

# An Exploratory Study of Tridentate Amine Extractants: Solvent Extraction and Coordination Chemistry of Base Metals with *Bis*((1*R*-benzimidazol-2-yl)methyl)amine

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Received July 19, 2012; revised August 25, 2012; accepted September 12, 2012

## ABSTRACT

Solvent extraction of base metals using *bis*((1-decylbenzimidazol-2-yl)methyl)amine (BDNNN) showed a lack of pH-metric separation of the metals. The extraction system was described quantitatively using the equilibria involved to derive the mathematical explanation for the two linear log D vs pH<sub>e</sub> plots for each metal ion extraction curve, and coordination numbers could also be extracted from the two slopes. The lack of separation was attributed to the absence of stereochemical “tailor making” since the complexes isolated from the reaction of the ligand, *bis*((1*H*-benzimidazol-2-yl)methyl)amine (NNN), with base metals suggested the formation of similar octahedral complex species from spectral and crystal structure evidence. The *bis* tridentate coordination observed was in agreement with information extracted from the extraction data. This investigation opens up an opportunity and an approach for the evaluation of amines as extractants but cautions against tridentate ligands.

**Keywords:** Base Metals; Tridentate; *Bis*((1*H*-benzimidazol-2-yl)methyl)amine; Extractive and Coordination Chemistry

## 1. Introduction

There is an increasing demand for substantial production of metals of high purity in the metallurgical industries in an attempt to meet the corresponding demand for both industrial and domestic applications. This has been the catalyst for the development of simpler and more economical routes for purification of metal ions from their ore solutions. The scale for example of nickel operations is limited, and therefore one has to maximise profit *via* processing efficiency rather than volume. The ultimate goal is to design processes that are environmentally friendly, cost-effective, time-saving and selective. Solvent extraction, a widely applied technique for the recovery of base metals [1,2], meets some of these principles since high boiling point and high flashpoint solvents are used and are recycled together with an extractant after the stripping step, and the system can be tuned through appropriate extractant design to achieve selectivity [3]. The basis of base metal ion separation is a unique property of the coordination chemistry of the particular metal ion. In the development of a metal ion specific extractant, it is necessary to consider the charac-

teristics of the metal ions from which the desired metal ion must be removed as well as its own [3]. Improvements of the chemical processes in the solvent extraction system require a thorough knowledge and investigation of the chemistry involved in order to achieve a meaningful advancement of this technology.

There has been an envisaged shift towards amine-based extractants, and this is motivated by the favourable properties that are offered by the nitrogenous ligands especially the aromatic amines as compared with oxygen-based extractants [3-5]. Some of these properties include the intermediate p*K*<sub>a</sub> values as well as  $\sigma$  and  $\pi$  bonding capabilities resulting in extractions in the low pH range and in a possibility of separation through bonding preferences respectively. The latter property has been dubbed “stereochemical tailor-making” by du Preez [5]. On the other hand, the strong aliphatic amine ligands with  $\sigma$ -donor only character show lack of relative preference for the metal ions but this can be improved if chelates are used, and also tend to form metal complexes at relatively high pH values which is undesirable [5]. The chelate effect has also been exploited effectively in a bidentate aromatic system (1-octyl-2,2'-pyridylimidazole) providing for effective separation of nickel from other base

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metals in strong acidic sulfate solutions with a possibility of back-extraction [3].

An extension of these systems to tridentate ligands would have an additional advantage of increasing the extraction equilibrium constants [6] due to the high complex formation constants for reactions of base metals and tridentate ligands [7,8], thereby requiring relatively low extractant-to-metal ratios to achieve quantitative extractions [6]. The only example of a tridentate amine extractant in the literature is that of a derivative of diethylenetriamine [9] but extractions occurred at relatively high pH values as expected due to high  $pK_a$  values of aliphatic amines [8], and the small  $\Delta pH_{0.5}$  values implied a lack of pH-metric separation of the later 3d metal ions [9]. It would be hoped that good separation factors of the metal chelates would be achieved through stereochemical considerations since nickel(II) is known to form the most stable spin free octahedral ( $O_h$ ) complexes of all base metal ions [10] while the copper(II) and cobalt(II) ions tend to form stable tetrahedral ( $T_d$ ) complexes [4,11]. This study, therefore, also interrogates the coordination chemistry aspects of base metals, that influence the extractions, with tridentate amine-based ligands.

In this account, we present the extractive and coordination chemistry of an aromatic tridentate ligand, *bis*((1*H*-benzimidazol-2-yl)methyl)amine (NNN) (**Figure 1(a)**), towards base metals in a sulfate/sulfonate medium. Dinonylnaphthalene sulfonic acid (DNNSA) (**Figure 1(b)**) was used as a bulky anion to ion-pair and transfer the cationic complexes formed in this extraction system (ion-association system) to the organic phase since the sulfate ion is known to have high hydration energies leading to lack of phase transferability [12]. The sulfate medium has become particularly important to explore since it is encountered in liquors produced in sulfate-based high nickel matte leach processes or those produced in sulfuric acid pressure leaching of laterites [13].

