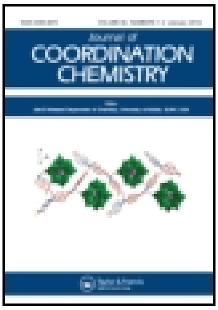
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:46
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

The coordination and extractive chemistry of the later 3d transition metals with bis((1R-benzimidazol-2-yl)methyl)sulfide

NOMAMPONDO P. MAGWA [a] , ERIC HOSTEN [b] , GARETH M. WATKINS [a] & ZENIXOLE R. TSHENTU [a]

[a] Department of Chemistry , Rhodes University , Grahamstown , South Africa

[b] Department of Chemistry , Nelson Mandela Metropolitan University , Port Elizabeth , South Africa

Accepted author version posted online: 08 Nov 2012.Published online: 12 Dec 2012.

To cite this article: NOMAMPONDO P. MAGWA , ERIC HOSTEN , GARETH M. WATKINS & ZENIXOLE R. TSHENTU (2013) The coordination and extractive chemistry of the later 3d transition metals with bis((1R-benzimidazol-2-yl)methyl)sulfide, Journal of Coordination Chemistry, 66:1, 114-125, DOI: 10.1080/00958972.2012.748192

To link to this article: http://dx.doi.org/10.1080/00958972.2012.748192

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 66, No. 1, 10 January 2013, 114–125

The coordination and extractive chemistry of the later 3d transition metals with *bis*((1*R*-benzimidazol-2-yl)methyl) sulfide

NOMAMPONDO P. MAGWA†, ERIC HOSTEN‡, GARETH M. WATKINS† and ZENIXOLE R. TSHENTU†*

†Department of Chemistry, Rhodes University, Grahamstown, South Africa
‡Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth, South Africa

(*Received 4 July 2012; in final form 26 September 2012*)

The coordination chemistry of the later 3d metal ions with *bis*((1*H*-benzimidazol-2-yl)methyl)sulfide (NSN) is investigated. All the complexes had general formula $[M(NSN)_2]X \cdot yH_2O$, where M = Co(II), Ni(II), Cu(II), and Zn(II), $X = SO_4^{2-}$) or (RSO_3^{2-}), and $y = 2$–5. The infrared and conductivity measurements provided evidence that the sulfate and sulfonate acted as counter anions in the isolation of these dicationic complexes. X-ray crystal structures of $[Co(NSN)_2](RSO_3)_2 \cdot 4H_2O$ and $[Ni(NSN)_2](RSO_3)_2 \cdot 2H_2O$ revealed a distorted octahedral geometry for these complexes. Extraction studies showed a lack of pH-metric separation of the later 3d metal ions with *bis*((1-octylbenzimidazol-2-yl) methyl)sulfide (BONSN) as an extractant, but that extractions occurred in the low pH range with an opportunity for back-extraction. This investigation suggests that tridentate ligands (of the nature investigated) are not feasible extractants for metal ions due to their lack of stereochemical "tailor making."

Keywords: Base metals; *Bis*((1*H*-benzimidazol-2-yl)methyl)sulfide; Tridentate; Extractive and coordination chemistry

1. Introduction

The upsurge in mineral markets provides motivation for the development of processes that improve dissolution of ores and separation of metal ions. The most commonly applied method in the separation of base metals is solvent extraction. Extractants currently available in industry, such as organophosphorus extractants (Cyanex reagents) and oxime-type extractants (LIX reagents), are oxygen donors [1, 2]. The major drawback with O-donor extractants is that they have high affinity for Fe(III) and other A type metal ions, necessitating precipitation of iron(III) prior to extraction of nickel and cobalt [3, 4]. However, N-donor ligands form stable complexes with borderline metals, such as the later 3d metal ions, and less stable complexes with A type metal ions such as ferric [5, 6]. This provides motivation for examination of N-donor ligands as potential extractants in separation of base metals.

---

*Corresponding author. Email: z.tshentu@ru.ac.za

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
http://dx.doi.org/10.1080/00958972.2012.748192

Aliphatic amines (R–NH_2, where R is an alkyl or aryl group) form metal complexes at relatively high pH due to their high protonation constants which lead to the hydrolysis of metal ions even under slightly acidic conditions. These strong ligands with only σ-donor character also show lack of preference for metal ions, however, this can be improved if chelates are used: for example, alkylated derivatives of ethylenediamine [7]. Aromatic nitrogen ligands, however, have a preference for metal ions which could relate to the possibility of σ and π bonding, and in addition, allow for complexation to occur even in strongly acidic solutions due to their lower pK_a values [7–9]. Extension of aromatic systems to bidentate amines provides for effective separation of nickel from other base metals in strong acidic solutions with low M : L ratios compared with monodentate aromatic nitrogen extractants, and there is reversibility of the extraction reaction [9]. A further expansion of these systems can be the introduction of tridentate ligands. Tridentate aliphatic amines, such as the derivatives of diethylenetriamine, also result in extractions at relatively high pH values and in small $\Delta pH_{0.5}$ values (0.2 for Ni/Co and ~1 for Cu/Zn and Zn/Co, respectively) [10]. This lack of selective separation may be attributed to thermodynamic and stereochemical factors. In this study, we explore the use of a potentially tridentate aromatic amine ligand as an extractant for the separation of base metals, especially, nickel from other later 3d metal ions.

