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Synthesis, Characterisation, and Equilibrium Studies of 1-(2-Ethyl-1,2,3,4-tetrahydro-quinazolin-2-yl)-ethanone Oxime and the Copper(II) Complex of Its Open-Chain Tautomer[1]

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Abstract—1-(2-ethyl-1,2,3,4-tetrahydro-quinazolin-2-yl)-ethanone oxime (ETQX, HL) and the Cu(II) complex of its open-chain tautomer were synthesised and characterised by elemental analysis, magnetic susceptibility, molar conductance, thermal analyses, and spectral (IR, NMR, AAS, LC-MS, and UV-Vis) studies. The accumulated data exhibited that the ligand underwent a ring-opening reaction upon formation of a mononuclear Cu(II) complex in which the chain tautomer acted as an *N,N,N*-donor. The Cu(II) complex was formed in a 1 : 1 (M : HL') ratio, as indicated by analytical results and the general formula was elucidated to be [Cu(HL')Cl]Cl.

The protonation constants of ETQX and the stability constants of the complex species formed with the Cu(II) of ETQX were studied by the potentiometric method at 25°C in 0.1 M KCl ionic medium. A complexation model for the Cu(II)-ETQX system was established with the software program "BEST" based on the potentiometric data. The concentration distribution curves of ETQX and Cu(II)-ETQX complex species in solution were evaluated by the SPE software program. The stoichiometry of the Cu(II) complex in solution was observed to be similar to that of the solid state Cu(II) complex.

Keywords: 1-(2-ethyl-1,2,3,4-tetrahydro-quinazolin-2-yl)-ethanone oxime, copper(II) complex, equilibrium studies, protonation constants, stability constants

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INTRODUCTION

Many Schiff base derivatives containing substituted oxime have been synthesised, characterised in detail, and used for complexation with certain transition metal ions [1, 2]. Formation of tetrahydroquinazolines is formally the synthesis of a Schiff base from aldehydes [3] or ketones with a ring-chain tautomeric equilibrium between the tetrahydroquinazolines and Schiff bases [3–6]. Recently, Sanmartín-Matalobos and co-workers have focused on controlling the tautomeric equilibrium between tetrahydroquinazolines and Schiff bases using metal coordination [7–9]. In the previous papers, we presented the synthesis and characterisation of 1,2,3,4-tetrahydroquinazoline derivatives containing the oxime group and their complexes with Ni(II) and Co(III) ions [10–15].

The coordination chemistry of Cu(II) complexes have received considerable attention due to their potential biological activity as antibacterial, anti-inflammatory, antioxidant, and antitumor agents [16–20].

In the current work, we have expanded synthesis and characterisation studies of 1,2,3,4-tetrahydroquinazoline oximes and their complexes and contributed to equilibrium studies thereof. A new ligand, ETQX, and its open-chain tautomer complex with Cu(II) were synthesised and characterised. The protonation constants of ETQX and the stability constants of the binary complexes that its ligand forms with Cu(II) were determined by the potentiometric method at 25°C in 0.1 M KCl ionic medium. ETQX contains two amine and one oxime groups, and its interactions with metals may be estimated using various binding models. The protonation constants of ETQX species and the stability constants of the Cu(II)–ETQX complexes were computed from titration data using the program BEST. Several models were tested, and the best one was chosen. The computer refinement of the titration data exhibited the presence of $CuLH^{2+}$, CuL^{+} and $CuLH_{-1}$ species in binary systems. Distribution diagrams of detectable species in the presence and the

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[1] The text was submitted by the authors in English.

Table 1. TG-DTA data of ETQX and the Cu(II) complex

Compound	Temperature range, °C	DTA$_{max}$, °C[a]	Total weight loss		Assignment
			found, %	calculated, %	
HL	168–332	159 (+)	0	0	[c]
		188 (–)			
		224 (–)	87.1	[b]	
		263 (–)			
	332–607	538 (–)	100	100	–
[Cu(HL')Cl]Cl	113–209	146 (–)	11.4	[b]	[c]
	209–433	261 (–)	32.2	[b]	[c]
		314 (–)			
	433–616	509 (–)	85.4	82.1	Cu

[a] (+) Endothermic, (–) exothermic. [b] Not computed. [c] Unknown.

absence of metal ions as function of pH were created using the program SPE.