## 2. Experimental

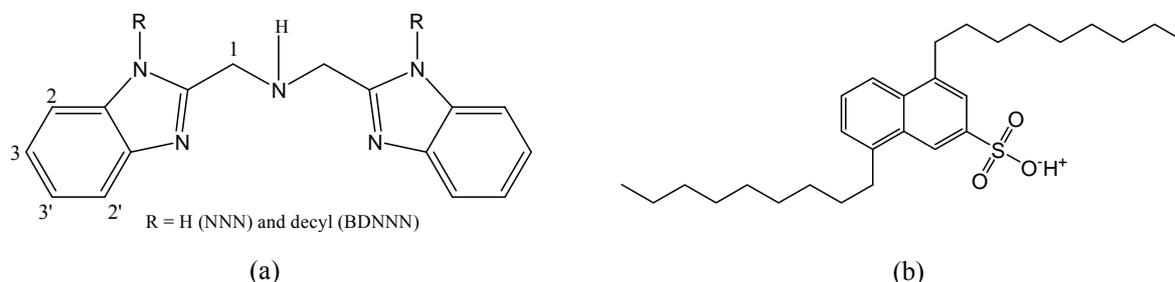
### 2.1. Materials

*o*-Phenylenediamine (99.5%, Sigma-Aldrich), iminodiacetic acid (98%, Sigma-Aldrich), hydrochloric acid

(32%, Merck Chemicals), ammonia (28%, Merck Chemicals), methanol (99%, Sigma-Aldrich), and ethyl acetate (98%, Sigma-Aldrich) were reagent grade chemicals used as received for the synthesis of *bis*((1*H*-benzimidazol-2-yl)methyl)amine (NNN). The reagent grade octylbromide (98%) was also obtained from Sigma-Aldrich and used as received for the synthesis of the extractant.  $NiSO_4 \cdot 6H_2O$  (98%),  $CuSO_4 \cdot 5H_2O$  (99%) were obtained from Merck chemicals.  $CoSO_4 \cdot 7H_2O$  (97.5%) was obtained from Fluka, while  $ZnSO_4 \cdot 7H_2O$  (99.5%) was obtained from BDH Chemicals. The copper(II), nickel(II), cobalt(II) and zinc(II) perchlorate hexahydrate salts which were used to prepare the metal(II) sulfonate salts using toluene-4-sulfonic acid (98%, Sigma-Aldrich) were obtained from Sigma-Aldrich. Analytical grade reagents were used without further purification in the preparations of the 0.10 M metal ion stock solutions in 3 M  $H_2SO_4$  solution. The ICP/AAS 1000 ppm metal standards, dissolved in 0.5 N nitric acid, were used to prepare standard solutions for the construction of calibration curves using distilled, deionized, milliQ water for the dilutions. Dinonylnaphthalene sulfonic acid (50 wt% in heptane), Shellsol 2325 (17 - 22 v/v% aromatic content) and 2-octanol (98%) were obtained from Sigma-Aldrich, Shell Chemicals (SA) and Merck Chemicals, respectively.

### 2.2. Instrumentation

$^1H$  NMR spectrometry was carried out on a Bruker AMX 400 MHz NMR spectrometer and reported relative to tetramethylsilane ( $\delta$  0.00). A Vario Elementary ELIII Microcube CHNS analyser was used for elemental analyses. A Thermo Electron (iCAP 6000 Series) inductively coupled plasma (ICP) spectrometer equipped with an OES detector was used for metal ion analysis. The Labcon micro-processor controlled orbital platform shaker model SPO-MP 15 was used for contacting the two phases of extraction. The pH measurements were performed on a Metrohm 827 pH meter using a combination electrode with 3 M KCl as electrolyte. The metal-complexes were characterised using infrared spectrometry on both Perkin Elmer 400 FTIR and 100 FTIR-ATR



**Figure 1.** The chemical structures of (a) *bis*((1*H*-benzimidazol-2-yl)methyl)amine (NNN for R = H, and BDNNN for R = Decyl) and (b) dinonylnaphthalene sulfonic acid (DNNSA).

spectrometers. The solid reflectance spectra of the metal complexes were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer UV-3100 with a MPCF-3100 sample compartment with samples mounted between two quartz discs which fit into a sample holder coated with barium sulfate. The spectra were recorded over the wavelength range of 2000 - 250 nm, and the scans were conducted at a medium speed using a 20 nm slit width. The Gallenkamp melting point apparatus (temperature range, 0°C - 350°C) was used to measure the melting points. The conductivity measurements were carried out on a A.W.R. Smith Process Instrumentation cc Laboratory Bench Meter Model AZ 86555 with ABS graphite cell probe using an aqueous standard which has a conductivity value of 135  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$  at 20°C for the calibration. All the complexes were prepared in DMF as a solvent to a concentration of  $10^{-3}$  M for the conductivity measurements.

## 2.3. Synthesis of the Ligand and Extractant

### 2.3.1. Bis((1*H*-benzimidazol-2-yl)methyl)amine (NNN)

The bis((1*H*-benzimidazol-2-yl)methyl)amine (NNN) was synthesized as reported elsewhere [14], except that iminodiacetic acid was used and the decolorization step using activated charcoal in methanol was necessary. The characterization data for the white precipitate of the free base was as follows: Yield: 84%, m.p., 268°C - 270°C. Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{OS}$  (%): C, 65.10; H, 5.80; N, 23.70. Found: C, 65.78; H, 5.80; N, 23.07.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 4.06 (4H, s, *H1*), 7.15 (4H, m, *H3, H3'*), 7.52 (4H, m, *H2, H2'*). IR ( $\text{cm}^{-1}$ ): 3208  $\nu(\text{N-H})$ , 3049  $\nu(\text{sec N-H})$ , 1592  $\nu(\text{C}=\text{N})$ .