Specificity for metals can be tuned through stereochemical "tailor making" [7]. Nickel(II) forms the most stable spin-free octahedral (O_h) complexes of all base metal ions [5], therefore, to achieve nickel specificity, it is important for the ligand to force six-coordination. Copper(II), on the other hand, forms stable tetrahedral (T_d) and square planar complexes while octahedral complexes are less common [11]. Cobalt and zinc also tend to form more stable T_d complexes compared with O_h complexes. These subtle stereochemical factors can be exploited when designing extractants for separation of base metals. Herein, we describe the application of an aromatic tridentate ligand, *bis*((1*H*-benzimidazol-2-yl)methyl) sulfide (NSN) (figure 1(a)) using extractive and coordination chemistry studies in sulfate and sulfonate media. Dinonylnaphthalene sulfonic acid (DNNSA) (figure 1(b)) was used as a bulky anion to ion-pair the cationic complexes formed in this extraction system for phase transferability.

2. Experimental

2.1. *Materials*

o-Phenylenediamine (99.5%, Sigma-Aldrich), 2,2'-thiodiacetic acid (98%, Sigma-Aldrich), hydrochloric acid (32%, Merck Chemicals), ammonia (28%, Merck Chemicals), methanol

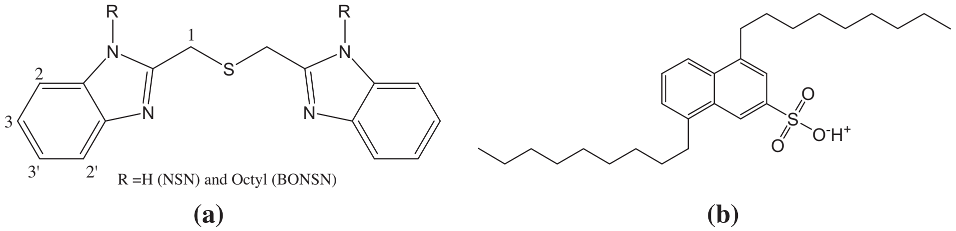


Figure 1. The chemical structures of (a) *bis*((1R-benzimidazol-2-yl)methyl)sulfide (NSN for R = H, and BONSN for R = Octyl) and (b) dinonylnaphthalene sulfonic acid (DNNSA).

(99%, Sigma-Aldrich), and ethyl acetate (98%, Sigma-Aldrich) were reagent grade chemicals used as received for synthesis of NSN. Reagent grade octylbromide (98%) was also obtained from Sigma-Aldrich and used as received for synthesis of the extractant. $NiSO_4 \cdot 6H_2O$ (98%) and $CuSO_4 \cdot 5H_2O$ (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 purification in preparation of 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 construction of calibration curves using distilled, deionized, milliQ water for dilutions. DNNSA (50 wt.% in heptane), Shellsol 2325 (17–22 v/v% aromatic content), and 2-octanol (98%) were obtained from Sigma-Aldrich, Shell Chemicals and Merck Chemicals, respectively.

2.2. *Instrumentation*

^{1}H-NMR spectrometry was carried out on a Bruker AMX 400 MHz NMR and reported relative to tetramethylsilane (δ 0.00). A Vario Elementary ELIII Microcube CHNS analyzer was used for elemental analyzes. A Thermo Electron (iCAP 6000 Series) inductively coupled plasma (ICP) spectrometer equipped with an OES detector was used for metal ion analysis. A 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 characterized using infrared spectrometry on both Perkin Elmer 400 FTIR and 100 FTIR-ATR 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 disks 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. A Gallenkamp melting point apparatus (temperature range, 0–350 °C) was used to measure the melting points. Conductivity measurements were carried out on a AWR 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 $\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$ at 20 °C for calibration. All the complexes were prepared in dimethylformamide (DMF) at 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)sulfide (NSN). The NSN was synthesized as reported elsewhere [12], except that 2,2’-thiodiacetic acid was used and the decolorization step using activated charcoal was not necessary. The characterization data for the white precipitate of the free base was as follows: Yield: 71%, m.p., 210–212 °C. Anal. Calcd for $C_{16}H_{16}N_4OS$ (%): C, 61.52; H, 5.16; N, 17.93; S, 10.26. Found: C, 61.15; H, 5.34; N, 17.97; S, 10.15. ^{1}H-NMR ($CDCl_3$) δ(ppm): 4.06 (4H, s, *H*1), 7.17 (4H, m, *H*3, *H*3′), 7.53 (4H, m, *H*2, *H*2′). IR (cm^{-1}): 3377 ν(N–H), 1534 ν(C=N), 1128 δ(C-S-C).

