

# Copper(II) Ion Complexation by the Tetradentate Phosphorus–Nitrogen Ligand $P_2N_2$ at the Water/1,2-DCE Interface

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Received August 4, 1993\*

The tetradentate ligand  $N,N'$ -bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine ( $P_2N_2$ ) has been synthesized and characterized by several analytical methods. The electrochemical properties of  $P_2N_2$  and its coordination ability with transition metal ions at the water/1,2-dichloroethane interface have been studied by cyclic voltammetry. It was found that  $P_2N_2$  can chelate copper(II) ion. The transfer of the  $Cu^{2+}$  facilitated by  $P_2N_2$  has been observed in the presence of  $Cl^-$ ,  $Br^-$ , or acetate anion in the aqueous phase. An interfacial reaction between the ligand and metal ion has been proposed. A unique selectivity of  $P_2N_2$  toward copper(II) makes it possible to use this hydrophobic ligand as an extractant in separation processes.

## Introduction

Solvent extraction has been widely applied to hydrometallurgical processing, especially for the recovery of metals from dilute solutions.<sup>1–4</sup> The process involves the transport of chemical species across liquid–liquid interfaces. One type of system that has recently attracted a great deal of interest is the interface between two immiscible electrolyte solutions. Charge-transfer reactions at this interface can be studied by electrochemical methods,<sup>5,6</sup> and these techniques have been shown to be very useful in understanding solvent extraction mechanisms and kinetics.<sup>7,8</sup>

Generally, the rate-determining step in the transfer of a metal ion assisted by an ionophore involves the formation of the metal complex only at the liquid interfacial region<sup>9,10</sup> or entirely in the bulk aqueous phase.<sup>2,3</sup> Hydrophobic ligands are usually employed in electrochemical studies of facilitated ion transfer across the liquid–liquid interface. These ligands are confined to the organic phase, and therefore, complex formation between the ligand and the metal ion occurs in the interfacial region.<sup>7,8</sup>

The kinetics and mechanism of single ion and facilitated ion transfers across liquid–liquid interfaces have been studied using various electrochemical techniques.<sup>5</sup> Most of the ions studied are alkaline, alkaline earth, and tetraalkylammonium ions and also some anions.<sup>11</sup> Facilitated cadmium ion transfer across the water/nitrobenzene interface has been studied in the presence of 2,2'-bipyridine (2,2'-bipy) in the nitrobenzene phase<sup>12,13</sup> and also that of  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Zn^{2+}$  ions from water to 1,2-dichloroethane with 1,10-phenanthroline (phen) as the

ligand.<sup>14</sup> However, these two ligands are soluble in water and simultaneous proton and ion transfer occurs. Also, the selectivity of 2,2'-bipy and phen toward transition metals is very poor. Other ligands, such as crown ethers and synthetic neutral cyclic or multicyclic ligands, have been used as ionophores to facilitate ion transfers,<sup>15</sup> but the electroassisted transition metal ions transfer using *multidonor* macrocyclic organic ligands has not yet been reported. Interestingly, the chelating ability and selectivity of these ligands toward transition metal ions increases with the incorporation of multidonor atoms in the molecule.

The purpose of the present work was to investigate the electrochemical properties of a new ligand,  $N,N'$ -bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine ( $P_2N_2$ ), and its coordination abilities to transition metal ions. This compound contains nitrogen and phosphorus as donor atoms and has an uncommon "PNNP" donor atom sequence, which results in an interesting coordination chemistry for transition metal complexes.<sup>16</sup> In the present work, the transfer properties of this ligand and of its complexes with transition metal ions  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ , and  $Zn^{2+}$  have been studied at the water/1,2-DCE interface (1,2-DCE = 1,2-dichloroethane).

## Experimental Section

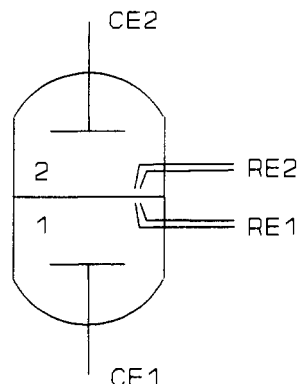
**Synthesis and Characterization of  $P_2N_2$ .**  $P_2N_2$  has been prepared according to literature methods,<sup>16</sup> by demetalation in benzene with NaCN of the deprotonated nickel(II) complex. This was obtained from the metal template catalyzed condensation of bis((2-(phenylphosphino)phenyl)amido)nickel(II)<sup>17</sup> with 1,3-bis((tolyl-*p*-sulfonyl)oxy)propane<sup>18</sup> in the presence of anhydrous potassium carbonate. The crude  $P_2N_2$  product was purified by chromatography (alumina column and benzene as eluent) and recrystallized from ethanol/benzene.