### 2.3.2. Bis((1-decylbenzimidazol-2-yl)methyl)amine (BDNNN)

The alkylated derivative of the ligand was prepared according to a literature method [15]. However, the purification step was carried out as follows: The resulting solution after the removal of the KBr salt was concentrated *via* rotary evaporation, and purified using a silica gel chromatographic column with ethyl acetate/methanol (4:1) solvent system. After the removal of the solvent by rotary evaporation the product was obtained as brown oil. Yield = 67%. Anal. Calcd. for  $\text{C}_{36}\text{H}_{59}\text{N}_5\text{O}_2$  (%): C, 72.81; H, 10.01; N, 11.79. Found: C, 72.95; H, 10.61; N, 11.86.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm):  $\delta$  0.89 (6H, t,  $\text{CH}_3$ ), 1.13 (24H, m,  $\text{CH}_3(\text{CH}_2)_6$ ), 1.01(4H, t,  $\text{CH}_2\text{-CH}_3$ ), 1.55(4H, t,  $\text{CH}_2\text{-CH}_2\text{N}$ ), 3.96 (4H, t,  $\text{CH}_2\text{-N}$ ), 4.02 (4H, s, *H1*), 7.26 (4H, q, *H3 & H3'*), 7.28 (2H, d, *H2*), 7.75 (2H, d, *H2'*). IR ( $\text{cm}^{-1}$ ): 1522  $\nu(\text{C}=\text{N})$ .

## 2.4. Syntheses of Metal Complexes

All the reactions for the formation of coordination complexes (sulfonate and sulfate compounds) were con-

ducted in absolute ethanol using the toluene-4-sulfonate salts of the metals, and inert conditions were adopted for the synthesis. 10 mL of hot ethanolic solution (60°C) containing 2 mmol of the ligand was added dropwise to 10 mL of the metal ion solution (1 mmol, respectively for each metal ion). The mixture was heated under reflux overnight and the precipitate that formed was filtered off, washed with ethanol and dried.

### 2.4.1. Sulfate Complexes

$[\text{Co}(\text{NNN})_2]\text{SO}_4\cdot 4\text{H}_2\text{O}$ : Color: pink. Yield = 51%, m.p., 252°C - 254°C. Anal. Calcd. for  $\text{C}_{32}\text{H}_{38}\text{N}_{10}\text{CoO}_8\text{S}$  (%): C, 49.17; H, 4.90; N, 17.92; S, 4.10. Found: C, 49.20; H, 4.46; N, 17.85; S, 4.86. IR ( $\text{cm}^{-1}$ ): 3242  $\nu(\text{N-H})$ , 1545  $\nu(\text{C}=\text{N})$ , 1037  $\nu_3(\text{SO}_4)$ , 226  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 66.

$[\text{Ni}(\text{NNN})_2]\text{SO}_4\cdot 3\text{H}_2\text{O}$ : Color: purple. Yield = 57%, m.p., 253°C - 255°C. Anal. Calcd. for  $\text{C}_{32}\text{H}_{36}\text{N}_{10}\text{NiO}_7\text{S}$  (%): C, 50.34; H, 4.75; N, 18.35; S, 4.20. Found: C, 50.64; H, 4.74; N, 18.28; S, 4.10. IR ( $\text{cm}^{-1}$ ): 3234  $\nu(\text{N-H})$ , 1538  $\nu(\text{C}=\text{N})$ , 1037  $\nu_3(\text{SO}_4)$ , 230  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 69.

$[\text{Cu}(\text{NNN})_2]\text{SO}_4\cdot 7\text{H}_2\text{O}$ : Color: green. Yield = 65%, m.p., 228°C - 229°C. Anal. Calcd. for  $\text{C}_{32}\text{H}_{44}\text{N}_{10}\text{CuO}_{11}\text{S}$  (%): C, 45.74; H, 5.28; N, 16.67; S, 3.82. Found: C, 45.81; H, 5.11; N, 16.41; S, 3.44. IR ( $\text{cm}^{-1}$ ): 3233  $\nu(\text{N-H})$ , 1565  $\nu(\text{C}=\text{N})$ , 1060 - 1088  $\nu_3(\text{SO}_4)$ , 224  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 71.

$[\text{Zn}(\text{NNN})_2]\text{SO}_4\cdot 11\text{H}_2\text{O}$ : Color: white. Yield = 64%, m.p., 221°C - 222°C. Anal. Calcd. for  $\text{C}_{32}\text{H}_{52}\text{N}_{10}\text{ZnO}_{15}\text{S}$  (%): C, 42.04; H, 5.73; N, 15.31; S, 3.51. Found: C, 41.96; H, 5.71; N, 15.00; S, 3.59. IR ( $\text{cm}^{-1}$ ): 3227  $\nu(\text{N-H})$ , 1548  $\nu(\text{C}=\text{N})$ , 1037  $\nu_3(\text{SO}_4)$ , 222  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 82.

### 2.4.2. Sulfonate Complexes

$[\text{Co}(\text{NNN})_2](\text{RSO}_3)_2\cdot 4\text{H}_2\text{O}\cdot 2\text{EtOH}$ : Color: red. Yield = 71%, m.p., 225°C - 226°C. Anal. Calcd. for  $\text{C}_{50}\text{H}_{64}\text{N}_{10}\text{CoO}_{12}\text{S}_2$  (%): C, 53.66; H, 5.67; N, 12.52; S, 5.73. Found: C, 53.60; H, 5.34; N, 12.67; S, 5.14. IR ( $\text{cm}^{-1}$ ): 3311  $\nu(\text{N-H})$ , 1551  $\nu(\text{C}=\text{N})$ , 1150-1161  $\nu_3(\text{RSO}_3)$ , 279  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 136.

$[\text{Ni}(\text{NNN})_2](\text{RSO}_3)_2\cdot 3\text{H}_2\text{O}\cdot 2\text{EtOH}$ : Color: purple. Yield = 58%, m.p., 246°C - 248°C. Anal. Calcd. for  $\text{C}_{50}\text{H}_{62}\text{N}_{10}\text{NiO}_{11}\text{S}_2$  (%): C, 54.50; H, 5.67; N, 12.71; S, 5.82. Found: C, 54.43; H, 5.58; N, 12.47; S, 5.70. IR ( $\text{cm}^{-1}$ ): 3313  $\nu(\text{N-H})$ , 1550  $\nu(\text{C}=\text{N})$ , 1151 - 1164  $\nu_3(\text{RSO}_3)$ , 246  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 139.

