A new Schiff base: Synthesis, characterization and optimization of metal ions-binding properties

Ahmet Bilgin, Seda Çetintaş, Elif Cerrahoğlu, Ufuk Yıldız & Deniz Bingöl


To link to this article: http://dx.doi.org/10.1080/01496395.2016.1201114
A new Schiff base: Synthesis, characterization and optimization of metal ions-binding properties
Ahmet Bilgin\textsuperscript{a}, Seda Çetin\textsuperscript{a}, Ş, Elif Cerrahoğlu\textsuperscript{b}, Ufuk Yildiz\textsuperscript{b}, and Deniz Bingöl\textsuperscript{b}
\textsuperscript{a}Department of Science Education, Kocaeli University, Kocaeli, Turkey; \textsuperscript{b}Department of Chemistry, Kocaeli University, Kocaeli, Turkey

ABSTRACT
In this study, a new Schiff base (H\textsubscript{4}TSTE) was synthesized and characterized by elemental analysis, FT-IR, NMR and MS spectral data. Liquid–liquid extraction process was performed for removal of Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) from aqueous solutions by means of H\textsubscript{4}TSTE. The extractions were investigated depending on the concentration of picric acid, metal ion and H\textsubscript{4}TSTE ligand. Response surface methodology (RSM) was first applied to optimize metal ion-binding properties of H\textsubscript{4}TSTE. The extraction efficiency was estimated to be >98% for all metals by models. Under the same conditions, the extraction efficiency was experimentally found to be >97% with a relative standard deviation within ±0.10 (N = 4), indicating the suitability of the models.

ARTICLE HISTORY
Received 14 January 2016
Accepted 9 June 2016

KEYWORDS
Metal ions; RSM; Schiff base; solvent extraction

Introduction
Schiff bases are condensation products caused by primary amines, aldehydes or ketones. Numerous Schiff bases and complexes are synthesized due to very flexible and variable structural characteristics. Schiff bases, giving the non-bonding electrons in \(\sigma_n\) molecular orbital of nitrogen in the azomethine group to metal ions, behave as ligands. Today, many scientists are working on the synthesis of new and well-organized Schiff bases. Schiff bases can be made stable with various metals in different oxidation states and thus the performance of many metal catalytic reactions can be controlled in this way.\textsuperscript{[1,2]} Metal complexes which are obtained depending on the groups in the structure of Schiff bases are coloured substances and thus largely used in the paint industry, especially in textile dyeing, as well as in polymer technology, pharmaceutical industry, medicine, agriculture, rocket fuel and the removal of heavy metals.\textsuperscript{[1]}

The solvent extraction process is one of the most versatile procedures for the removal, separation and enrichment of metallic species compared to other known techniques such as biological processes, combined chemical and biochemical degradation, chemical oxidation, coagulation and membrane treatments. Experimental designs that provide a large amount of useful information from a reduced number of experiments have many advantages such as a relatively low cost and possibilities to evaluate interactions among variables.\textsuperscript{[3]} In application of response surface methodology in the optimization of analytical procedures, optimization is often required to improve the response because of its above advantages to classical one-variable-a-time optimization. The central composite design (CCD) is still the symmetrical second-order experimental design most utilized to rapidly optimize an analytical method.\textsuperscript{[4–11]} The sequential single-factor-at-a-time approach requires all factors but one to be held constant while a univariate search is carried out on the factor of interest.\textsuperscript{[12]}

In this study, a new Schiff base, \(N,N',N'',N'''\)-tetrasalicylidylen-3,3',4,4'-tetraaminodiphenyl ether (H\textsubscript{4}TSTE), was synthesized by reacting 3,3',4,4'-tetraaminodiphenyl ether and salicylaldehyde and then characterized by elemental analysis, FT-IR, NMR and MS spectral data. The heavy metal ions binding properties of the Schiff base (H\textsubscript{4}TSTE) ligand were investigated depending on picric acid, metal ions and H\textsubscript{4}TSTE concentration using chloroform as solvent.

