

Binding ability of 2,6-bis(methylthiomethyl)pyridine with proton, palladium(II) and copper(II) in aqueous solutions

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Abstract

The acidity constant of the tridentate ligand 2,6-bis(methylthiomethyl)pyridine (L) and formation constants of its Pd(II) and Cu(II) complexes $[\text{PdLTu}]^{2+}$ and $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ have been determined in aqueous solutions by potentiometric and spectrophotometric techniques. The acidity constant as determined by potentiometry is $\log K = 4.04 \pm 0.04$ (4.01 ± 0.02 by spectrophotometry), whereas the formation constants for the Pd(II) and Cu(II) species are $\log K = 28.92 \pm 0.09$ and 4.6 ± 0.1 (4.41 ± 0.04), respectively. Some preliminary results on the high selectivity for Pd(II) over Cu(II) of a macroporous polystyrene-divinylbenzene resin bearing the same chelating group are also reported.

Introduction

Noble metals tend to form their most stable complexes with chelating ligands containing N and especially S as donor atoms. Therefore the functionalization of polymers with ligands of this type is expected to give chelating resins which can be promising for the selective extraction of noble metals from aqueous solutions [1, 2].

Since the selective behaviour of a chelating resin is mainly based on the different stabilities of the metal complexes formed by the immobilized ligand at appropriate pH values, the knowledge of the formation constants for the metal–ligand complexes of interest is an important prerequisite [2].

With this idea in mind, we set out to investigate the tridentate ligand 2,6-bis(methylthiomethyl)pyridine, which has been selected as a model compound, with the aim of determining the formation constants of its Pd(II) and Cu(II) complexes. The present paper reports the results of such a study and some preliminary results on the high selectivity for Pd(II) over Cu(II) obtained by a polystyrene–divinylbenzene resin bearing the aforesaid complexing group.

A full description of the synthesis of the chelating resin and batch extraction studies which have now been performed will be reported in a forthcoming paper.

Experimental

Materials

N,N-dimethylformamide (DMF) was purified by distillation from CaH_2 and stored over 4 Å molecular sieves in a dark bottle [3]. Thionyl chloride was distilled before use. Other solvents and reagents were generally used without further purification.

Physical measurements

^1H NMR spectra were taken on a Varian FT 80-A spectrometer in CDCl_3 using SiMe_4 as internal standard. IR and electronic spectra were recorded on Perkin-Elmer 683 and Perkin-Elmer Lambda 5 spectrophotometers, respectively. pH measurements were carried out with a Metrohm 654 pH-meter. Metal ion concentrations were calculated with a Perkin-Elmer 2380 atomic absorption spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory of the University of Padua.

Preparations

2,6-Bis(chloromethyl)pyridine

It was prepared by a known procedure [4] except that crystallization was carried out in ethanol–water.

2,6-Bis(methylthiomethyl)pyridine (L)

Into an ice-cooled solution of 2,6-bis(chloromethyl)pyridine (3.52 g, 20 mmol) in DMF (50 cm^3) was added sodium methanethiolate (3.1 g,

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44 mmol) and the mixture was allowed to warm to room temperature. After 24 h of stirring the solvent was evaporated and the resulting residue partitioned between chloroform (200 cm³) and water (100 cm³). The organic phase was washed with water, dried with sodium sulfate and evaporated to dryness to give an oily product. Chromatography of this residue over silica gel eluted with chloroform yielded 3.41 g (86%) of L, as an oil. ¹H NMR (δ): 7.64 (1H, t, J 7.6), 7.23 (2H, d), 3.78 (4H, s, CH₂-py), 2.05 (6H, s, CH₃).

2,6-Bis(methylthiomethyl)-3-hydroxypyridine

The synthetic procedures for the preparation of the title ligand are described elsewhere [5].

Polymer-supported ligand

The chelating resin was prepared from macroporous polystyrene-divinylbenzene (Janssen, 22–50 mesh, average pore diameter 800 Å). The copolymer was chloromethylated according to the procedure reported in the literature [6] and then reacted with 2,6-bis(methylthiomethyl)-3-hydroxypyridine in *N,N*-dimethylformamide in the presence of caesium carbonate at 75 °C for 48 h. The content of the immobilized ligand was determined to be 1.48 mmol g⁻¹ resin from the analyses of N (2.07%) and S (9.49%).