2.3.2. *Bis*((1-octylbenzimidazol-2-yl)methyl)sulfide (BONSN). The alkylated derivative of the ligand was prepared according to a literature method [13]. However, the purification step was carried out as follows: the resulting solution after removal of the KBr salt was concentrated via rotary evaporation and purified using a silica gel chromatographic column with ethyl acetate/methanol (4:1). After removal of the solvent by rotary evaporator, the product obtained was a white precipitate. Yield = 63%, m.p., 76–78 °C. Anal. Calcd for $C_{32}H_{50}N_4O_2S$ (%): C, 69.27; H, 9.08; N, 10.10; S, 5.78. Found: C, 68.83; H, 9.45; N, 10.04; S, 5.83. ^{1}H-NMR ($CDCl_3$) δ(ppm): ^{1}H-NMR ($CDCl_3$) δ(ppm): δ 0.81 (6H, t, CH_3), 1.17 (20H, m, $CH_3(\mathbf{CH_2})_5$), 1.65 (4H, t, CH_2–$\mathbf{CH_2}$N), 4.14 (4H, t, $\mathbf{CH_2}$–N), 4.21 (4H, s, *H*1), 7.19 (4H, q, *H3 & H3'*), 7.51 (2H, d, *H2*), 7.59 (2H, d, *H2'*). IR (cm^{-1}): 1503 ν(C=N), 1137 δ(C–S–C).

2.4. *Syntheses of metal complexes*

2.4.1. Preparation of metal sulfonate salts, $M(RSO_3)_2 \cdot 6H_2O$ (M = Co, Ni, Cu and Zn). A solution of toluene-4-sulfonic acid (RSO_3H) (10 mmol) was mixed with equimolar potassium hydroxide (10 mmol) in absolute ethanol to produce toluene-4-sulfonate salt (equation (1)) which was filtered and left to dry at room temperature.

$$RSO_3H + KOH \rightarrow K^+RSO_3^- + H_2O\,(R = \text{toluene}) \tag{1}$$

$$2K^+RSO_3^- + M(ClO_4)_2 \rightarrow M(RSO_3)_2 + 2KClO_4(s) \tag{2}$$

To potassium toluene-4-sulfonate (2 mmol) was added $M(ClO_4)_2 \cdot 6H_2O$ (1 mmol) dissolved in 30 mL absolute ethanol (equation (2)), after which, the potassium perchlorate salt was removed by centrifugation and filtration. The metal sulfonate salts were purified by slow recrystallization in acetone to form crystals.

2.4.2. Preparation of sulfate and sulfonate complexes. All reactions for the coordination complexes (sulfonate and sulfate compounds) were conducted in absolute ethanol and inert conditions were adopted for the synthesis. Hot ethanolic solution (60 °C) of 10 mL 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 overnight under reflux and the precipitate was filtered off and washed with ethanol. Single crystals of cobalt and nickel complexes suitable for X-ray diffraction were obtained upon slow evaporation of the synthetic mother liquors at room temperature.

(a) Sulfate complexes. **$[Co(NSN)_2]SO_45H_2O$**: Color: mauve. Yield = 57%, m.p., 242–243 °C. Anal. Calcd for $C_{32}H_{38}N_8CoO_9S_3$ (%): C, 46.09; H, 4.59; N, 13.44; S, 11.54. Found: C, 46.13; H, 4.68; N, 13.52; S, 11.79. IR (cm^{-1}): 3191 ν(N–H), 1547 ν(C=N), 1068–1095 $\nu_3(SO_4)$, 349 ν(M–N), 244 ν(M–S). Conductivity (10^{-3} M, $Ohm^{-1}\,cm^2\,mol^{-1}$): 68.

$[Ni(NSN)_2]SO_44H_2O$: Color: pink. Yield = 48%, m.p., 245–246 °C. Anal. Calcd for $C_{32}H_{36}N_8NiO_8S_3$ (%): C, 47.13; H, 4.45; N, 13.74; S, 11.79. Found: C, 47.07; H, 4.17; N, 13.72; S, 11.99. IR (cm^{-1}): 3189 ν(N–H), 1545 ν(C=N), 1064–1090 $\nu_3(SO_4)$, 348 ν(M–N), 250 ν(M–S). Conductivity (10^{-3} M, $Ohm^{-1}\,cm^2\,mol^{-1}$): 71.

[Cu(NSN)$_2$]SO$_4$4H$_2$O: Color: green. Yield = 64%, m.p., 248–249 °C. Anal. Calcd for $C_{32}H_{36}N_8CuO_8S_3$ (%): C, 46.85; H, 4.42; N, 13.66; S, 11.73. Found: C, 46.79; H, 4.17; N, 13.25; S, 11.67. IR (cm^{-1}): 3186 ν(N–H), 1545 ν(C=N), 1060–1088 ν_3(SO$_4$), 340 ν(M–N), 243 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 74.

[Zn(NSN)$_2$]SO$_4$2H$_2$O: Color: white. Yield = 52%, m.p., 249–252 °C. Anal. Calcd for $C_{32}H_{32}N_8ZnO_6S_3$ (%): C, 48.88; H, 4.10; N, 14.25; S, 12.23. Found: C, 48.98; H, 4.15; N, 14.35; S, 12.27. IR (cm^{-1}): 3187 ν(N–H), 1545 ν(C=N), 1060–1080 ν_3(SO$_4$), 338 ν(M–N), 296 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 85.