$[\text{Cu}(\text{NNN})_2](\text{RSO}_3)_2\cdot 12\text{H}_2\text{O}$ : Color: blue. Yield = 68%, m.p., 201°C - 202°C. Anal. Calc. for  $\text{C}_{46}\text{H}_{68}\text{N}_{10}\text{CuO}_{18}\text{S}_2$  (%): C, 46.95; H, 5.82; N, 11.90; S, 5.45. Found: C, 46.48; H, 5.47; N, 11.76; S, 5.85. IR ( $\text{cm}^{-1}$ ): 3213  $\nu(\text{N-H})$ , 1550  $\nu(\text{C}=\text{N})$ , 1147 - 1172  $\nu_3(\text{RSO}_3)$ , 262  $\nu(\text{M-N})$ . Conductivity ( $10^{-3}$  M,  $\text{ohm}^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1}$ ): 141.

[Zn(NNN)<sub>2</sub>](RSO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O·2EtOH: Color: white. Yield = 62%, m.p., 201°C - 202°C. Anal. Calc. for C<sub>50</sub>H<sub>62</sub>N<sub>10</sub>ZnO<sub>11</sub>S<sub>2</sub> (%): C, 54.17; H, 5.64; N, 12.63; S, 5.78. Found: C, 54.50; H, 5.64; N, 12.30; S, 5.53. IR (cm<sup>-1</sup>): 3304 ν(N-H), 1549 ν(C=N), 1172 - 1187 ν<sub>3</sub>(RSO<sub>3</sub>), 258 ν(M-N). Conductivity (10<sup>-3</sup> M, ohm<sup>-1</sup>·cm<sup>2</sup>·mole<sup>-1</sup>): 147.

## 2.5. Solvent Extraction Procedure

All the extractions were carried out at 25°C (±1°C) in a temperature controlled laboratory. Equal volumes (10 mL) of 0.001 M metal ion solution (aqueous layer) and 80% 2-octanol/shellsol solution (organic layer containing the extractant BDNNN and the counterion DNNSA) were pipetted into 50 mL conical separating funnels. The contents in the funnel were shaken using an automated orbital platform shaker for 30 minutes at an optimised speed of 200 rpm. A minimum period of 60 minutes was observed before harvesting the raffinate. The raffinate were filtered through a 33 mm millex-HV Millipore filter (0.45 μm) and diluted appropriately for analysis by ICP. The percentage extractions (%E) of the metal ions were calculated from the concentrations of the metal ions in the aqueous phase using equation 1 below:

$$\%E = \left( \frac{C_i - C_s}{C_i} \right) \times 100 \quad (1)$$

where  $C_i$  is the initial solution concentration (mg/L) and  $C_s$  is the solution concentration after extraction.

The extraction efficiencies were investigated as a function of pH, and all the extraction curves were plotted with Sigma Plot 11.0.

## 2.6. X-Ray Structure Determination and Refinement

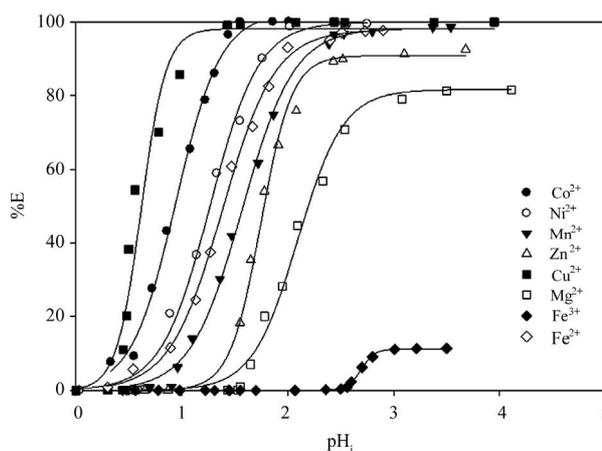
Single crystals of [Cu(NNN)<sub>2</sub>](RSO<sub>3</sub>)<sub>2</sub>·12H<sub>2</sub>O, suitable for X-ray diffraction, were obtained by slow evaporation of the ethanolic mother liquor of this complex at room temperature. X-ray diffraction studies were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal structures were solved by direct methods using *SHELXTL* [16]. All non-hydrogen atoms were refined anisotropically. C-bound H atoms were placed in calculated positions and refined as riding atoms, with bond lengths 0.95 (aromatic CH), 0.99 (CH<sub>2</sub>), 0.98 (CH<sub>3</sub>) Å and with  $U_{iso}(H) = 1.2$  (1.5 for methyl)  $U_{eq}(C)$ . Hydrogens bonded to nitrogen were located on a Fourier map and allowed to refine freely. Hydrogens on water molecules were restrained to an O-H bond length of 0.84 Å and H-O-H angle of 110°. Diagrams and publication material were generated using *SHELXTL*, *PLATON* [17] and *ORTEP-3* [18].

## 3. Results and Discussion

### 3.1. Solvent Extraction Studies

These studies were carried out in dilute synthetic sulfate solutions. The extractant (BDNNN) was used for the extraction studies while the ligand (NNN) was used to study the coordination chemistry involved. The complexes of the extractant were oily and not easily isolated hence we used the NNN ligand for the coordination chemistry studies. The decyl groups of the extractant (BDNNN) would be positioned away from the coordination sphere and therefore the use of the ligand (NNN) would not change the coordination chemistry of the extractant from a steric hindrance point of view.