Chloro[2,6-bis(methylthiomethyl)pyridine]-palladium(II) chloride, [PdLCl]Cl (1)

To Pd(CH₃CN)₂Cl₂ (0.2 g, 0.771 mmol) dissolved in the minimum amount of dichloromethane was added dropwise a solution of L (0.153 g, 0.771 mmol) in dichloromethane (10 cm³). A deep yellow product precipitated at once which was filtered off and washed with dichloromethane and *n*-hexane. *Anal.* Found: C, 28.45; H, 3.35; N, 3.65. Calc. for C₉H₁₃NCl₂S₂Pd: C, 28.68; H, 3.45; N, 3.72%.

Thiourea[2,6-bis(methylthiomethyl)pyridine]-palladium(II) perchlorate, [PdLTu](ClO₄)₂ (2)

1 (0.1 g, 0.266 mmol) was suspended in methanol (70 cm³) and then a solution of AgClO₄ (0.11 g, 0.531 mmol) in methanol (10 cm³) was added in the dark. After 1 h the AgCl precipitated was filtered off and to the filtrate, concentrated to a small volume, was added thiourea (Tu) (0.0202 g, 0.266 mmol). The resulting precipitate was dissolved by addition of further methanol. After standing for 30 min, addition of diethyl ether to the clear solution caused precipitation of the deep yellow product which was recrystallized from methanol–diethyl ether. *Anal.*

Found: C, 20.49; H, 2.81; N, 7.15. Calc. for C₁₀H₁₇N₃Cl₂O₈S₃Pd: C, 20.67; H, 2.93; N, 7.24%.

Tetrathioureapalladium(II) chloride [PdTu₄]Cl₂ (3)

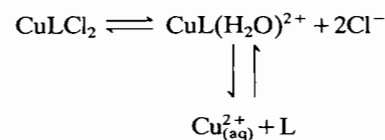
To a solution of Pd(CH₃CN)₂Cl₂ (0.2 g, 0.771 mmol) in dichloromethane (50 cm³) was added dropwise thiourea (0.5 g, 6.6 mmol) dissolved in the minimum amount of methanol. The resulting deep orange precipitate was filtered off and characterized by comparison of its IR spectrum with that reported in the literature [7].

Tetrathioureapalladium(II) perchlorate, [PdTu₄](ClO₄)₂ (4)

3 (0.150 g, 0.311 mmol) was dissolved in methanol and treated with AgClO₄ (0.129 g, 0.622 mmol) in the dark. The precipitated AgCl was filtered off immediately and the product separated by addition of diethyl ether. *Anal.* Found: C, 7.93; H, 2.61; N, 18.43. Calc. for C₄H₁₆N₈Cl₂O₈S₄Pd: C, 7.87; H, 2.64; N, 18.38%.

Dichloro[2,6-bis(methylthiomethyl)pyridine]-copper(II), [CuLCl₂] (5)

L (0.2 g, 1 mmol) was dissolved in ethanol (50 cm³) and treated dropwise with a solution of CuCl₂·2H₂O (0.171 g, 1 mmol) in the minimum amount of ethanol. The resulting deep green precipitate was filtered off, washed repeatedly with acetone and dried. *Anal.* Found: C, 32.19; H, 3.90; N, 4.11. Calc. for C₉H₁₃NCl₂S₂Cu: C, 32.38; H, 3.90; N, 4.20%. This complex is stable as a five-coordinate, undissociated species in the solid state [8] or in nitromethane solution in the presence of excess L. When dissolved in water, it dissociates immediately according to



Determination of the acidity constant of the ligand

Potentiometric method

An aqueous solution of L·HCl (250 cm³, 1 × 10⁻³ mol dm⁻³) was prepared *in situ* by dissolving L (0.0498 g, 0.25 mmol) in HCl (25 cm³, 1 × 10⁻² mol dm⁻³, *I* = 0.1 mol dm⁻³, NaCl) and subsequent dilution to the required volume with a NaCl solution (0.1 mol dm⁻³). Aliquots (50 cm³ each) of this solution were titrated with NaOH (9.6 × 10⁻³ mol dm⁻³, *I* = 0.1 mol dm⁻³) in a thermostatted potentiometric cell

(25 °C) under a nitrogen stream. Prior calibration of the potentiometer was carried out with standard Metrohm buffer solutions (pH 4 and 7).