(b)Sulfonate complexes. **[Co(NSN)$_2$](RSO$_3$)$_2$4H$_2$O**: Color: orange. Yield = 59%, m.p., 263–264 °C. Anal. Calcd for $C_{46}H_{50}N_8CoO_{10}S_4$ (%): C, 52.02; H, 4.74; N, 10.55; S, 12.08. Found: C, 52.09; H, 4.83; N, 10.75; S, 12.11. IR (cm^{-1}): 3410 ν(N–H), 1542 ν(C=N), 1167 ν_3(SO$_3$), 399 ν(M–N), 319 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 131.

[Ni(NSN)$_2$](RSO$_3$)$_2$2H$_2$O: Color: pink. Yield = 48%, m.p., 266–268 °C. Anal. Calcd for $C_{46}H_{46}N_8NiO_8S_4$ (%): C, 53.86; H, 4.52; N, 10.92; S, 12.48. Found: C, 53.98; H, 4.54; N, 10.96; S, 12.11. IR (cm^{-1}): 3412 ν(N–H), 1542 ν(C=N), 1165 ν_3(SO$_4$), 396 ν(M–N), 314 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 134.

[Cu(NSN)$_2$](RSO$_3$)$_2$4H$_2$O: Color: green. Yield = 43%, m.p., 211–212 °C. Anal. Calcd for $C_{46}H_{50}N_8CuO_{10}S_4$ (%): C, 51.79; H, 4.72; N, 10.50; S, 12.02. Found: C, 51.84; H, 4.96; N, 10.92; S, 12.51. IR (cm^{-1}): 3413 ν(N–H), 1539 ν(C=N), 1161 ν_3(SO$_4$), 392 ν(M–N), 336 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 138.

[Zn(NSN)$_2$](RSO$_3$)$_2$4H$_2$O: Color: white. Yield = 62%, m.p., 213–214 °C. Anal. Calcd for $C_{46}H_{50}N_8ZnO_{10}S_4$ (%): C, 51.70; H, 4.72; N, 10.49; S, 12.00. Found: C, 51.75; H, 4.79; N, 10.54; S, 12.08. IR (cm^{-1}): 3392 ν(N–H), 1535 ν(C=N), 1180 ν_3(SO$_4$), 399 ν(M–N), 332 ν(M–S). Conductivity (10^{-3} M, Ohm^{-1} cm^2 mol^{-1}): 141.

2.5. *Solvent extraction procedure*

All extractions were carried out at 25(±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 BONSN and the counterion DNNSA) were pipetted into 50 mL conical separating funnels. They were shaken using an automated orbital platform shaker for 30 min at an optimized speed of 200 rpm. A minimum period of 60 min was observed before harvesting the raffinates. The raffinates 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 (3):

$$\%\mathrm{E} = \left(\frac{C_\mathrm{i} - C_\mathrm{s}}{C_\mathrm{i}}\right) \times 100 \tag{3}$$

where, C_i is the initial solution concentration (mg L^{-1}) 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*

The single crystals of $[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$ and $[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$ were obtained by slow evaporation of their ethanolic mother liquors at room temperature for one week. X-ray diffraction studies were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods using *SHELXTL* [14]. All nonhydrogen atoms were refined anisotropically. Carbon-bound hydrogens were placed in calculated positions and refined as riding atoms with bond lengths 0.95 (aromatic CH), 0.99 (CH_2), and 0.98 (CH_3) 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 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 [15], and ORTEP-3 [16].

3. Results and discussion

3.1. *Synthesis and general considerations*

The ligand, NSN, was synthesized by condensation/cyclization between 2,2'-thiodiacetic acid and *o*-phenylenediamine [12] while the extractant, *bis*((1-octyl-1-benzimidazol-2-yl) methyl)sulfide (BONSN), was prepared by alkylation of NSN in the presence of a base [13]. BONSN was used for the extraction studies while NSN was used to study the coordination chemistry involved. The complexes of the extractant were oily and not easily isolated: hence, we used NSN for the coordination chemistry. The octyl groups of the extractant (BONSN) are positioned away from the coordination sphere and, therefore, the use of the ligand (NSN) would not change the coordination chemistry from a steric hindrance point of view.

The complexes were prepared by reaction of two-molar equivalents of the ligand with respect to $M(II)X{\cdot}yH_2O$, where M = Co(II), Ni(II), Cu(II), Zn(II) and ($X = SO_4^{2-}$) and (RSO_3^{2-}) ($y = 2$–5), in ethanol under inert conditions. The elemental analyzes suggest $[M(NSN)_2]X{\cdot}yH_2O$. The molar conductivity data in DMF show that the sulfate and sulfonate complexes have molar conductance values of 67–90 and 131–167 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, indicating that the sulfate complexes behaved as 1:1 electrolytes while the sulfonate complexes were 1:2 electrolytes [17]. This behavior in solution suggested noncoordinated counter-anions. Both sulfate and sulfonate complexes were prepared to elucidate the nature of these anions with respect to involvement in the inner or outer coordination sphere. This was done for both anions since the extraction studies were carried out in a sulfate medium and a bulky sulfonate was also used to replace the sulfate. This replacement was done owing to the lack of phase transferability of the sulfate complexes due to the high hydration energies of this anion [18].