The use of low  $pK_a$  groups (benzimidazoles) on the ligand was expected to result in metal extractions from highly acidic solutions in comparison with tridentate aliphatic amine extractants based on diethylenetriamine [9]. This was well exploited but also resulted in lack of room for back-extraction of some metals (like Cu(II), Co(II) and possibly Ni(II)) at the "left legs" of their extraction curves. The lack of pH-metric separation of the base metal ions, however, was evident from the small  $\Delta pH_{0.5}$  values (**Figure 2**). Interestingly, the order of the extraction of the metal ions somewhat followed the Irving-Williams stability order [19] in the shifting of the curves towards the acidic region with the exception of Co(II) and Ni(II) extractions, which could be influenced by kinetic effects [20]. It is also noteworthy to report on the hard ions (Mn<sup>2+</sup> and Mg<sup>2+</sup>) extracting ability of this tridentate ligand but with rejection of Fe(III) in the pH range 0 - 2.6, which is attractive for the latter but not the former.



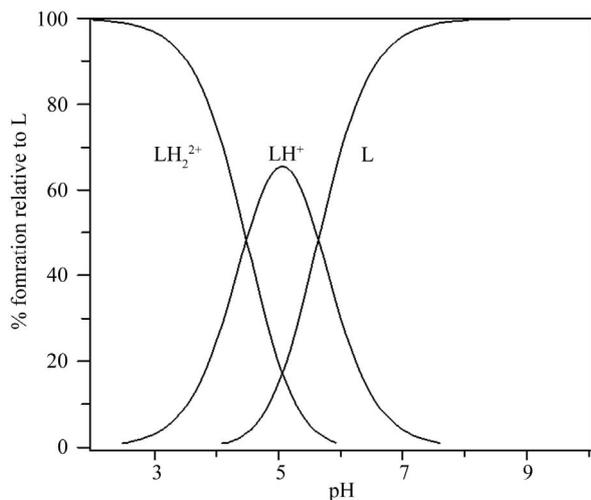
**Figure 2.** A plot of %E vs initial pH of equimolar concentrations (0.001 M) of Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>, extracted with BDNNN (at M:L ratio 1:40) and 0.02 M DNNSA in 2-octanol/Shellsol 2325 (8:2) from a dilute sulfate medium.

It is clear, therefore, that the move towards tridentate ligands, even with low  $pK_a$  aromatic nitrogen groups and a strong aliphatic amine group, is not sufficient to successfully exploit the low pH range interactions with metal ions since extraction isotherms are pushed further into the low pH range thereby compromising back-extraction. These ligands also lack selectivity for the important borderline metal ions which can possibly be tuned through bonding preferences. The coordination chemistry studies (Section 3.2) were, therefore, conducted to try and elucidate the underlying aspects of bonding that influenced the extraction isotherms observed.

In a quantitative treatment for this solvent extraction system, similar to that applied for a chelating system (HL) [6], the protonation, complexation and phase distribution equilibria can be used to describe the system mathematically with respect to the distribution ratio of a metal ion ( $M^{n+}$ ), and also give insight into the coordination numbers involved in the extraction reaction. The protonation equilibria which were studied using potentiometry in the pH range of 2 - 10 by Hay *et al.* [7] showed two constants for *bis*((1*H*-benzimidazol-2-yl)methyl)amine (NNN, L), and they were 5.64 and 10.12 respectively for the cumulative protonation steps ( $LH^+$  and  $LH_2^{2+}$ ). The species distribution plot, constructed from the above constants using the computer program HYSS [21], is given in **Figure 3** for the pH-metric speciation involved for L in the aqueous phase.

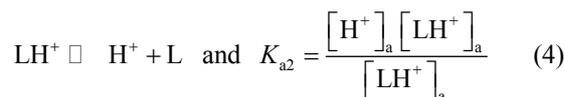
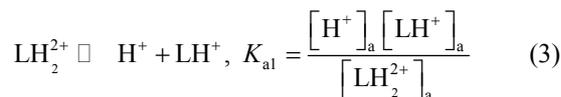
The chelating agent (L) must distribute between the organic and aqueous phases to effect coordination in the aqueous phase, and that distribution coefficient is represented by  $K_D(L)$ :

$$(L)_a \rightleftharpoons (L)_o \text{ and } K_D(L) = \frac{[L]_o}{[L]_a} \quad (2)$$

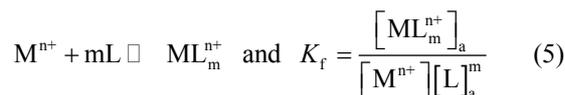


**Figure 3.** Protonation species distribution diagram for *bis*((1*H*- benzimidazol-2-yl)methyl)amine (NNN, L).

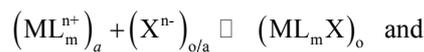
However, in the aqueous phase the following two protonation equilibria may exist depending on pH:



Then, the metal ion chelates with the neutral ligand to form a cationic complex:



It must be borne in mind, however, that the metal ion will replace proton(s) in the pH ranges under investigation but the protonation equilibria will accommodate this in the mathematical treatment. Finally, the chelate which is ion-paired by an anion (in our case two sulfonate anions represented by  $X^{n-}$ ) to form an extractable species,  $[ML_m]X$ , distributes itself between the organic and aqueous phases:



$$K_D (ML_m^{n+}) = \frac{[ML_m X]_o}{[ML_m^{n+}]_a} \quad (6)$$

The distribution ratio (D), defined as the ratio of the concentration of the total metal species in the organic phase to that in the aqueous (regardless of its mode), is given by expression 7, on the assumption that the metal chelate distributes largely in the organic phase and that the metal ion does not hydrolyse in the aqueous phase.