The tetradentate  $P_2N_2$  ligand was characterized by elemental analyses, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR spectroscopy, and mass spectroscopy.

\* Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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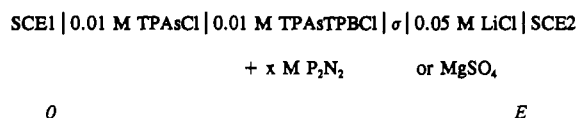


**Figure 1.** Schematic diagram of the four-electrode cell used in the study of charge-transfer reactions at the immiscible electrolyte interface. CE1, RE1 and CE2, RE2 are counter and reference electrodes in the organic and aqueous phases, respectively. The number 1 refers to the organic phase, and the number 2 refers to the aqueous phase.

The compound was found to be stable in air for long periods of time.

**Electrochemistry at the Water/1,2-DCE Interface.** All chemicals used were of analytical grade or better. Tetraphenylarsonium tetrakis(4-chlorophenyl)borate (TPAsTPBCl) was prepared from tetraphenylarsonium chloride (TPAsCl, Fluka) and sodium tetrakis(4-chlorophenyl)borate (NaTPBCl, Fluka) as previously described.<sup>19</sup> 1,2-Dichloroethane (1,2-DCE, Aldrich) was used without further purification. The supporting electrolyte was 0.01 M TPAsTPBCl in the organic phase and 0.05 M LiCl, MgSO<sub>4</sub>, or Li<sub>2</sub>SO<sub>4</sub> (BDH, AnalaR) in the aqueous phase. Acetic acid (0.5 M) or 0.05 M sodium acetate solution and dilute NaOH or HCl solution (all AnalaR BDH) were employed to adjust the pH of the aqueous solution. The solutions of metal ions tested were prepared from the corresponding chloride or sulfate salts: cupric sulfate (CuSO<sub>4</sub>, AnalaR, BDH), cadmium(II) sulfate (CdSO<sub>4</sub>, AnalaR, BDH), cobalt chloride (CoCl<sub>2</sub>, 98%, Aldrich), manganous chloride (MnCl<sub>2</sub>, AnalaR, BHD), nickel sulfate (NiSO<sub>4</sub>, Johnson Matthey, specpure), and zinc chloride (ZnCl<sub>2</sub>, AnalaR, BDH).

Voltammetric measurements were carried out using a four-electrode potentiostat and a waveform generator (PPR1, Hitek, High Wycombe, England) as described elsewhere.<sup>20</sup> The four-electrode cell with an interfacial area of 0.287 cm<sup>2</sup> employed is schematically shown in Figure 1. It consists of two Pt counter electrodes and two reference electrodes that probed the interfacial potential through Luggin capillaries. The potential  $E$  applied refers to cell A, and all potentials are defined with respect to the organic phase. A flow of positive charge from the aqueous to the organic phase is taken as a positive current. The cell A diagram is as follows:



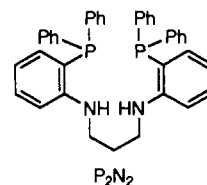
All potentials are reported in the Galvani potential scale, which were calculated from

$$E = \Delta_o^w \phi - \Delta_o^w \phi_{\text{TPAs}^+} \quad (1)$$

where  $\Delta_o^w \phi$  is the interfacial Galvani potential and  $\Delta_o^w \phi_{\text{TPAs}^+}$  is the organic reference liquid junction potential. The details of the calculation of  $\Delta_o^w \phi$  and  $\Delta_o^w \phi_{\text{TPAs}^+}$  have been previously described.<sup>19</sup> The standard transfer potential of TPAs<sup>+</sup> across the water/1,2-DCE interface,  $\Delta_o^w \phi_{\text{TPAs}^+}^0$ , was taken as  $-0.364 \text{ V}$ .<sup>21</sup>

## Results and Discussion

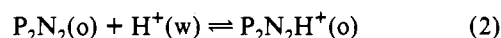
**(i) Cyclic Voltammetric Studies of the Ligand at the Water/1,2-DCE Interface.** The ligand P<sub>2</sub>N<sub>2</sub> contains two tertiary phosphines and two secondary amino groups. Secondary amines



are weak bases, but in P<sub>2</sub>N<sub>2</sub>, the basicity of this group increases due to conjugation with the electron donor phosphino group. Therefore, P<sub>2</sub>N<sub>2</sub> can easily effect facilitated proton transfer.