3.2. *Spectroscopic studies*

3.2.1. Infrared spectroscopy. In the IR spectrum of the ligand, absorption at 3377 cm^{-1} is attributed to v(N–H) [19]. The C=N stretch of the benzimidazole ring appeared at 1534 cm^{-1} [20, 21]. Upon complex formation, the band shifted to higher frequencies (1535–1550 cm^{-1}), confirming bond formation between the metal and nitrogen of benzimidazole. Complexation resulted in an increase in the double-bond character of C=N, perhaps due to the π-acidity of the benzimidazole ring. Far infrared spectra of the sulfate and sulfonate complexes displayed two bands between 240–336 cm^{-1} and 338–406 cm^{-1} which were assigned to ν(M–S) and ν(M–N), respectively [22, 23]. A strong and broad peak at 1060–1095 cm^{-1} is present in spectra of complexes, characteristic of uncoordinated sulfate [21, 24]. The infrared spectra of these complexes suggest that all three donors of the ligand are involved in coordination and that both sulfate and sulfonate are noncoordinating. The geometry of the complexes was confirmed by UV–vis solid reflectance electronic studies as well as X-ray crystallography as discussed in Sections 3.2.2 and 3.3, respectively.

3.2.2. Electronic spectroscopy. The crystal field theory predicts three d–d transitions for an octahedral Co(II) complex, $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ (ν_2), and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3) [25]. These absorptions were observed at 1011, 549, and 476 nm, respectively (figure 2). For the nickel complexes, bands were observed at 978 and 549 nm which may be ascribed to $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ (ν_1) and $^3A_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ (ν_2), respectively, for an octahedral symmetry, assuming that the third transition ($^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ (ν_3) is masked by the intra-ligand transition. Similar complexes of nickel(II), with a distorted octahedral coordination geometry, have been obtained with four nitrogens of benzimidazole and two amine nitrogens from secondary aliphatic amine in place of sulfur [26–28]. The electronic spectrum of the Cu(II) complex showed one band and a shoulder at 775 and 395 nm, respectively, which were ascribed to $^2B_{1g} \longrightarrow {}^2B_{2g}$ and $^2B_{1g} \longrightarrow {}^2A_{1g}$, consistent with distorted octahedral geometry [25].

3.3. *Crystal structures*

The ORTEP diagrams of $[Co(NSN)_2](RSO_3)_2 \cdot 4H_2O$ and $[Ni(NSN)_2](RSO_3)_2 \cdot 2H_2O$ are illustrated in figures 3 and 4; selected crystallographic data are presented in table 1: and selected bond lengths and angles in table 2. The crystal structures of both $[Co(NSN)_2](RSO_3)_2 \cdot 4H_2O$ and $[Ni(NSN)_2](RSO_3)_2 \cdot 2H_2O$ consist of discrete cationic complexes and relatively isolated sulfonate anions (figures 3 and 4). The closest contacts that the sulfonate

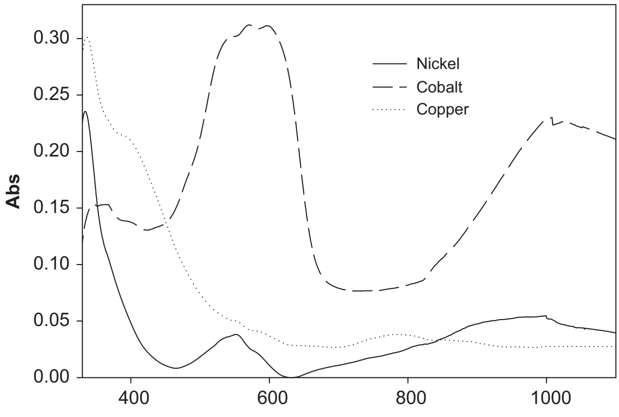


Figure 2. The UV–vis solid reflectance spectra of $[M(NSN)_2]SO_4 \cdot yH_2O$ (M = Co, Ni, and Cu; y = 2–5).

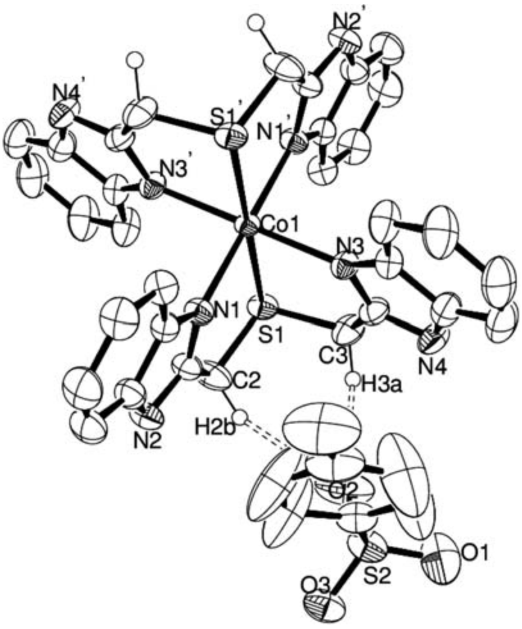


Figure 3. The ORTEP diagram of $[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$ showing the atom labeling scheme with ellipsoids drawn at 50% probability. One toluene-4-sulfonate and four waters have been omitted for clarity.