Spectrophotometric method

Aliquots (5 cm³ each) of a solution of L (5.64 × 10⁻⁴ mol dm⁻³, from 0.0562 g in 500 cm³ properly diluted with 0.1 mol dm⁻³ NaCl) were treated with various different amounts of aqueous HCl or NaOH. Each resulting solution was diluted to 10 cm³ by addition of 0.1 mol dm⁻³ NaCl so that the analytical concentration of L and the ionic strength were kept constant at 2.82 × 10⁻⁴ and 0.1 mol dm⁻³, respectively. The pH and the absorbance of the resulting solutions were then recorded in the range 220–350 nm.

Determination of formation constants

Potentiometric method for [CuL(H₂O)]²⁺

L (0.474 g, 2.38 mmol) was dissolved in 0.111 mol dm⁻³ HClO₄ (24.6 cm³) and brought to 100 cm³ with 0.1 mol dm⁻³ NaClO₄. The resulting solution (25 cm³) was then diluted to 250 cm³ by means of the same NaClO₄ solution. Aliquots (50 cm³ each) were titrated with a 2.63 × 10⁻² mol dm⁻³ solution of CuCl₂, the ionic strength being adjusted to 0.1 mol dm⁻³ with NaClO₄. The pH was recorded after each addition on a thermostatted potentiometric cell at 25 °C under a nitrogen stream.

Spectrophotometric method for [CuL(H₂O)]²⁺

A H₃PO₄/KH₂PO₄ buffer solution at pH 2.82 and ionic strength 0.1 mol dm⁻³ was prepared by mixing 0.1 mol dm⁻³ H₃PO₄ (100 cm³) with 0.1 mol dm⁻³ KH₂PO₄ (800 cm³) and taking to 1000 cm³ with 0.1 mol dm⁻³ NaClO₄. CuCl₂·H₂O (0.171 g, 1 mmol) was dissolved in the buffer solution (60 cm³) and taken to 100 cm³ with water. Proper dilution with buffer gave a final Cu(II) solution (200 cm³, 2 × 10⁻⁴ mol dm⁻³) with *I* = 0.1 and pH = 2.82. Variable volumes of a solution of L (0.399 g, 2 mmol) in phosphate buffer at pH 2.82 (100 cm³) were then added to aliquots (5 cm³ each) of the copper chloride solution, the final volumes being adjusted to 10 cm³ with the buffer solution. The analytical concentrations of L and Cu(II) in the solutions were in the range 5 × 10⁻⁵ to 2 × 10⁻³ and 1 × 10⁻⁴, respectively. The absorption spectra of the resulting solutions were recorded in the range 350–450 nm with 1 cm path length cells placed in the thermostatted cell compartment of a Perkin-Elmer Lambda 5 spectrophotometer. The buffer solution was used as a blank in the reference cell.

Spectrophotometric method for [PdLTu]²⁺

[PdTu₄](ClO₄)₂ (0.061 g, 0.1 mmol) was dissolved in 2 × 10⁻² mol dm⁻³ Tu solution (*I* = 0.1 mol dm⁻³, NaClO₄). To aliquots (5 cm³ each) of this solution were added variable aliquots of L at the same ionic strength, the final volume being adjusted to 10 cm³ with 0.1 mol dm⁻³ NaClO₄. The analytical concentrations of Tu, Pd and L were 1 × 10⁻², 1 × 10⁻⁴ and in the range 1 × 10⁻⁵ to 2.3 × 10⁻⁴ mol dm⁻³, respectively. The absorptions of the resulting solutions were recorded in the range 320–400 nm against 0.1 mol dm⁻³ NaClO₄ as a blank.

Data reduction and analysis

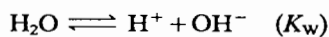
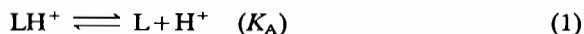
Mathematical and statistical analysis of titration data was carried out on an IBM PS/2 70 personal computer equipped with an INTEL 80387 math co-processor by the use of a locally adapted version of Marquardt's non-linear regression algorithm [9] written in TURBOBASIC (Borland). 3D plots were obtained with the SURFER package (Golden Software).

Selective metal extractions

Samples of resin (100 mg each) were contacted in a batch process with mixed aqueous solutions of Pd(II) and Cu(II) at 25 °C and pH 1 (HCl). The metal ion solutions had the same concentration of Pd(II) (3 mmol dm⁻³) but differed in the Cu(II)/Pd(II) mole ratio. After 48 h at 25 °C the metal ions sorbed on the resin were stripped with 5% thiourea in 1 mol dm⁻³ HCl. The metal ion contents of the stripping solution were monitored by atomic absorption spectroscopy.