Figure 2 shows cyclic voltammograms of cell A with  $2 \times 10^{-4} \text{ M P}_2\text{N}_2$  in the organic phase. A voltammetric peak at  $\Delta_o^w \phi_{1/2} = 0.256 \text{ V}$  can be seen in neutral solutions (pH = 7.1). The peak current increases with the concentration of P<sub>2</sub>N<sub>2</sub> in the organic phase.

The voltammograms are pH dependent. For an acid solution (pH = 3.1) the peak was shifted to 0.22 V, with a very large peak current compared with that observed for neutral solutions. This indicates that the proton transfer occurs at the interface. The following equilibrium exists:



In summary, the proton transfer facilitated by P<sub>2</sub>N<sub>2</sub> across the water/1,2-DCE interface does occur at potentials close to 0.25 V when neutral or acidic solutions are used. This has been previously observed<sup>18</sup> for amines studied at the liquid/liquid interface.

**(ii) Transfer of Cu<sup>2+</sup> Assisted by P<sub>2</sub>N<sub>2</sub>.** Figure 3 shows the changes in the cyclic voltammograms for ion transfer on addition of Cu<sup>2+</sup> to the aqueous solution. The ligand transfer peak at  $\Delta_o^w \phi_{1/2} = 0.25 \text{ V}$  is relatively smaller than that in the acidic solution. When Cu<sup>2+</sup> is present in the aqueous phase and the organic phase does not contain P<sub>2</sub>N<sub>2</sub>, only the capacitive current can be observed (Figure 3(I')). Therefore, copper ion transfer is not possible in the potential window available when P<sub>2</sub>N<sub>2</sub> is absent. In the presence of both CuSO<sub>4</sub> and P<sub>2</sub>N<sub>2</sub> one well-defined peak with a half-wave potential of  $-0.150 \pm 0.005 \text{ V}$  was observed. This peak was detected in excess of either P<sub>2</sub>N<sub>2</sub> or CuSO<sub>4</sub>. Also, an increase of the second peak at positive potentials (Figure 3(II)) was observed, which corresponds to facilitated proton transfer by P<sub>2</sub>N<sub>2</sub>. This increase is due to the slight acidification of the aqueous solution on addition of CuSO<sub>4</sub>. However, there is a half-wave potential separation between the two peaks of about 400 mV which does not interfere with the analysis of assisted transfer of Cu<sup>2+</sup> ion from water to 1,2-DCE.

At a constant P<sub>2</sub>N<sub>2</sub> concentration, the peak current is proportional to the square root of the sweep rate and, also, the peak current is proportional to the concentration of CuSO<sub>4</sub>. This behavior can be analyzed with the Randles-Sevcik equation for a diffusionally controlled processes,<sup>23</sup>

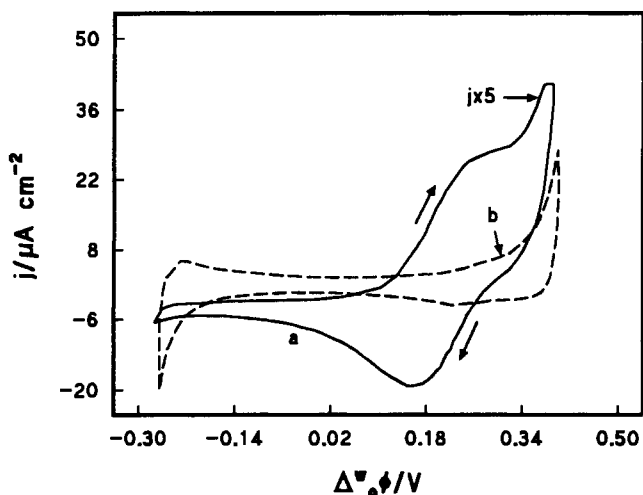
$$I_p = 2.69 \times 10^5 AD^{1/2}v^{1/2}C^0 \quad (3)$$

where  $I_p$  is the peak current in amperes,  $A$  is the interfacial area in cm<sup>2</sup>,  $D$  is the diffusion coefficient in cm<sup>2</sup> s<sup>-1</sup>,  $v$  is the scan rate in V s<sup>-1</sup>, and  $C^0$  is the bulk concentration in mol dm<sup>-3</sup>. When excess ligand is present in the organic phase,  $C^0$  is the Cu<sup>2+</sup> bulk concentration. From eq 3, the diffusion coefficient of the complex was calculated to be  $4.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