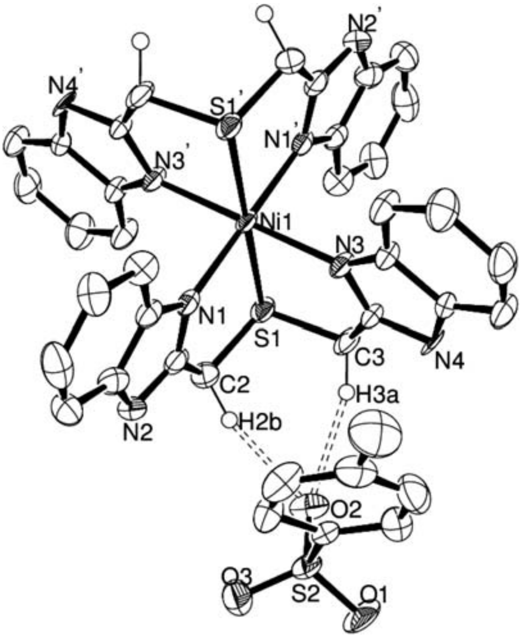


Figure 4. The ORTEP diagram of $[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$ showing the atom labeling scheme with ellipsoids drawn at 50% probability. One toluene-4-sulfonate anion and two waters have been omitted for clarity.

Table 1. Selected crystallographic data for $[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$ and $[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$.

Compound	$[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$	$[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$
Chemical formula	$C_{32}H_{28}CoN_8S_2,2(C_7H_7O_3S),4(H_2O)$	$C_{32}H_{28}N_8NiS_2,2(C_7H_7O_3S),2(H_2O)$
Formula weight	1062.15	1025.88
Crystal color	Red	Pink
Crystal system	Monoclinic	Triclinic
Space group	*P21/c*	$P\bar{1}$
Temperature (K)	200	200
Crystal size (mm^3)	0.17 × 0.25 × 0.26	0.04 × 0.05 × 0.15
a (Å)	10.9513(2)	9.748(5)
b (Å)	9.5582(2)	10.568(5)
c (Å)	23.6177(5)	11.981(5)
α (°)	90	78.130(5)
β (°)	101.726(1)	76.849(5)
γ (°)	90	87.413(5)
V (Å)	2420.58(8)	1176.2(10)
Z	2	1
D_{calc} ($g\,cm^3$)	1.457	1.448
μ/mm^{-1}	0.593	0.652
F (000)	1106	534
Wavelength (Å)	0.71073	0.71069
Theta min–max (°)	2.3, 28.4	1.8, 28.5
S	1.03	0.92
Tot. uniq. data, R(int)	22,584, 6047, 0.019	19,058, 5797, 0.469
Observed data $[I > 2.0\sigma(I)]$	4946	2212
R	0.0476	0.0581
R_w	0.1367	0.1123

ions have with the complex molecules are as follow: H(2)–O(2) = 2.560(1) and H(3)–O(2) = 2.360(1) for the cobalt complex and H(2)–O(2) = 2.300(1) and H(3)–O(2) = 2.340(1) for the nickel complex.

The metal ions, Co(II) and Ni(II), are surrounded by two ligands, each tridentate (two N of benzimidazole and a sulfur). The geometries for both complexes are distorted octahedral with the equatorial plane formed by the four benzimidazole nitrogens while the sulfurs occupy apical positions. These distortions are evidenced by the nonorthogonal angles in the x, y, and z axes intersections around the metal despite linear N–M–N′ and S–M–S′ bonds (table 2). The plane that bisects the ligands and parallel to S–M–S presents a vertical plane of symmetry for these molecules as evidenced by the bond lengths and angles. The equatorial distances for cobalt complex are Co–N1 and Co–N1′ = 2.118(2) Å and Co–N3 and Co–N3′ = 2.119(2) Å, while axial Co–S distance is 2.488(6) Å. For the nickel complex, the equatorial distances are Ni–N1 and Ni-N1′ = 2.097(3) Å and Ni–N3 and Ni–N3′ = 2.104(3) Å, while the axial Ni–S distances are 2.488(6) Å. For both complexes, the Co–S, Co–N, Ni–S, and Ni–N bond lengths fall in the range normally observed for octahedral compounds [29–32].

This pattern of coordination for NSN is similar to that of *bis*((2-benzimidazol-2-yl)ethyl) sulfide in *bis*[*bis*((2-benzimidazol-2-yl)ethyl)sulfide]nickel(II) nitrate (but with a methylene instead of an ethylene spacer between the benzimidazole and sulfur) [33]. The X-ray crystal structures of copper complexes similar to $[Cu(NSN)_2](RSO_3)_2{\cdot}2H_2O$ have been reported [34–39]. The isostructural nature of these complexes $\{[M(NSN)_2]SO_4{\cdot}yH_2O$ (M = Co, Ni, and Cu; $y = 2–5)\}$ led us to conclude that the lack of separation between these metal ions with *bis*((1-octylbenzimidazol-2-yl)methyl)sulfide as extractant (Section 3.4) is influenced by the lack of stereochemical "tailor making."

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$ and $[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$.