Results and discussion

The acidity constant of LH⁺ was determined by potentiometric titration of LH⁺Cl⁻ with strong base from weighted non-linear least-squares fits of pH versus added titrant volume according to the model



$$[\text{H}^+] - K_W/[\text{H}^+] + (cV - c_0V_0\alpha_0)/V_T = 0 \quad (2)$$

where *c* = concentration of titrating NaOH (mol dm⁻³), *c*₀ = concentration of titrated LH⁺Cl⁻ (mol dm⁻³), *V*₀ = initial titrated volume (cm³), *V* = volume of titrant added (cm³), *V*_T = *V*₀ + *V*, *α*₀ = *K*_A / ([H⁺] + *K*_A) = 1 / (1 + 10^{pK_A - pH}).

Marquardt's algorithm was used with p*K*_A (= -log *K*_A) as the refinable parameter. The function minimized was Σ*w*_{*i*}(pH_{obs} - pH_{calc})² with the weighting scheme *w*_{*i*} = 1 / (pH_{*i*+1} - pH_{*i*-1})² to avoid lending too

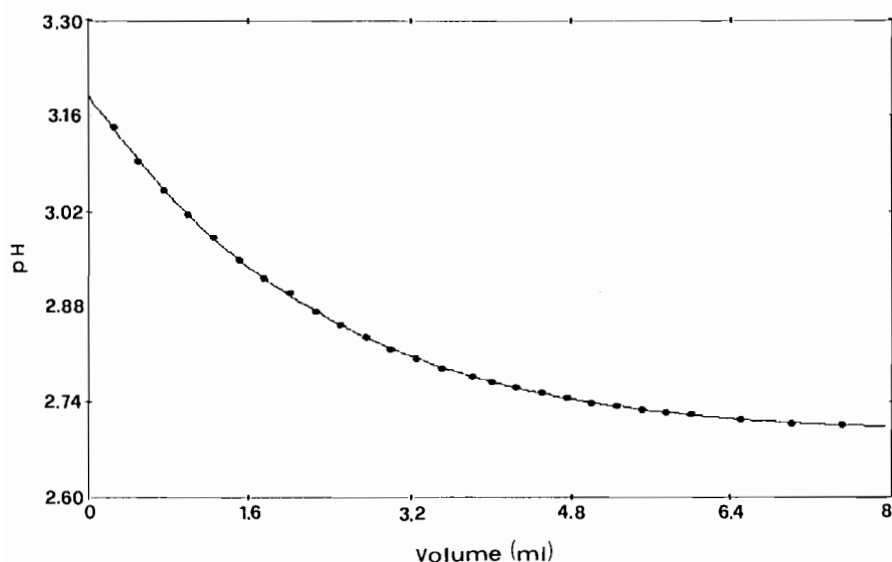


Fig. 1. Potentiometric titration of LH^+ $2.38 \times 10^{-3} \text{ mol dm}^{-3}$ with Cu^{2+} $2.63 \times 10^{-2} \text{ mol dm}^{-3}$ ($V_0 = 50 \text{ cm}^3$, $I = 0.1 \text{ mol dm}^{-3}$, NaClO_4).