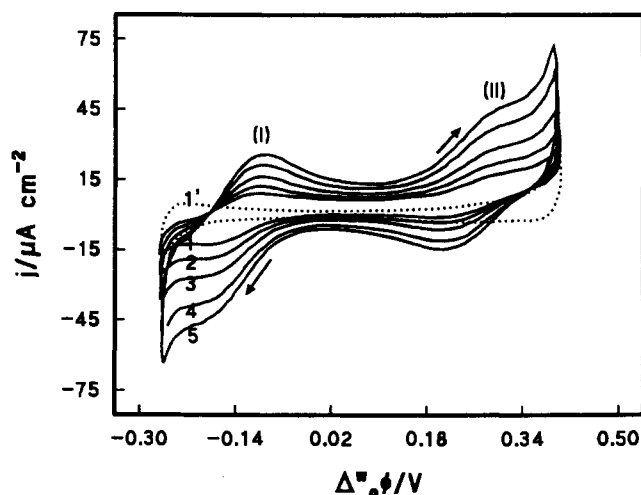
The peak separation was always close to 60 mV for sweep rates from 12 to 100 mV s<sup>-1</sup>, the theoretical value for transfer of monovalent ions. This means that, in the present case, the transferred species must be singly charged. These results indicate that coupled anion transfer must occur since the complexation of Cu<sup>2+</sup> by the neutral ligand P<sub>2</sub>N<sub>2</sub> gives a doubly charged complex.

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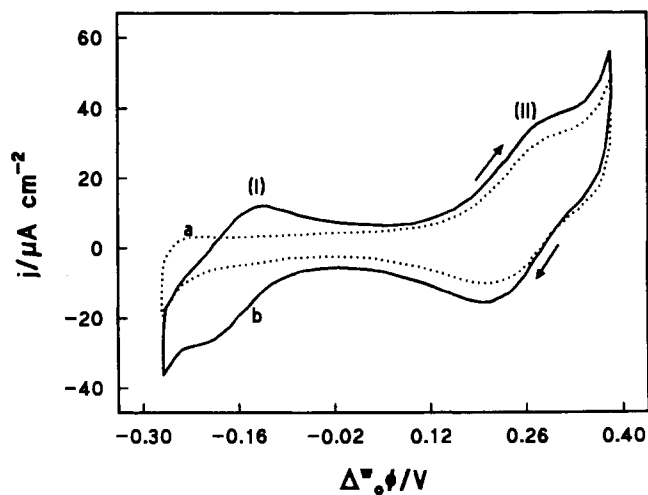
**Figure 2.** Cyclic voltammograms of  $2 \times 10^{-4}$  M P<sub>2</sub>N<sub>2</sub> at the water/1,2-DCE interface. Base electrolyte solutions: 0.01 M TPAsTPBCl in the organic phase and 0.05 M LiCl in the aqueous phase. The pH was 3.0 (a) and 7.1 (b), respectively. Sweep rate:  $0.05 \text{ V s}^{-1}$ .



**Figure 3.** Cyclic voltammograms of  $1.0 \times 10^{-4}$  M copper(II) transfer facilitated by  $1.0 \times 10^{-3}$  M P<sub>2</sub>N<sub>2</sub> in 1,2-DCE at different sweep rates ( $\text{mV s}^{-1}$ ): (1) 12; (2) 25; (3) 50; (4) 100; (5) 150. Dotted line (1'): CV obtained in the absence of copper in the aqueous phase,  $\nu = 50 \text{ mV s}^{-1}$ . The solution compositions were 0.01 M TPAsTPBCl in the organic phase and 0.05 M LiCl in the aqueous phase.

In order to investigate this unusual effect, experiments were carried out using Li<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub>, instead of LiCl, as aqueous supporting electrolyte. In these cases, no complex transfer current could be detected when both Cu<sup>2+</sup> and P<sub>2</sub>N<sub>2</sub> were present. Addition of excess LiCl to the sulfate electrolytes resulted in the appearance of a transfer peak located at the same half-wave potential as that observed for the LiCl solution (Figure 4). This clearly illustrates that Cl<sup>-</sup> is involved in the process of complexation between the ligand and Cu<sup>2+</sup>. In the presence of aqueous bromide or acetate the transfer current was also observed (results are not shown), but the peak current in the acetate solution was much smaller than that observed for LiCl.