Materials and methods

Materials
Methanol (Sigma) was distilled over MgSO\textsubscript{4} under N\textsubscript{2} and stored over 4 Å molecular sieves and thoroughly degassed with N\textsubscript{2} prior to use. Salicylaldehyde (Sigma) was distilled under reduced pressure. As described in the literatures, 3,3',4,4'-tetraaminodiphenyl ether was prepared.\textsuperscript{[13,14]} Other reagents were received from commercial suppliers. Conventional procedures were used for purification.

CONTACT Deniz Bingöl denizbingol1@gmail.com, deniz.bingol@kocaeli.edu.tr Department of Chemistry, Kocaeli University, 41380 Kocaeli, Turkey. © 2016 Taylor & Francis
of all solvents. All the synthesis reactions were performed under an inert atmosphere using standard Schlenk techniques, unless otherwise noted.

**Measurement**

Transmission infrared spectra were recorded on a Fourier Transform Infrared (FT-IR) spectrophotometer (Schimadzu FTIR-8201 PC) in the spectral range from 4000 to 400 cm⁻¹ with samples in KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer with DMSO-₆ as solvent at ambient temperature. Tetramethyldisilane was used as the internal standard and the chemical shifts were given in parts per million (ppm) relative this standard. Mass spectrum was recorded on Bruker Daltonics MICRO-TOF mass spectrometer with an orthogonal electrospray ionization source. Melting point of the prepared compound was determined on an electrothermal digital melting point apparatus (Barnstead Electrothermal IA9100) and was uncorrected. Concentration of the metal ions remaining in the aqueous phase was determined by flame atomic absorption spectrometry (FAAS) (Perkin Elmer AAnalyst 800 model).

**Synthesis of N,N,N',N''-tetrusalicylidene-3,3',4,4'-tetraaminophenyl ether, 3, (H₅TSTE)**

A sample of 3,3',4,4'-Tetraaminodiphenyl ether (2.303 g, 10 mmol) was dissolved in 150 mL of dry methanol at 70°C under N₂ and then 4.3 mL of salicylaldehyde (4.885 g, 40 mmol) in 15 mL of dry methanol was added dropwise to the warm solution. The solution was refluxed overnight, turning a deep yellow colour within the first few hours. The reaction system was then chilled to below 0°C and filtered to isolate the crude yellow product, which was washed several times with cold methanol (5 mL) and followed by diethyl ether (10 mL). The crude ligand was recrystallized from degassed 1,2-dichloroethane after the addition of colorizing carbon, dried at 50°C in vacuo over P₂O₅. Yield: 5.70 g, 88%. Mᵣ = 222–224°C. Anal. calcd. for C₄₀H₃₀N₄O₅: C, 74.29; H, 4.68; N, 8.66%. Found: C, 74.56; H, 4.47; N, 8.49%. FT-IR (KBr, cm⁻¹): 3400–3363 (–OH), 3060–3048 (=CH aromatic), 1618 (imine –N=CH–), 1570, 1487, 1458 (aromatic –C=C–), 1364 (N–C), 1272 (aromatic etheric band, Ar–O–Ar), 1181, 1150 (phenol C=O), 970, 752. ¹H NMR (DMSO-₆, δ, ppm): 13.10 (s, 2H, OH), 12.80 (s, 2H, OH), 8.98 (s, 2H, –N=CH–), 8.82 (s, 2H, –N=CH–), 6.27–7.66 (m, 22H, ArH). ¹³C NMR (DMSO-₆, δ, ppm): 166.3 (–N=CH–), 164.5 (–N=CH–), 162.2, 161.5, 160.4, 158.6, 146.0, 135.0, 134.2, 133.7, 132.8, 131.7, 121.9, 121.4, 120.9, 119.5, 118.3, 112.0, 108.9, 106.7 (all aromatic-C). MS (MICRO-MS, m/z): calcd. for [M+1]⁺ 647.2294; found [M+1]⁺ 647.2632.

**Solutions preparation**

Five different metal ions [Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II)] were investigated in the present study with a separate analysis for each. Synthetic solutions were prepared by dissolving Cu(NO₃)₂·2.5H₂O (p.a.), Mn (NO₃)₂·4H₂O (p.a.), Ni(NO₃)₂·6H₂O (p.a.), Pb(NO₃)₂ (p.a.) and Zn(CH₃COO)₂·2H₂O (p.a.).