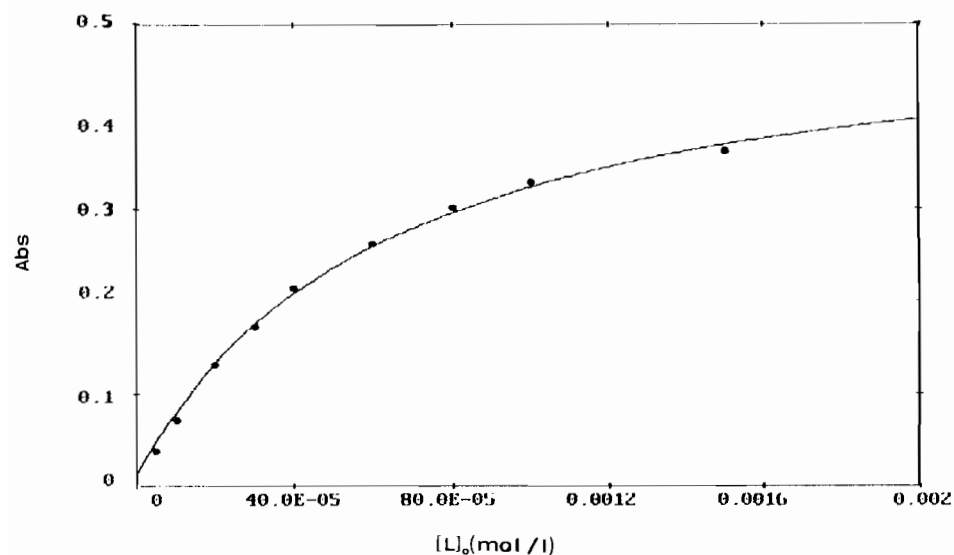


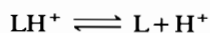
Fig. 2. Spectrophotometric titration of Cu^{2+} $1 \times 10^{-4} \text{ mol dm}^{-3}$ with L at $\text{pH} = 2.82$, $I = 0.1 \text{ mol dm}^{-3}$ (NaClO_4) at $\lambda = 375 \text{ nm}$.

much influence to the less accurate pH values in the steeply-rising portion of the titration curve [10]. During each iterative cycle implicit eqn. (2) was solved numerically for pH at each data point by a modified iterative bisection equation solver using the current value of parameter $\text{p}K_A$ [11]. The partial derivative of the object function with respect to the parameter was approximated by a numerically efficient forward differentiation scheme [12]. Convergence was rapidly reached to an optimized $\text{p}K_A$ value

of 4.04 ± 0.04 (uncertainties quoted throughout this paper are one standard error of estimate from the inverse covariance matrix). At convergence the experimental pH values agreed with those calculated from eqn. (2) within 0.06 pH unit (weighted standard error of fit = 1.3). The residuals were randomly scattered and approximated a normal distribution.

The acidity constant of LH^+ was also determined by spectrophotometric titration and unweighted non-linear regression of absorbance versus observed pH

data according to the model



$$A_\lambda = \epsilon_{\text{LH}}[\text{LH}^+] + \epsilon_{\text{L}}[\text{L}]$$

$$[\text{L}] = c_0 \alpha_0 = c_0 / (1 + 10^{\text{p}K_{\text{A}} - \text{pH}})$$

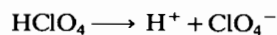
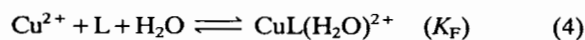
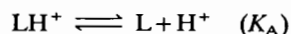
$$[\text{LH}^+] = c_0 - [\text{L}]$$

where A_λ is the absorbance at wavelength λ (295 nm), c_0 is the analytical concentration of L (2.8×10^{-4} mol dm $^{-3}$), ϵ_{LH} and ϵ_{L} the extinction coefficients of LH^+ and L, respectively, at λ . The optimized parameters were in this case $\text{p}K_{\text{A}}$ and ϵ_{LH} ($\epsilon_{\text{L}} \cong 0$ at 295 nm). The resulting value for $\text{p}K_{\text{A}}$ (4.01 ± 0.02) is in excellent agreement with that obtained from potentiometric titration.

Copper complex

The formation constant of the complex $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ was determined by both potentiometric and spectrophotometric methods.

For the former, a solution of L and HClO_4 was titrated with a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at a constant ionic strength of 0.1 mol dm $^{-3}$ (NaClO_4), the pH being measured directly. Non-linear regression of pH versus titrant volume data was carried out according to the model



The optimized parameters were $\log K_{\text{F}}$ and $\text{p}K_{\text{A}}$; the latter could also be held fixed at the value derived from potentiometric titration of LH^+ (see earlier), thereby providing a check on the consistency of data and the overall experimental layout. During each iterative cycle, the concentrations of all species involved were determined by solving the equilibrium and mass balance equation system at the current