$$D \approx \frac{[ML_m X]_o}{(M^{n+})_a} \quad (7)$$

Substituting Equations (6) and (5) respectively into Equation (7) yields Equation (8), depicting the formation constant and the concentration of the ligand in the aqueous phase as important parameters as well as the distribution coefficient of the chelate:

$$D = K_D (ML_m^{n+}) K_f [L]_a^m \quad (8)$$

which can be transformed to Equation (9) if Equation (2) is substituted into Equation (8), indicating that the concentration of L in the aqueous phase is dependent on its concentration in the organic phase and that its distribution between the two phases affects the distribution ratio of the complex formed:

$$D = \frac{K_D (ML_m^{n+}) K_f}{K_D (L)^m} [L]_0^m \quad (9)$$

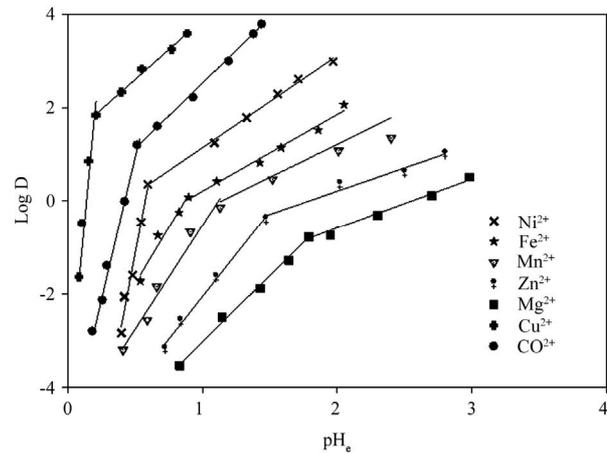
However, since the extractions are carried out at low pH, it is necessary to consider the two protonation equilibria respectively because these species occur over wide pH ranges (**Figure 3**), and competition of metal ions with protons for the ligand occurs early with pH due to the higher formation constants [7] compared with protonation constants thereby resulting in release of the protons from the ligand. Now, substituting Equation (4), and Equations (3) and (4), respectively, into Equation (8) yields the following respective Equations (10) and (11):

$$D = K_D (ML_m^{n+}) K_f K_{a2}^m \frac{[LH^+]^m}{[H^+]_a^m} \quad (10)$$

$$\text{And } D = K_D (ML_m^{n+}) K_f K_{a2}^m K_{a1}^m \frac{[LH_2^{2+}]_a^m}{[H^+]_a^{2m}} \quad (11)$$

Therefore, in the pH range where only one protonation equilibrium (Equation (4)) is involved then a plot of log D vs pH (from taking the logarithms of both sides in equation 10) should yield a straight line with slope m (number of ligands bonded to the metal ion  $M^{n+}$ ). But in the highly acidic region where the second proton equilibrium (Equation (3)) is also active, then a plot of log D vs pH should yield a straight line with slope (2 m).

A plot of log D vs pHe (since the extraction isotherms relate to the equilibrium condition) for this extraction system is presented in **Figure 4**. There is a clear change in the slope of each curve and respectively become steeper with an increase in the order of stabilization of metal ions [19]. The higher pH range for  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$  and  $Ni^{2+}$  is represented by a slope in the range 1 - 2 with nickel at  $m = 1.97$  while it peaks close to 3 - 4 ( $\approx 2$  m) respectively at the lower pH range with the exception of nickel (slope = 15) which gets seriously affected by the extremely acidic medium. This observation is somewhat in agreement with the mathematical model described here for this complex equilibria system suggesting two ligands per metal ion are involved in the coordination. These observations (as well as those discussed below) are also in line with the protonated ligand species observed in **Figure 3** (for the protonation equilibria). The extremely acidic region (affecting the copper and cobalt curves, and to a minor extent the nickel curve in the acidic end) is only characterised by a slope of ca. (3 m - 2 m) for copper and cobalt at the higher pH end (around the pH where other metal ions also have a slope close to 4). This occurred mainly because our mathematical modelling does not take into account the third protonation equilibrium which is possible under those



**Figure 4.** A plot of log D vs equilibrium pH ( $pH_e$ ) for the extraction of 0.001 M  $M^{2+}$  ( $M = Mg^{2+}$ ,  $Zn^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Cu^{2+}$ ) with 0.002 M BDNN and 0.02 M DNNSA from sulfate medium.

highly acidic conditions where cobalt and copper are extracted. This third protonation constant was also not determined by potentiometry by Hay *et al.* [7] due to the inaccessibility of the measurement in that pH range by potentiometry. According to our mathematical treatment, involving the third equilibrium should result in a slope 3 m = 6 at the lower pH end for cobalt and copper (and to some extent nickel), however, it is much steeper with slopes of 12, 15 and 26 for cobalt, nickel and copper respectively.

It is possible, however, that not only the double (slope = 2 m) and the triple (slope = 3 m) protonation equilibria dominate in the pH range where extractions of copper and cobalt ions occur but complex multiple protonations ( $i$  m,  $i = 1, 2, 3, \dots$ ) with  $i$  exceeding 3 from the hydrogen bonding with the rings'  $\pi$  electrons [22], hence the coordination number (m) cannot be calculated accurately from data in that pH range. It seems though that a linear plot of the points (calculated at the intersections of the two lines from each metal ion extraction data) at the vertices of the two linear plots, respectively for each metal ion, gives a negative slope  $\approx 1.6$  which is in agreement with the coordination numbers of 2 involved for all the metals (discussed in Section 3.2), but a mathematical treatment has not been provided herein. This observation may be coincidental, and therefore one cannot conclude on an isolated study. Once it is verified for other extraction studies with extractants similar to the one studied here, a mathematical function may be derived.