**Metal extraction analyses**

The extraction of metal picrates from the aqueous phase to chloroform phase by a newly synthesized Schiff base (H₅TSTE) was examined by liquid–liquid extraction. For this purpose, the metal picrate solutions were prepared as the aqueous phase and then the metal picrates were extracted to chloroform phase from the aqueous phase containing H₅TSTE. Optimal pH (8.2) and time (1 h) were determined by pretests in which the highest metal ion extractions were obtained. Slightly basic metal-picrate solutions (10 mL) buffered by NH₃–NH₄Cl buffer (pH 8.2) and ligand solutions (10 mL) prepared in chloroform by dissolving in very little DMF (0.3 mL), were stirred in magnetic stirrer for 30 min. Afterwards, the extraction solution was reconstituted on an orbital shaker at 250 rpm and 25°C for 1 h. The extraction solution was taken to separator funnel, after shaking for 5 min; it was allowed to stand for phase separation for 15 min. Concentration of remaining metal ions in the aqueous phase was determined by FAAS (Perkin Elmer AAnalyst 800 model), fitted with a deuterium arc background corrector. The extracted amount of metal ions, (q) or efficiency (%) was calculated as the amount of the metal bound to ligand or the amount of the metal ions removed from the aqueous phase:

\[
q = \left(\frac{C_0 - C_e}{C_e}\right) \times 100
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium liquid-phase concentrations of metal ions (mg/L or mol/L), \(V\) is the volume of metal ion solutions (L), and \(W\) is the mass of H₅TSTE used (g).
Response surface methodology

To optimize the extraction process, response surface methodology (RSM) approach, which provides a shorter time and an assessment in detail of extraction conditions, was applied to obtain the best extraction efficiency and to investigate the effects and interactions of the factors on the extraction efficiency.

According to experimental design which was determined by CCD, all tests were performed with two replications using 10 mL aqueous solution of metal picrate and 10 mL solution of the organic ligand. The effect of picric acid concentration (mol/L), initial metal ion concentration (mg/L) and ligand concentration (mol/L) onto extraction were examined. A CCD was done using Minitab software version 16.

Results and discussion

Characteristics of Schiff base

$N,N',N'',N'''$-tetrasalicylidene-$3,3',4,4'$-tetraaminodiphenyl ether, 3, ($H_4$TSTE) was synthesized by condensation reaction of $3,3',4,4'$-tetraaminodiphenyl ether 2[13,14] with salicylaldehyde 1 in dry methanol for a period of overnight (Fig. 1). Final purification of the Schiff base 3 by recrystallization from degassed 1,2-dichloroethane after the addition of decolorizing carbon afforded 3 in 88% yield, for which elemental analyses and MICRO-TOF MS mass spectral data were satisfactory: $[M+1]^+$ 647.2632. NMR spectra are particularly useful in monitoring the transformation of the salicylaldehyde 1 to the Schiff base $H_4$TSTE. In $^1$H NMR spectrum of $H_4$TSTE the disappearance of the amine proton signals belonging to the tetraamine compound (2) proves the condensation reaction between compound 1 and 2. In addition to aromatic proton signals in the region 6.27–7.66, $^1$H NMR spectrum of $H_4$TSTE showed new signals belong to OH and imine ($-N=CH-$) protons at $\delta = 13.10$ (s, 2H, OH), 12.80 (s, 2H, OH), 8.98 (s, 2H, $-N=CH-$), 8.62 (s, 2H, $-N=CH-$) ppm, respectively. On account of non-equivalent OH and imine protons in $H_4$TSTE have different chemical environments and give different signals. The $^1$H NMR spectrum of $H_4$TSTE is in accordance with the proposed structure. With the addition of D$_2$O in (3) the chemical shifts of O–H at 13.10 and 12.80 ppm were displaced with deuterium. The proton-decoupled $^{13}$C NMR spectrum of $H_4$TSTE clearly indicates the presence of non-equivalent imine carbon atoms with peaks at $\delta = 166.3$ and 164.5 ppm, respectively. It also displays eighteen different singlets, at $\delta = 162.2$, 161.5, 160.4, 158.6, 146.0, 135.0, 134.2, 133.7, 132.8, 131.7, 121.9, 121.4, 120.9, 119.5, 118.3, 112.0, 108.9 and 106.7 ppm, corresponding aromatic carbon atoms due to the non-equivalent aromatic carbon atoms in $H_4$TSTE.[16,17]

