation time up to 300 s; an adsorption time of 80 s was used for the optimization study, and a higher adsorption time with the samples.

3.2.1. Analytical parameters. The calibration graph for determination of nickel was obtained under optimized conditions (figure 4): pH 5.5 (100 µL of 0.4 mol L^{-1} BR buffer); $C_{L(\mathbf{2})}$ 0.15 µmol L^{-1}; t_{ads} 80 s; E_{ads} −0.70 V. If $C_{L(\mathbf{2})}$ is 0.15 µmol L^{-1}, adsorptive curves of Ni(II) at concentrations from 0.1 to 5.0 µg L^{-1} produce a linear calibration plot ($r = 0.998$), but if $C_{L(\mathbf{2})}$ is 0.3 µmol L^{-1}, the plot is linear until 15.0 µmol L^{-1}. The precision expressed as the relative standard deviation (RSD) was 0.60% for seven successive measurements of the same sample containing 4.9 µg L^{-1} of Ni(II). The limit of detection (LOD) was calculated according to Miller [26] and was 0.2 µg L^{-1}. These results are similar (0.1 µg L^{-1}) to those obtained by us using the commercial ligand 1-nitroso-2-napthol [20].

3.2.2. Interference studies and validation of the method. The usefulness of the present method was evaluated by determining Ni(II) in certified reference waste water

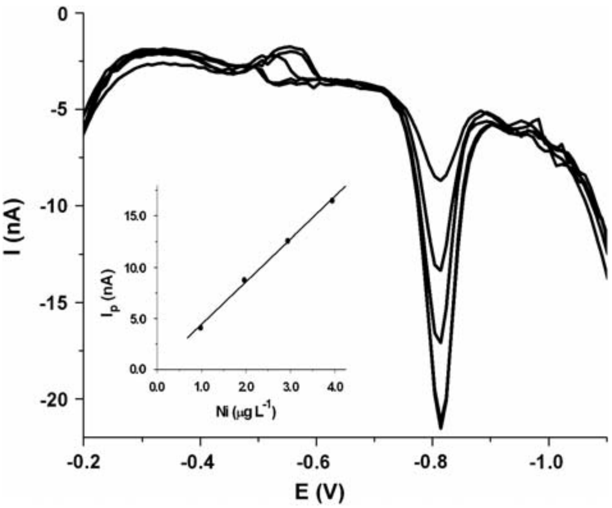


Figure 4. Adsorptive voltammograms (top) and corresponding calibration plot (bottom) of Ni(II) standard solutions. Conditions: pH = 5.5; $C_{L(\mathbf{2})} = 0.15$ µmol L^{-1}; $E_{ads} = -0.70$ V; $t_{ads} = 80$ s.

(SPS–WW1) containing 1000 $\mu g\,L^{-1}$ of Ni in the presence of Al, As, Cd, Co, Cr, Cu, Fe, Mn, P, Pb, V, and Zn. An aliquot of 50 µL of water sample (4.9 $\mu g\,L^{-1}$ of Ni in solution) and aliquots of ligand were added into the electrochemical cell to observe the signal of free ligand. Ni(II) was quantified by standard addition method obtaining $5.2 \pm 0.4\ \mu g\,L^{-1}$ (RE 6.1%). Experimental conditions: pH 5.5; C_L: 0.3 $\mu mol\,L^{-1}$, t_{ads}: 80 s; E_{ads}: −0.70 V. However, only with **2** was it possible to carry out this analytical application. Probably, **3** does not form a complex with nickel under these experimental conditions or the formed complex has a different charge and is not adsorbed onto the electrode.

Metal ions can interfere with the measurement by complexing with **2**, and this consumes the ligand or both by complexing and producing reduction peaks that overlap with, or even completely suppress, the Ni-L(**2**) complex peak. The first problem was solved by adding excess ligand and using the standard addition method for the determination. In voltammetric determination of Ni(II), the main interferences may be caused by the presence of Co(II), Al (III), and Zn(II) because their reduction potentials are close to that of Ni(II). However, in this case in the presence of **2** no signals were observed due to these metal ions.

4. Conclusions

We have synthesized and characterized two new [(N–C–N)Br] ligands formed by reacting 2-bromo-1,3-bis(bromomethyl)benzene with 1,2,3-triazole and benzotriazole. The molecular structure of 2-bromo-1,3-bis(benzotriazol-1-ylmethyl)benzene (**3**) was confirmed by X-ray diffraction. 2-Bromo-1,3-bis(triazol-1-ylmethyl)benzene (**2**) gave the best results in analysis of Ni(II). The present work shows that these new ligands can be explored for trace metal analysis, and further studies with the other ligands are in progress in our laboratory.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-806476. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: /44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We thank "Fondo de Desarrollo Científico y Tecnológico" (FONDECYT), Chile, for financial support under projects Nos. 1060597 11980002 and 1080524. JH and EN acknowledge Pontificia Universidad Católica de Chile (VRAI), CONICYT and MECESUP for doctoral fellowships.

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