Both chloride and acetate anions can coordinate to copper(II), forming CuCl<sup>+</sup> or Cu(CH<sub>3</sub>COO)<sup>+</sup>,<sup>24</sup> although the stability constants are rather small compared with that of the copper amine complex. In the presence of chloride the appearance of the complex transfer current can be described in terms of enhancement effects by these anions, as observed by Freiser *et al.*<sup>25</sup> for extraction processes. Generally, monodentate ligands such as acetate or



**Figure 4.** Cyclic voltammograms obtained in the absence (a) and presence (b) of  $2.0 \times 10^{-3}$  M LiCl in the aqueous phase. The base electrolyte in the aqueous phase was 0.05 M Li<sub>2</sub>SO<sub>4</sub>. The concentrations of Cu<sup>2+</sup> and P<sub>2</sub>N<sub>2</sub> were  $1.0 \times 10^{-4}$  and  $2.0 \times 10^{-3}$  M, respectively;  $\nu = 50 \text{ mV s}^{-1}$ .

thiocyanate give metal complexes that react more rapidly than do the free, or hydrated, ions;<sup>25</sup> with multidentate ligands, the free metal ion reacts more rapidly with P<sub>2</sub>N<sub>2</sub> than the complex. Therefore, in the present case, it is more likely that Cu<sup>2+</sup> first coordinates with Cl<sup>-</sup>, followed by the reaction of CuCl<sup>+</sup> with P<sub>2</sub>N<sub>2</sub>.

It has already been reported that extraction of Cu<sup>2+</sup> by cyclic and acyclic tetrathioethers from water to 1,2-DCE is affected by anions in the aqueous phase through ion pair formation, making the transfer of the complex much easier.<sup>12</sup> However, for the tetrathioether-copper(II) system, the sulfate ion is not extracted at all with the copper(II)-tetrathioether complex cation.<sup>26</sup> Similar results were obtained in the present study. As shown in Figure 4b, only when Cl<sup>-</sup> was present in the aqueous phase was the assisted transfer observed, strongly suggesting that an interaction between the complex and Cl<sup>-</sup> is associated with the transfer process (this will be discussed below). It was found that the enhancement of ion transfer due to Cl<sup>-</sup> is much greater than that for CH<sub>3</sub>COO<sup>-</sup>. However, in electroassisted solvent extraction at the liquid/liquid interface it is difficult to exclude at present the formation of the neutral species (CuP<sub>2</sub>N<sub>2</sub>)<sup>2+</sup>SO<sub>4</sub><sup>2-</sup>, which evidently would not contribute to the current.

The half-wave potential,  $\Delta_o^w \phi_{1/2}$ , changes with the concentrations of P<sub>2</sub>N<sub>2</sub> (for [Cl<sup>-</sup>] = 0.05 M) and of Cl<sup>-</sup> (for [P<sub>2</sub>N<sub>2</sub>] =  $1 \times 10^{-3}$  M). In both cases,  $1 \times 10^{-4}$  M Cu<sup>2+</sup> was used in the aqueous phase. It was found that  $\partial(\Delta_o^w \phi_{1/2})/\partial(\log(C_{P_2N_2})) = -54 \pm 5 \text{ mV}$  (regression coefficient  $r = 0.999$ ) and  $\partial(\Delta_o^w \phi_{1/2})/\partial(\log(C_{Cl^-})) = 59 \pm 5 \text{ mV}$  (with  $r = 0.995$ ). These results indicate that the reaction orders ( $P_i$ ) for assisted Cu<sup>2+</sup> transfer are  $P_{Cl^-} = +1$  and  $P_{P_2N_2} = -1$ . However, the **positive** shift in the half-wave potential with increase in chloride concentration is opposite to that observed in the complexation between metal ions and neutral ligands.<sup>12-14</sup> Effects of chloride in the process discussed here can be 2-fold: (a) ion pairing of hydrated Cu<sup>2+</sup> with chloride, with the further reaction of CuCl<sup>+</sup> with the ligand in the organic phase being energetically more favorable than that of Cu<sup>2+</sup>, due to the large desolvation Gibbs energies involved in the transfer and further coordination of the naked ion; (b) ion pairing between protonated P<sub>2</sub>N<sub>2</sub>H<sup>+</sup> and Cl<sup>-</sup>, giving a neutral form of the ligand, P<sub>2</sub>N<sub>2</sub>HCl, in the organic phase. In order to prove that the ligand is protonated in the form of P<sub>2</sub>N<sub>2</sub>HCl, a simple direct extraction experiment was carried out by mixing equal volumes of  $1.0 \times 10^{-4}$  M P<sub>2</sub>N<sub>2</sub> in 1,2-DCE with 0.05 M LiCl aqueous solution (pH = 3). After separation, the organic