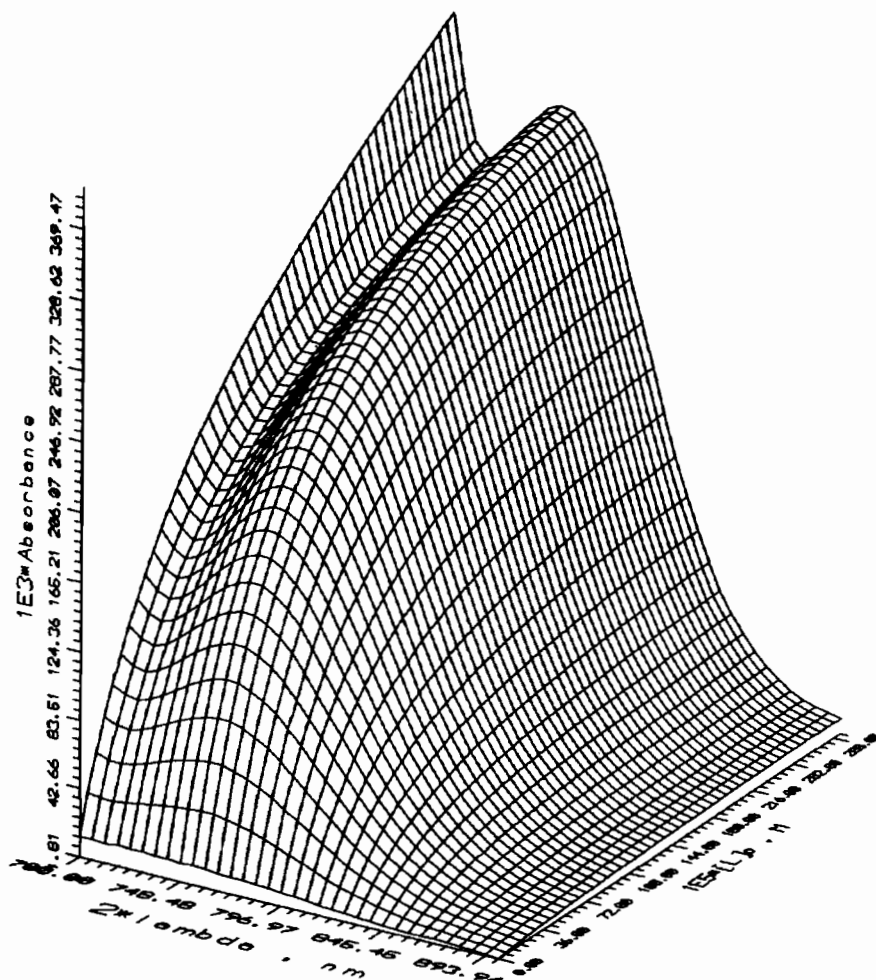
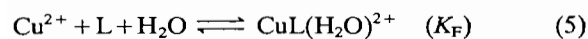
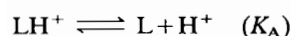


Fig. 3. 3D representation of the spectrophotometric titration of $\text{Cu}^{2+} \times 10^{-4}$ mol dm $^{-3}$ with L at $\text{pH} = 2.82$ in the range 350–450 nm.

parameter values by means of a Newton equation system solver based on LU decomposition/back substitution schemes [13].

The optimized parameters turned out to be $\log K_F = 4.6 \pm 0.1$ and $pK_A = 4.04 \pm 0.1$, the latter being identical to the potentiometric value. The fit of calculated to observed pH is shown in Fig. 1.

The $\log K_F$ parameter was also obtained from spectrophotometric titration of a CuCl_2 solution buffered at pH 2.82 ($0.1 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4/\text{KH}_2\text{PO}_4$ buffer) with a buffered solution of L at constant ionic strength ($0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$). Non-linear regression of absorbance versus titrant concentration data was carried out, the latter ranging from 5×10^{-5} to $2 \times 10^{-3} \text{ mol dm}^{-3}$ (analytical metal concentration: $1 \times 10^{-4} \text{ mol dm}^{-3}$).



pH = 2.82

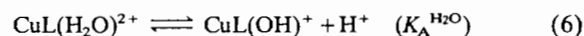
$$A_\lambda = \epsilon_{\text{LH}^+}[\text{LH}^+] + \epsilon_{\text{CuL}(\text{H}_2\text{O})^{2+}}[\text{CuL}(\text{H}_2\text{O})^{2+}] + \epsilon_{\text{Cu}}[\text{Cu}^{2+}]$$

During each iterative cycle the already mentioned equation system solver was used to determine the concentrations of all species of relevance to the model. The parameters optimized were $\log K_F$ and $\epsilon_{\text{CuL}(\text{H}_2\text{O})^{2+}}$. At convergence these appear to be strongly correlated, as shown by the highly negative parameter correlation coefficient (-0.942). This is an intrinsic feature of the model unlikely to be alleviated by

experimental design, which may make the spectrophotometric method less reliable than the potentiometric one. Indeed, $\log K_F$ turns out to be 4.41 ± 0.04 as the average of values at five different wavelengths, in satisfactory agreement with the value from potentiometric titration. Spectral changes for a typical titration are shown in Fig. 2 for $\lambda = 375 \text{ nm}$.