### 3.2. Coordination Chemistry Studies

The elemental analyses data suggested the following empirical formulae;  $[M(NNN)_2]X \cdot xH_2O \cdot yEtOH$  ( $M = Co, Ni, Cu$  and  $Zn$ ;  $X = SO_4^{2-}$  or  $(RSO_3^-)_2$ ,  $x = 3 - 12$  and  $y = 0 - 2$ ). The involvement of two ligands per metal ion is

in agreement with what was observed in the extraction studies. Complexes of Fe(II), Fe(III) and other hard ions could not be isolated with a good level of purity but *bis*-coordination is implied by the slopes of the extraction data. The molar conductivity data in DMF showed that the sulfate and sulfonate complexes have molar conductance values of 66 - 82 and 136 - 147  $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ , respectively. This indicated that all the sulfate complexes behaved as 1:1 electrolytes while the sulfonate complexes were 1:2 electrolytes [23]. This behavior in solution suggested the non-coordinated nature of the counter-anions. Both the sulfate and sulfonate complexes were prepared in order to elucidate the nature of these anions respectively with respect to their innocence to coordination, and the full structural analyses are discussed in Sections 3.2.1 and 3.2.2 below. Both the sulfate and sulfonate complexes were prepared since the extraction studies were carried out in a sulfate medium and a bulky sulfonate anion was also used to replace the sulfate ion.

### 3.2.1. Spectral Analysis

The C=N stretching vibration of the benzimidazole rings of the free ligand (NNN) appeared at  $1592\text{ cm}^{-1}$  [24,25], and coordination-induced frequencies were observed in the range  $1548 - 1565\text{ cm}^{-1}$  upon complex formation. The lowering in the double bond character of C=N is perhaps due to the influence of the benzimidazole groups being *trans* to each other. The far infrared spectra of the sulfate and sulfonate complexes displayed bands in the range  $222 - 279\text{ cm}^{-1}$  which were assigned to the  $\nu(\text{M-N})$  [26]. A strong and broad peak in the range  $1137 - 1188\text{ cm}^{-1}$  and  $1050 - 1090\text{ cm}^{-1}$  was present in the spectra of sulfate and sulfonate complexes respectively, and this is typical of the uncoordinated sulfate and sulfonate ions [27]. The infrared spectra of these complexes suggested that all the three donor atoms of the ligand are involved in the coordination sphere and that both the sulfate and sulfonate anions are non-coordinating. The geometry of the complexes was confirmed by UV-Vis solid reflectance electronic studies as well as by single crystal X-ray crystallography (Section 3.2.2).

Three d-d transitions that are expected in the visible region of the spectrum for an octahedral Co(II) complex are;  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_2$ ) and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) [28]. These absorption bands were observed at 1095, 544 and 482 nm respectively (Figure 5). For the nickel complexes the bands were observed at 919, 585 and 555 nm which may be assigned to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3\text{A}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_2$ ) and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transitions respectively for an octahedral symmetry [28]. The electronic spectrum of the Cu(II) complex showed one broad band at 619 nm which was ascribed to the  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  and, assuming that the second transition ( ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ) is masked by the intraligand

transition, this is consistent with a distorted octahedral geometry [28].

### 3.2.2. X-Ray Structural Analysis

An ORTEP diagram of the crystal structure of  $[\text{Cu}(\text{NNN})_2](\text{RSO}_3)_2\cdot 12\text{H}_2\text{O}$  is presented in Figure 6. The selected crystallographic data is presented in Table 1, and selected bond lengths and angles in Table 2.

The crystal structure of  $[\text{Cu}(\text{NNN})_2](\text{RSO}_3)_2\cdot 12\text{H}_2\text{O}$  conclusively depicted that the complex is cationic with relatively isolated sulfonate anions (Figure 6). The closest contact that the sulfonate ion has with the cationic molecule is  $\text{H}(23)\text{-O}(31) = 2.560(1)$ . The two ligands are

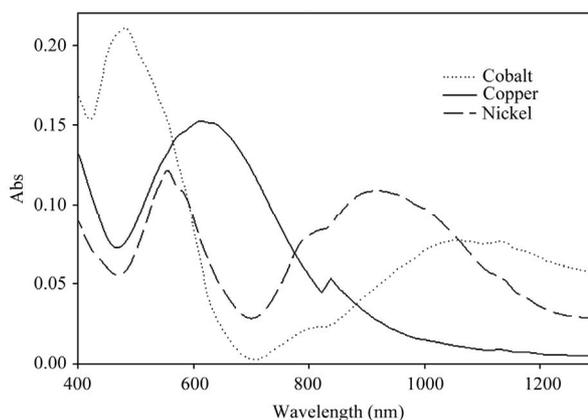


Figure 5. The UV-Vis solid reflectance spectra of  $[\text{M}(\text{NNN})_2]\text{SO}_4\cdot x\text{H}_2\text{O}$  ( $\text{M}=\text{Co}, \text{Ni}$  and  $\text{Cu}$ ;  $x = 3 - 12$ ).

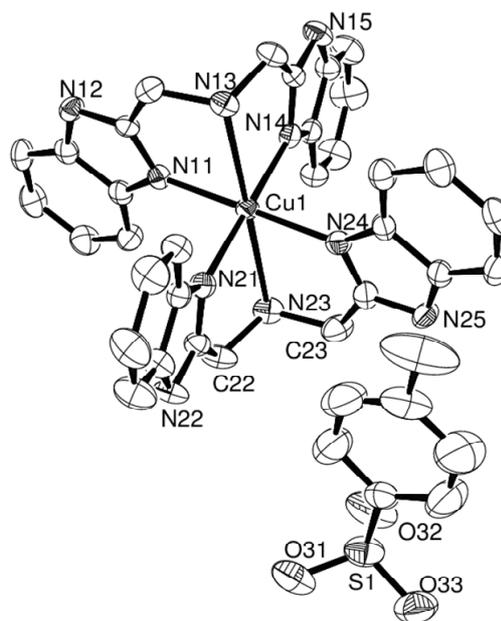


Figure 6. ORTEP diagram of  $[\text{Cu}(\text{NNN})_2](\text{RSO}_3)_2\cdot 12\text{H}_2\text{O}$  showing the atom labeling scheme and ellipsoids drawn at 50% probability level. One toluene-4-sulfonate anion and twelve water molecules have been omitted for clarity.