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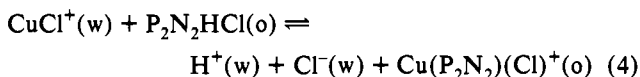
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**Table 1.** Possible Reactions for Facilitated Cu<sup>2+</sup> Transfer by P<sub>2</sub>N<sub>2</sub> at the Water/1,2-DCE Interface and the Expected Relationship between the Half-Wave Potential and Concentration of the Ligands (L = P<sub>2</sub>N<sub>2</sub>)

case	possible reactions at the interface	linear relation of Δ <sub>0</sub> <sup>w</sup> φ <sub>1/2</sub> with
1	Cu <sup>2+</sup> (w) + Cl <sup>-</sup> (w) + L(o) = CuLCl <sup>+</sup> (o)	-ln([Cl <sup>-</sup> ][L])
2	CuCl <sup>+</sup> (w) + L(o) = Cl <sup>-</sup> (w) + CuL <sup>2+</sup> (o)	ln([Cl <sup>-</sup> ]/[L]) <sup>2</sup>
3	Cu <sup>2+</sup> (w) + HLCl(o) = H <sup>+</sup> (w) + CuLCl <sup>+</sup> (o)	-ln([Cl <sup>-</sup> ][L])
4	Cu <sup>2+</sup> (w) + Cl <sup>-</sup> (w) + HLCl(o) + H <sup>+</sup> (w) + CuLCl(o)	no charge transfer
5	Cu <sup>2+</sup> (w) + Cl <sup>-</sup> (w) + HLCl(o) = (CuHLCl <sub>2</sub> ) <sup>-</sup> (o)	-ln([Cl <sup>-</sup> ] <sup>2</sup> [H <sup>+</sup> ][L])
6	CuCl <sup>+</sup> (w) + HLCl(o) = H <sup>+</sup> (w) + Cl <sup>-</sup> (w) + CuLCl <sup>+</sup> (o)	ln([H <sup>+</sup> ][Cl <sup>-</sup> ]/[L])

phase was brought to contact with an excess of NaOH of known concentration, which was then titrated with standard HCl. It was found that 69% (±10%) of P<sub>2</sub>N<sub>2</sub> was present as the form of P<sub>2</sub>N<sub>2</sub>HCl.

In order to account for the observed reaction orders, several possible pathways for the facilitated Cu<sup>2+</sup> ion transfer across the interface can be considered, as summarized in Table 1. Only case 6 yields reasonable results which can best explain the experimental results. The reaction proposed is



This considers that the species transferred is the CuCl<sup>+</sup> complex, which on coordination to P<sub>2</sub>N<sub>2</sub>HCl results in proton (and, hence, Cl<sup>-</sup>) displacement. When the ligand is in excess in the organic phase, the process is controlled by diffusion of aqueous CuCl<sup>+</sup>. At equilibrium, the potential difference established at the water/1,2-DCE interface, Δ<sub>0</sub><sup>w</sup>φ<sub>i</sub> (i = Cu(P<sub>2</sub>N<sub>2</sub>)(Cl))<sup>+</sup>, the transferred species), is given by<sup>5</sup>

$$\Delta_0^w \phi_i = \Delta_0^w \phi_i^\circ + \frac{RT}{zF} \ln \frac{a_i^\circ}{a_i^w} \quad (5)$$

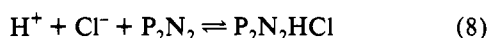
where Δ<sub>0</sub><sup>w</sup>φ<sub>i</sub><sup>0</sup> is the standard transfer potential and a<sub>i</sub><sup>0</sup> and a<sub>i</sub><sup>w</sup> are the activities in the organic and aqueous phase, respectively. From (5),

$$\Delta_0^w \phi_i = \Delta_0^w \phi_i^\circ + \frac{RT}{zF} \ln \frac{[\text{H}^+][\text{Cl}^-][\text{CuP}_2\text{N}_2\text{Cl}^+]}{[\text{P}_2\text{N}_2\text{HCl}][\text{CuCl}^+]} \quad (6)$$

where the activity and diffusion coefficients of the species involved in the organic and aqueous phases are included in the formal potential, Δ<sub>0</sub><sup>w</sup>φ<sub>i</sub><sup>0</sup>. At the half-wave potential,

$$\Delta_0^w \phi_{1/2} = \Delta_0^w \phi_i^\circ + \frac{RT}{F} \ln \frac{[\text{H}^+][\text{Cl}^-]}{[\text{P}_2\text{N}_2\text{HCl}]} \quad (7)$$