A 3D-representation in the wavelength range 350–450 nm is shown in Fig. 3.

The contribution to the models in eqns. (4) and (5) by the hydroxo species from the equilibrium in eqn. (6) was not taken into account as its concentration is expected to be negligible at the pH values prevailing in both types of titration.



As a matter of fact, pH measurements at metal concentrations around $2 \times 10^{-2} \text{ mol dm}^{-3}$ indicate that $pK_A^{\text{H}_2\text{O}}$ for the aquo species should be about 7, much higher than the highest pH attained in all our experiments.

Palladium complex

Preliminary potentiometric titrations according to eqn. (4) have shown that the formation constant for the palladium complex is higher by several orders of magnitude than that of its copper analog. Therefore we determined the formation constant of the mixed L–Tu complex $[\text{PdLTu}]^{2+}$ by a spectrophotometric study of competition equilibria in the presence of a large excess of Tu over the metal (1×10^{-2} versus $1 \times 10^{-4} \text{ mol dm}^{-3}$ at $I = 0.1 \text{ mol dm}^{-3}$, NaClO_4):

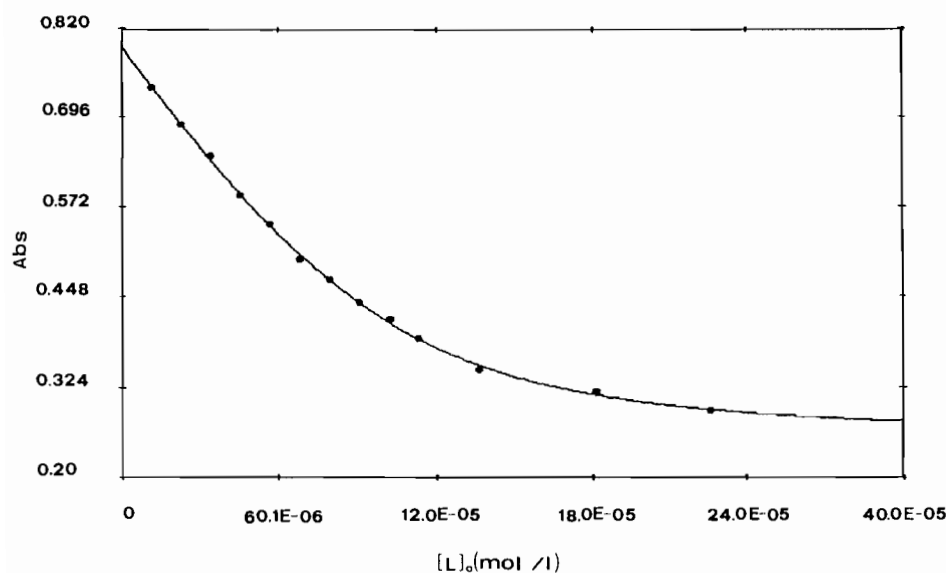


Fig. 4. Spectrophotometric titration of $[\text{PdTu}_4]^{2+} 1 \times 10^{-4} \text{ mol dm}^{-3}$ with L in the presence of Tu $1 \times 10^{-2} \text{ mol dm}^{-3}$ at $\lambda = 320 \text{ nm}$.