The FT-IR spectrum of the Schiff base $H_4$TSTE shows no characteristic absorption assignable to either NH$_2$ or C=O function in the precursor materials, but exhibits a broad resonance at 3400–3363 cm$^{-1}$, which can be attributed to O–H stretching of the phenolic hydroxyl groups. The appearance of a strong band at 1618 cm$^{-1}$, which has been assigned to the $-N=CH-$ stretching vibration, establishes the presence of the completely condensed the Schiff base $H_4$TSTE.[16,17] Strong band at 1272 cm$^{-1}$ and medium peak at 1150 cm$^{-1}$ are also observed. These are assigned to the usual modes of aromatic etheric Ar–O–Ar and phenol C–O groups, respectively.

Liquid–liquid extraction

The experiment conditions and the average results for 20 experiments containing different combination of factors are shown in Table 1. According to design matrix (Table 1), the order was randomized to avoid systematic errors in the experiments.

In the evaluation of experimental designs, a mathematical model is provided to relate the response variable with the factor effects. Results were evaluated using analysis of variance (ANOVA) in 95% confidence level. One of the applications of ANOVA is the development of an analytical procedure, and is use as a preliminary step in the experimental optimization of procedures. Almost all the main factors and a few their interactions

![Figure 1. Synthesis of the Schiff base 3, H_4TSTE.](image-url)
indicated probability of less than 0.05 were significant at 95% confidence level. But, these interactions that \( P \)-values \( > 0.05 \) were not statistically significant impact at 95% confidence level on the extraction process and they will not contribute to the model. Therefore, these interactions should be removed from the model. In addition, if the model presents the coefficient of determination \( (R^2) \) above 90% then it is considered excellent. This is only one criterion to evaluate the model goodness of fit. The regression models for metal ions-binding properties of a new Schiff base were given with goodness of fit. The regression models for metal ions—ligand interactions were found as single effective interaction.

As a result of the optimization of the factors by CCD; for Cu(II), Mn(II), Ni(II), Pb(II), and Zn(II) extraction efficiency can be estimated to be 99.66%, 81.57%, 50.78%, 76.17%, 99.98% using ligand concentration of \( 1.01 \times 10^{-4} \) (mol/L), initial metal concentration of \( 24.63 \) (mg/L) and picric acid of \( 2.02 \times 10^{-4} \) (mol/L), respectively.

The Schiff base, \( \text{H}_2\text{TSTE} \), showed higher uptake affinity for Cu(II) and Zn(II) cations. This behaviour can be due to the high complexing capacity of \( \text{H}_2\text{TSTE} \) towards the Cu(II) and Zn(II) ions. First of all, pH plays a significant role in the extraction of ions due to the presence of hydrogen ions \( (\text{H}^+) \) in solution which compete with positively charged species. The highest uptake affinity of the Schiff base reached at pH 8.2. The higher affinity of \( \text{H}_2\text{TSTE} \) towards the Cu(II) and Zn(II) ions at pH 8.2 could be explained by the ease coordination of the phenoxy ion over that of the phenolic –OH group and also the enhanced basicity of the C≡N nitrogen in the alkaline medium.