For the equilibrium



when  $K[\text{H}^+][\text{Cl}^-] \gg 1$ , i.e. for large values of the association constant ( $K$ ) of P<sub>2</sub>N<sub>2</sub>,  $[\text{P}_2\text{N}_2\text{HCl}] \approx [\text{P}_2\text{N}_2]$ . From eq 7,

$$\Delta_0^w \phi_{1/2} = \Delta_0^w \phi_i^\circ + \frac{RT}{F} \ln \frac{[\text{H}^+][\text{Cl}^-]}{[\text{P}_2\text{N}_2]} \quad (9)$$

a result in agreement with the reaction orders for Cl<sup>-</sup> and P<sub>2</sub>N<sub>2</sub>.

For the other extreme situation, i.e.  $C_{\text{Cu}^{2+}} \gg C_{\text{P}_2\text{N}_2}^\circ$  and  $C_{\text{Cl}^-} \gg C_{\text{P}_2\text{N}_2}^\circ$ , the half-wave potential was independent of the metal ion concentration when  $C_{\text{Cl}^-}$  and  $C_{\text{P}_2\text{N}_2}^\circ$  were fixed. This kind of reaction at the liquid/liquid interface was only observed by Matsuda *et al.*<sup>15</sup> for the transfer of Ba<sup>2+</sup> facilitated by 18-crown-6 (18C6). In the present case, the transfer process involves ion pair formation, protonation of the ligand, and displacement of proton and chloride ions, as discussed above.

The results presented above give evidence that a [Cu(P<sub>2</sub>N<sub>2</sub>)(Cl)]<sup>+</sup> species is formed in the organic phase in the process of Cu<sup>2+</sup>-assisted transfer. As far as the conformation is concerned,

copper(II) usually forms two types of complexes, square pyramidal and tetragonal. The structure of the complex between copper(II) and 1,8-bis(2-pyridyl)-3,6-dithiooctane (pdto) has been studied.<sup>27</sup> This ligand contains an *NSSN* donor atom sequence, which is very similar to that in the P<sub>2</sub>N<sub>2</sub> molecule. It was found that the structure of the perchlorate salt of Cu(pdto)<sup>2+</sup> is essentially square pyramidal, with the perchlorate group above the nitrogen and sulfur atoms plane. For the Cu(P<sub>2</sub>N<sub>2</sub>)<sup>2+</sup> complex, the four phenyl groups in the ligand molecule cause large steric effects on the binding of axial ligands to the central metal ion, although the ligand is an acyclic molecule. The overall complex conformation is likely to be distorted tetrahedral as that found for the Ni(P<sub>2</sub>N<sub>2</sub>)<sup>2+</sup> complex.<sup>16</sup> The combination of Cu(P<sub>2</sub>N<sub>2</sub>)<sup>2+</sup> with Cl<sup>-</sup> may be in the form of ion pairing or of Cl<sup>-</sup> binding to Cu<sup>2+</sup> ion in the complex.

(iii) **Formation of Complexes between P<sub>2</sub>N<sub>2</sub> and Other Transition Metal Ions.** Since P<sub>2</sub>N<sub>2</sub> was first synthesized,<sup>16</sup> there has been a great deal of interest in the unusual *PNNP* donor atom sequence. The coordination chemistry of this multidentate ligand with nickel and rhodium has been reported.<sup>16</sup> For the latter case only two phosphorus atoms chelate with the central ion, leaving two nitrogen donor atoms free. Apart from copper(II), complexation of P<sub>2</sub>N<sub>2</sub> with other transition metal ions might occur at the liquid/liquid interface. This can be detected by the metal ion transfer currents, and for this reason, the transfer of Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, and Zn<sup>2+</sup> has been investigated.