**Table 1. Selected crystallographic data for [Cu(NNN)<sub>2</sub>](RSO<sub>3</sub>)<sub>2</sub>·12H<sub>2</sub>O.**

Compound	[Cu(NNN) <sub>2</sub> ](RSO <sub>3</sub> ) <sub>2</sub> ·12H <sub>2</sub> O
Chemical formula	C <sub>54</sub> H <sub>86</sub> CuN <sub>10</sub> O <sub>18</sub> S <sub>2</sub>
Formulae weight	4514.66
Crystal color	Blue
Crystal system	Tetragonal
Space group	I4
Temperature (K)	200
Crystal size (mm <sup>3</sup> )	0.05 × 0.11 × 0.50
a (Å)	34.4165(11)
b (Å)	34.4165(11)
c (Å)	9.3238(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å <sup>3</sup> )	11044.0(9)
Z	2
D <sub>calc</sub> (g/cm <sup>-3</sup> )	1.358
μ/mm <sup>-1</sup>	0.545
F(000)	4696
Wavelength (Å)	0.71073
Theta Min-Max (°)	1.9, 28.3
S	0.98
Tot., Uniq. Data, R(int)	91906, 13572, 0.095
Observed data [I > 2.0 sigma(I)]	8997
R	0.0507
R <sub>w</sub>	0.1218

tridentately coordinated to the copper(II) ion in the formation of a tetragonally distorted O<sub>h</sub> geometry with the four benzimidazoles in the square plane while the two aliphatic amines occupy the apical positions. The five-membered chelate rings have bite angles in the range 74.8° - 77.0°. The aliphatic amines are bonded *trans* to each other and the Cu-N lengths of 2.509 and 2.547 Å are rather long possibly due to Jahn-Teller distortion. However, the Cu-N (benzimidazole) lengths are rather short (average of 2.014 Å) due to the π-acidity character of the benzimidazole group.

An X-ray crystal structure of the copper complex similar to [Cu(NNN)<sub>2</sub>](RSO<sub>3</sub>)<sub>2</sub>·12H<sub>2</sub>O was presented by Berends and Stephan [29] but no crystallographic pa-

**Table 2. Selected bond lengths (Å) and angles (°) for [Cu(NNN)<sub>2</sub>](RSO<sub>3</sub>)<sub>2</sub>·12H<sub>2</sub>O.**

Bond lengths			
Cu1-N11	1.998(14)	Cu1-N21	2.045(14)
Cu1-N13	2.509(14)	Cu1-N23	2.547(14)
Cu1-N14	2.040(14)	Cu1-N24	2.012(15)
Bond angles			
N11-Cu1-N13	77.0(5)	N13-Cu1-N24	104.0(5)
N11-Cu1-N14	86.5(6)	N14-Cu1-N21	179.9(8)
N11-Cu1-N21	93.6(6)	N14-Cu1-N23	105.3(5)
N11-Cu1-N23	103.1(5)	N14-Cu1-N24	93.9(6)
N11-Cu1-N24	179.0(6)	N21-Cu1-N23	74.8(5)
N13-Cu1-N14	75.9(5)	N21-Cu1-N24	86.0(6)
N13-Cu1-N21	104.0(5)	N23-Cu1-N24	75.9(5)
N13-Cu1-N23	178.9(4)	C22-N23-C23	114.2(14)

rameters were reported because the complete refinement of the model was unsuccessful, and the ORTEP diagram presented was based on parameters obtained in “best” model. A similar nickel complex crystal structure has also been reported [30,31] but had a different arrangement of the donor groups, for example the aliphatic amine groups from each ligand were bonded *trans* to the benzimidazole group of another ligand. The similarity in the geometry of these base metal complexes afforded us to conclude that the lack of pH-metric separation with the use of *bis*((1-decylbenzimidazol-2-yl)methyl)amine as extractant (Section 3.1) is influenced by the lack of stereochemical “tailor making”.

#### 4. Conclusion

The combination of two low pK<sub>a</sub> aromatic nitrogenous groups of benzimidazole with a strong aliphatic amine, in the design of a tridentate ligand, resulted in extraction curves that are pushed deep as a function of pH possibly due to the high complex formation constants of tridentate coordination and the relatively low protonation constants of the benzimidazole groups. This may compromise the stripping of the metal ions from the loaded organic phase through pH adjustment to lower pH. The Fe(III) rejection ability of this tridentate ligand in the range where the other later 3d metal ions extract is remarkable. It can be concluded that the exploitation of the subtle stereochemical aspects of coordination for the extraction of base metals is lacking with tridentate ligands (at least those of the nature presented here). This leads us to propose the evaluation of a bidentate derivative, [2-methylaminomethyl-(1-*R*-benzimidazole), *R* = octyl or decyl],

as a potential extractant of base metal ions. We have also demonstrated, for the first time, that the ion-association solvent extraction system studied here can be interpreted quantitatively for the complexation aspect of the formation of the cationic complex species to describe the two linear log D vs  $\text{pH}_c$  plots, and to extract information on coordination numbers from the extraction data using the respective slopes for each extraction curve.

## 5. Supporting Information

CCDC 891865 contains the supplementary crystallographic data for  $[\text{Cu}(\text{NNN})_2](\text{RSO}_3)_2 \cdot 12\text{H}_2\text{O}$ . These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## 6. Acknowledgements

The authors thank Mr F. Chindeka (DST/Mintek-NIC, Rhodes University Chemistry Department) for the micro-analysis results. We also acknowledge Shell Chemicals (SA) (Pty) Ltd for supplying Shellsol 2325. We would also like to thank Mr A. S. Ogunlaja and Mr P. Kleyi for their assistance. For financial support, we thank the National Research Foundation (NRF-CPRR grant).

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