The results of the model were found to be consistent with experimental results in the same conditions; the difference between the results was less than 5% for studied metals. The agreement between the experimental values and the estimated values \( (R^2_{\text{adj}} \text{ (Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II)) = 98.51%, 98.85%, 99.62%, 99.87% and 99.25%, respectively}) showed that CCD can be used to removal of metals with liquid-liquid extraction as a suitable model.
The visualization of the predicted model equation can be obtained by the surface response plot. A response surface is the graph of a system response plotted as a function of one or more of the system factors (i.e. 'independent variables'). Response surface plots are plotted to see the effect of three variables (concentrations of PA, M and L) on the extraction efficiency. The analysis provides a better understanding of both effects of variables and their interaction on the response. Figure 2 shows examples of response surfaces that can be fit by the

Figure 2. The response surface plots of q (mg/g) and extraction (%) versus to L (mol/L) and metal ions concentration (mg/L) at PA: $2.08 \times 10^{-4}$ mol/L for extraction of five metal ions.
Table 2. The regression models for metal ion-binding properties of a new Schiff base (at coded units).

<table>
<thead>
<tr>
<th></th>
<th>Extraction (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>qCu</td>
<td>Cu% = 99.081 + 0.157.PA – 1.095.Cu(II) + 2.7221.L – 0.859.Cu(II) + 3.165.L² + 2.171.Cu(II)*L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R² adj: 99.25%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S: 4.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>qMn</td>
<td>Mn% = 78.486 + 0.0086.PA – 4.337.Mn(II) + 5.3991.L – 2.314.PA² – 3.294.Mn(II) + 1.395.Mn(II)*L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R² adj: 98.51%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S: 0.49</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R² adj: 99.62%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S: 0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R² adj: 99.87%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S: 1.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>qZn</td>
<td>Zn% = 98.384 – 0.2591.PA – 5.028.Zn(II) + 2.201.L + 1.725.PA² – 5.605.Zn(II) + 1.514.Zn(II)*L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R² adj: 99.25%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S: 0.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

models of equations in Table 2. These figures might represent extraction of five metal ions as a function of metal ions and ligand concentration at PA 2.08 × 10⁻⁴ mol/L. As can be seen in Figure 2, the metal extraction efficiencies are almost the same and initially increase and then decrease with increasing initial metal concentration. In addition, the metal extraction efficiencies are strongly L concentration-dependant.

This study indicated that the prepared novel Schiff base, H₄TSTE, can effectively extract Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions from aqueous solution in the following decreasing order: Pb(II) (302.78 mg/g) > Cu(II) (269.54 mg/g) > Zn(II) (260.74 mg/g) > Mn(II) (215.36 mg/g) ≫ Ni(II) (46.86 mg/g) using ligand concentration of 1.55 × 10⁻² (mol/L), initial metal concentration of 50.80 (mg/L) and picric acid concentration of 1.5 × 10⁻⁵ (mol/L). The extraction values of H₄TSTE for the metal cations in chloroform have been decreased in order Cu(II) > Zn(II) > Mn(II) > Pb(II) > Ni(II). Cu(II) is found to be the best extracted metal cation for the studied Schiff base and demonstrated to form more stable complex than other divalent cations. The extra stability of Cu(II) ion can be explained by taking into account of Jahn–Teller distortion of the d⁹ ion. With respect to increasing electronegativity of the metals, the electronegativity difference between metal atom and donor atom of the ligand will decrease, hence the metal–ligand bond would have more covalent character which may result in greater stability of the metal chelates.²²,²³

Conclusions
The synthesis and characterisation of a novel Schiff base H₄TSTE as an extractant are presented. The novel Schiff base H₄TSTE was prepared by the condensation reaction of 3,3',4,4'-tetraaminodiphenyl ether with salicylaldehyde. Response surface method (RSM) approach was used to determine the optimal experimental conditions for solvent extraction method. The extraction values of H₄TSTE for the metal cations in chloroform have been decreased in order Cu(II) > Zn(II) > Mn(II) > Pb(II) > Ni(II). Cu(II) is found to be the best extracted metal cation for the studied Schiff base and demonstrated to form more stable complex than other divalent cations. The suitable medium for the uptake of the metal ions by H₄TSTE was at pH 8.2. This is due to the availability of the maximum electron density on the O and N atoms of the functional groups, which is needed for coordination with the metal ion to form the ligand–metal complex. Extraction efficiencies were found to be >98% for...
all metal ions. Experimental values and predicted values from the model were quite compatible, and CCD can be used as a suitable model for the removal of metal ions with a new Schiff base by liquid–liquid extraction method using a limited number of experiments.

References