$[Co(NSN)_2](RSO_3)_2{\cdot}4H_2O$		$[Ni(NSN)_2](RSO_3)_2{\cdot}2H_2O$	
Co1–S1	2.488(1)	Ni1–S1	2.447(1)
Co1–N1	2.118(2)	Ni1–N1	2.097(3)
Co1–N3	2.119(2)	Ni1–N3	2.104(3)
Co1–S1′	2.488(1)	Ni1–S1'	2.447(1)
Co1–N1′	2.118(2)	Ni1–N1′	2.097(3)
Co1–N3′	2.119(2)	Ni1–N3′	2.104(3)
S1–Co1-N1	82.38(5)	S1–Ni1–N1	83.30(9)
S1–Co1–N3	82.72(5)	S1–Ni1–N3	83.18(9)
S1–Co1–S1′	180.00(1)	S1–Ni1–S1′	180.00(1)
S1–Co1–N1′	97.62(5)	S1–Ni1–N1′	96.71(9)
S1–Co1–N3′	97.28(5)	S1–Ni1–N3′	96.82(9)
N1–Co1–N3	87.66(7)	N1–Ni1–N3	88.84(12)
S1′–Co1–N1	97.62(5)	S1′–Ni1–N1	96.71(9)
N1–Co1–N1′	180.00(1)	N1–Ni1–N1′	180.00(1)
N1–Co1–N3′	92.34(7)	N1–Ni1–N3′	91.16(12)
S1′–Co1–N3	97.28(5)	S1′–Ni1–N3	96.82(9)
N1′–Co1–N3	92.34(7)	N1′–Ni1–N3	91.16(12)
N3–Co1–N3′	180.00(1)	N3–Ni1–N3′	180.00(1)
S1′–Co1–N1′	82.38(5)	S1′–Ni1–N1′	83.30(9)
S1′–Co1–N3′	82.72(5)	S1′–Ni1–N3′	83.18(9)
N1′–Co1–N3′	87.66(7)	N1′–Ni1–N3′	88.84(12)

3.4. *Extraction studies*

These studies were carried out in dilute synthetic sulfate solutions. The purpose of this study was to investigate selectivity towards nickel(II) through forcing six-coordination while the other metal ions adopt other geometries. In addition, the use of low pK_a groups on the ligand was expected to result in extractions in highly acidic solution in comparison with tridentate aliphatic amine extractants based on diethylenetriamine. The latter property was well exploited but the lack of pH-metric separation of the base metal ions was

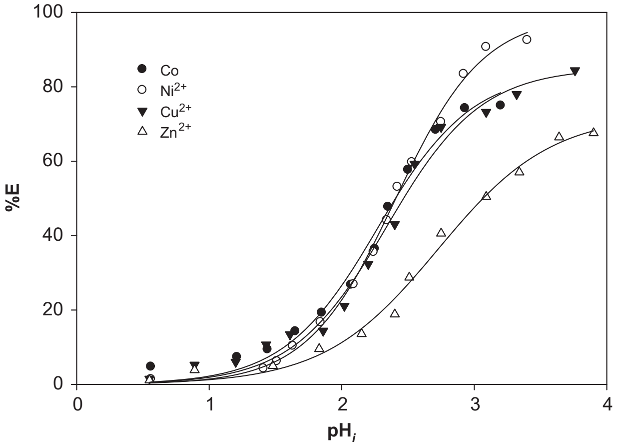


Figure 5. A plot of %E vs. initial pH of equimolar concentrations (0.001 M) of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} extracted with BONSN (at M:L ratio 1:20) and 0.02 M DNNSA in 2-octanol/Shellsol 2325 (8:2) from a dilute sulfate medium.

evident, especially for Co(II), Ni(II), and Cu(II) (figure 5). It seems, however, that there would also be an opportunity for effective back-extraction of some of the metal ions into the aqueous phase as evidenced by the pH at the "left leg" of these extraction isotherms.

It is clear from the clustering of the curves that this extractant resulted in a similar coordination pattern with all the metals, an observation similar to the solid-state chemistry discussed above. The coordination chemistry studies conducted were a way of verifying this phenomenon. It is also clear, therefore, that the move towards tridentate ligands, even with low pK_a aromatic nitrogen groups, is not sufficient to exploit selectivity through bonding preferences.

4. Conclusion

The results presented in this article provide empirical evidence that the behavior of base metals in a solvent extraction system can be interpreted by using solid state studies. It can be concluded that subtle stereochemical aspects of coordination for the extraction of base metals is lacking with tridentate ligands (at least those of the nature presented here). The use of low pK_a aromatic nitrogen donors, however, provides for the exploitation of the low pH range for the extraction of base metal ions with an opportunity for back-extraction.

Supplementary material

CCDC 887449 and 887450 contain the supplementary crystallographic data for $[Co(NSN)_2](RSO_3)_2 \cdot 4H_2O$ and $[Ni(NSN)_2](RSO_3)_2 \cdot 2H_2O$, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank Mr. F. Chindeka (DST/Mintek-NIC, Rhodes University Chemistry Department) for the microanalysis results. We would also like to thank Shell Chemicals (SA) (Pty) Ltd. for supplying Shellsol 2325. For financial support, we thank the National Research Foundation (NRF-CPR20100406000010238).