When 0.01 M TPAsTPBCl + 1.0 × 10<sup>-3</sup> M P<sub>2</sub>N<sub>2</sub> and 0.05 M LiCl were used as supporting electrolytes, the presence of Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, or Zn<sup>2+</sup> in the aqueous solution resulted in cyclic voltammograms which were indistinguishable from those of the base electrolytes. However, addition of copper(II) to the above mentioned metal ions mixture yielded the copper(II) ion transfer current and no interference with copper transfer current could be seen due to the presence of the other metal ions. For the purpose of electroassisted separations by P<sub>2</sub>N<sub>2</sub>, the specific transport of copper(II) from water to 1,2-DCE is possible in the presence of the metal ions above mentioned.

In order to confirm that the assisted transfer potential of the transition metal ions investigated was much more positive than that of Cu(II), partition experiments with control of the interfacial potential by a partitioning quaternary ammonium ion were carried out. The procedure has been previously described.<sup>30</sup> The results for the extraction of four metal ions with P<sub>2</sub>N<sub>2</sub>, when the interfacial Galvani potential was fixed at 64 mV with tetraethyl-ammonium as a partition ion, are given in Table 2. Within experimental error, the results show that cadmium, nickel, and zinc are not extracted from the aqueous to the organic phase, while copper does. These results are in good agreement with those obtained from the cyclic voltammetric investigation.

Although the Ni<sup>2+</sup> complex with P<sub>2</sub>N<sub>2</sub> has been synthesized by the template effect and the complex has been isolated as the

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**Table 2.** Extraction of Metal Ions with  $1.0 \times 10^{-3}$  M P<sub>2</sub>N<sub>2</sub><sup>a</sup>

metal	% remaining in the aqueous phase	
	1 h	2 h
Cu <sup>2+</sup>	80.3	65.0
Cd <sup>2+</sup>	97.0	98.0
Ni <sup>2+</sup>	102.0	103.0
Zn <sup>2+</sup>	100.4	98.8

<sup>a</sup> The interfacial potential was fixed at 64 mV with tetraethylammonium as a partition ion; the aqueous phase contained 0.05 M LiCl and  $5 \times 10^{-4}$  M of the respective metal ion. The results are presented as the amount of metal found in the aqueous phase after contacting with the organic phase for the period of time as indicated.

dinitrate salt,<sup>16</sup> the formation of the complex at the liquid/liquid interface is very different from the direct homogeneous complex synthesis. In the former case, both ligand and metal ion have to be desolvated in one phase and resolvated in the other,<sup>7</sup> possibly followed by the formation of an ion pair in the organic phase.<sup>14</sup> If Ni<sup>2+</sup> ion shows the same complexation properties with P<sub>2</sub>N<sub>2</sub> as Cu<sup>2+</sup>, a doubly charged complex will be formed, the transfer of which may be outside the available potential window, and this might be the reason that no transfer currents could be detected in the present work. For the other metal ions studied, there is no information available of their complexation with P<sub>2</sub>N<sub>2</sub>. Further work is needed to understand the significant difference in complex formation of P<sub>2</sub>N<sub>2</sub> with copper and the other metal ions studied.

However, the ligand P<sub>2</sub>N<sub>2</sub> can be used as an extractant for the specific separation of copper from other transition metals.

### Conclusions

The neutral extractant P<sub>2</sub>N<sub>2</sub> shows acid-base properties. In neutral and acidic solutions, facilitated proton transfer by P<sub>2</sub>N<sub>2</sub> across the water/1,2-DCE interface occurs at the very positive potential side of the potential window.

The formation of complexes between P<sub>2</sub>N<sub>2</sub> and Cu<sup>2+</sup> occurs, and the transfer of Cu<sup>2+</sup> across the water/1,2-DCE interface has been observed. However, under the same experimental conditions, no assisted transfer of Cd<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, or Zn<sup>2+</sup> could be observed, which is in agreement with extraction results.

A 1:1 copper to ligand complex stoichiometry has been found, and its transfer across the interface is diffusionally controlled. The presence of chloride in the aqueous solution is necessary for the assisted Cu<sup>2+</sup> transfer by P<sub>2</sub>N<sub>2</sub>. The special selectivity of the ligand toward transition metals opens up the possibility of separating Cu<sup>2+</sup> by electrochemical techniques from the other metal ions studied using P<sub>2</sub>N<sub>2</sub> as an extractant.

**Acknowledgment.** Financial support from the Commission of the European Communities, DG XII, Recycling of non-Ferrous Metals Programme, Contract MR2A-CT91-0012, is gratefully acknowledged.