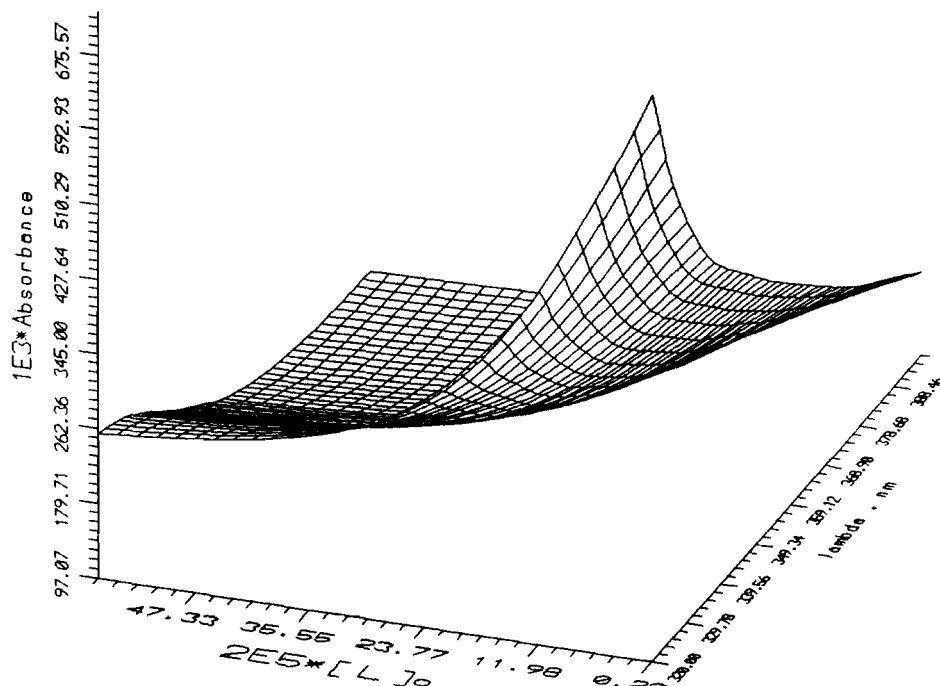
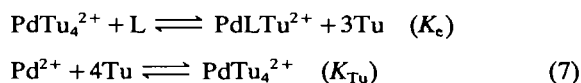


Fig. 5. 3D representation of the spectrophotometric titration of $[\text{PdTu}_4]^{2+}$ with L in the presence of Tu in the range 320–400 nm.



$$A_\lambda = \epsilon_{\text{PdLTu}}[\text{PdLTu}^{2+}] + \epsilon_{\text{PdTu}_4}[\text{PdTu}_4^{2+}]$$

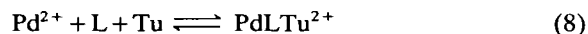
To a solution of previously prepared $[\text{PdTu}_4](\text{ClO}_4)_2$ were added variable amounts of solutions of L in the presence of excess Tu and the absorbance of the resulting mixture was recorded in the range 320–400 nm. Non-linear least-squares fit of absorbance versus added [L], by the methods described above, gave a value of -1.18 ± 0.09 for

TABLE 1. Selective metal extractions from solutions containing Pd(II) and Cu(II) at pH 1 and $T = 25^\circ\text{C}$

| Cu(II)/Pd(II) mol ratio ^a | Pd(II) on the resin (mmol g ⁻¹) | Cu(II) on the resin (mmol g ⁻¹) |
|---|---|---|
| 1 | 0.30 | ND ^c |
| 150 | 0.30 | 0.07 |
| 350 | 0.30 | 0.16 |
| In absence of Cu(II) ^a | 0.30 | |
| In absence of Pd(II) ^b | | ND ^c |

^a3 mmol dm⁻³ of Pd(II). ^b3 mmol dm⁻³ of Cu(II). ^cND = not detectable (<0.5 mg metal g⁻¹ dry resin).

$\log K_e$ as the average of values at five different wavelengths. Since $\log K_{\text{Tu}}$ is known from the literature to be 30.1 [14], $\log K_F$ for the equilibrium



turns out to be $\log K_F = \log K_e + \log K_{\text{Tu}} = 28.92 \pm 0.09$.

Spectral changes for a typical titration are shown in Fig. 4 for $\lambda = 320$ nm.

A 3D-representation in the wavelength range 320–400 nm is shown in Fig. 5.

At the highest concentration of added L (2.26×10^{-4} mol dm⁻³) the spectrum of the resulting solution was close to that of an authentic sample of independently prepared $[\text{PdLTu}](\text{ClO}_4)_2$.

Selective metal extraction

The palladium complex displays a formation constant extremely higher than its copper counterpart, which certainly overwhelms the fact that the ligands being exchanged are different (Tu versus H₂O). This suggests that a polymer functionalized with 2,6-bis(methylthiomethyl)pyridine groups would display sorption selectivity for Pd(II) in mixtures of Pd(II) and Cu(II).

Sorption experiments of Pd(II) in the presence of Cu(II) at various Cu(II)/Pd(II) mol ratios at pH 1 and $T = 25^\circ\text{C}$ confirmed the expected selectivity (Table 1). In fact, the capacity of the resin for Pd(II) (0.30 mmol g⁻¹ dry resin) is not affected by increasing

concentrations of Cu(II), although in the presence of 350 fold concentration of Cu(II), the sorption of Cu(II) on the resin increases significantly.

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