References

[1] W.A. Rickelton, D.S. Flett, D.W. West. *Solvent Extr. Ion Exch.*, **2**, 815 (1984).
[2] D.S. Flett. *J. Organomet. Chem.*, **690**, 2426 (2005).
[3] A.K. De, S.M. Khopkar, R.A. Chalmers. *Solvent Extr. Met.*, Van Nostrand Reinhold, New York (1970).
[4] A. Feather, W. Bouwer, A, Swarts, V. Nagel. *J. South Afr. Inst. Min. Metall.*, 457 (2002).
[5] J.G.H. du Preez, J. Postma, S. Ravindran, B.J.A.M. van Brecht. *Solvent Extr. Ion Exch.*, **15**, 79 (1997).
[6] R.G. Pearson. *J. Am. Chem. Soc.*, **85**, 581 (1963).
[7] J.G.H. du Preez. *Solvent Extr. Ion Exch.*, **18**, 679 (2000).
[8] J.G.H. du Preez, T.I.A. Gerber, W. Edge, V.L.V. Mtotywa, B.J.A.M. van Brecht. *Solvent Extr. Ion Exch.*, **19**, 143 (2001).
[9] A.I. Okewole, N.P. Magwa, Z.R. Tshentu. *Hydrometallurgy*, **121–124**, 81 (2012).
[10] S.O. Bondareva, Y. Murinov, V.V. Lisitskii. *Russ. J. Inorg. Chem.*, **52**, 796 (2007).
[11] G. Wilkison, R.D. Gillard, J.A. McCleverty. *Comprehensive Coordination Chemistry, Late Transition Elements*, Vol. 5, pp. 596–681, Pergamon Press, Oxford (1987).

[12] J.V. Dagdigian, C.A. Reed. *Inorg. Chem.*, **18**, 2623 (1979).
[13] M. Haring. *Helv. Chim. Acta*, **42**, 1845 (1959).
[14] Bruker. *SHELXTL-5.1. (includes XS, XL, XP, XSHELL)*, Bruker AXS Inc., Madison, Wiskonsin, USA (1999).
[15] A.L. Spek. *J. Appl. Crystallogr.*, **36**, 7 (2003).
[16] L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997).
[17] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[18] K.A. Allen. *J. Phys. Chem.*, **60**, 943 (1956).
[19] N.L. Alpert, W.E. Keiser, H.A. Symanski. *Theory and Practice of Infrared Spectroscopy*, 2nd Edn, p. 280, Heyden & Sons Ltd, New York (1970).
[20] C.N.R. Rao. *Chemical Applications of Infrared Spectroscopy.* pp. 265–266, Academic Press, New York (1963).
[21] L.J. Bellamy. *Advances in Infrared Group Frequencies*, pp. 49–224, Barnes & Noble, Inc., New York (1968).
[22] J.V. Hodgson, G. Percy, D.A. Thornton. *J. Mol. Struct.*, **66**, 81 (1980).
[23] E.S. Raper, J.L. Brooks. *J. Inorg. Nucl. Chem.*, **39** 2163 (1977).
[24] Z. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, p. 239, John Wiley and Sons, New York (1978).
[25] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, pp. 554–557, Elsevier, New York (1984).
[26] M. Hvastijova, J. Kohout, M. Okruhlica. *Transition Met. Chem.*, **18**, 579 (1993).
[27] P.D. Bauer, M.S. Mashuta, R.J. O'Brein, J.F. Richardson, R.M. Buchanan. *J. Coord. Chem.*, **57**, 361 (2004).
[28] R. Carballo, A. Castineiras. *Polyhedron*, **12**, 1083 (1993).
[29] T. Pandiyan, J.G. Hernandez, N.T. Medina, S. Bernes. *Inorg. Chim. Acta*, **357**, 2570 (2004).
[30] K. Takahashi, Y. Nishidas, S. Kida. *Bull. Chem. Soc. Jpn.*, **57**, 2628 (1984).
[31] M.S. Lah, M. Moon. *Bull. Korean Chem. Soc.*, **18**, 406 (1997).
[32] E. Kwaskowska-Chec, M. Kubiak, T. Glowiak, J.J. Zoilkowski. *J. Chem. Crystallogr.*, **25**, 837 (1995).
[33] T. Pandiyan, K. Panneerselvam, M. Soriano-Garcia, C. Duran de Bazua, E.M. Holt. *Acta Crystallogr., Sect. C*, **52**, 1137 (1996).
[34] F.J. Rietmeijer, P.J.M.W.L. Birker, S. Gorter, J. Reedijk. *J. Chem. Soc., Dalton Trans.*, 1191 (1982).
[35] J.C. Lockhart, W. Clegg, M.N.S. Hill, D.J. Rushton. *J. Chem. Soc., Dalton Trans.*, 3541 (1990).
[36] J.V. Dagdigian, V. Mckee, C.A. Reed. *Inorg. Chem.*, **21**, 1332 (1982).
[37] H.P. Berends, D.W. Stephan. *Inorg. Chim. Acta*, **93**, 173 (1984).
[38] A.W. Addison, P.J. Burke, K. Henrick, T.N. Rao. *Inorg. Chem.*, **22**, 3645 (1983).
[39] R. Balamurugan, M. Palaniandavar, R.S. Gopalan, G.U. Kulkarni. *Inorg. Chim. Acta*, **357**, 919 (2004).