RESULTS AND DISCUSSION

The analytical and spectral data of ETQX and the Cu(II) complex of its imine tautomer are presented in the experimental section. The C, H, N, and M contents were in good agreement with the chemical formulae of ETQX and [Cu(HL')Cl]Cl. The mass spectrum of the free ligand, which contained the molecular ion peak at m/z = 219.8 $(HL)^+$, indicated formation of the desired structure. The molar conductance value measured in methanol solution (~10^{-3} M) at room temperature for the Cu(II) complex indicated that the Cu(II) complex was a 1 : 1 electrolyte [21] with one chloride ion present outside the coordination sphere. The room temperature magnetic moment of the Cu(II) complex indicated paramagnetic nature of the complex with a μ_{eff} = 1.73 BM and one unpaired electron. This result was in accord with the normal range for mononuclear Cu(II) species with $S = 1/2$ confirming the square-planar geometry of the Cu(II) complex [22].

UV-Vis spectra. The electronic spectrum of ETQX in methanol exhibited three dominating absorption bands with two bands at 245 nm and 208 nm, that represented (π–π*) intra-ligand transitions, whereas the third band at 300 nm represented the (*n*–π*) intra-ligand transition. The bands underwent a shift to higher or lower energy in the spectrum of Cu(II) complex, suggesting the coordination of imine, amine and oxime nitrogen atoms with the central Cu(II) ion.

The electronic spectrum of [Cu(HL')Cl]Cl in methanol exhibited intense bands at 316, 237, and 206 nm that were assigned to intra-ligand (*n*–π* and π–π*) transitions associated with the aromatic ring and C=N chromophores. The spectrum of the Cu(II) complex exhibited a low-intensity *d*–*d* band at approximately 619 nm, which could be assigned to the square-planar copper(II) environment [22–24]. This finding was supported by magnetic susceptibility measurements.

FT-IR spectra. There were two main features of the infrared spectrum of the newly formed ligand ETQX. The first one was absence of the characteristic carbonyl group band at 1671 cm^{-1} specific to PDO, the second feature was appearance of the band at 1606 cm^{-1} assigned to the stretching vibration of the oxime –C=N group that confirmed the condensation reaction. The FT-IR spectrum of ETQX exhibited fairly strong bands at 3393 and 3280 cm^{-1} attributable to the ν(N–H) mode. The oxime (–OH) stretching vibration of the ligand appeared as a broad peak with maximum at 2877 cm^{-1}, shifted significantly to lower frequencies as a result of the intramolecular hydrogen bonding (N····H–O). The bands observed at 1303 and 885 cm^{-1} were attributed to the vibrations of (–C–N–) and (N–O), respectively. The data are in accord with those that had been previously reported for 1,2,3,4-tetrahydroquinazoline oximes [10–15].

In the FT-IR spectrum of the Cu(II) complex, the band at 3201 cm^{-1} was associated with the (–OH) stretching vibration of the oxime group. The FT-IR spectrum of the Cu(II) complex comparison with that of the free ligand indicated that the ν(C=N$_{oxime}$) band

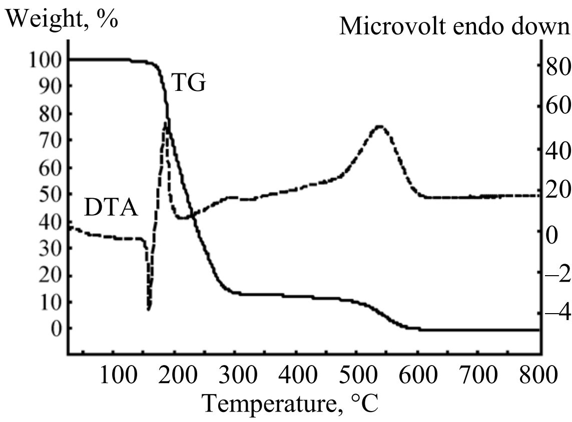


Fig. 1. TG and DTA curves of ETQX.

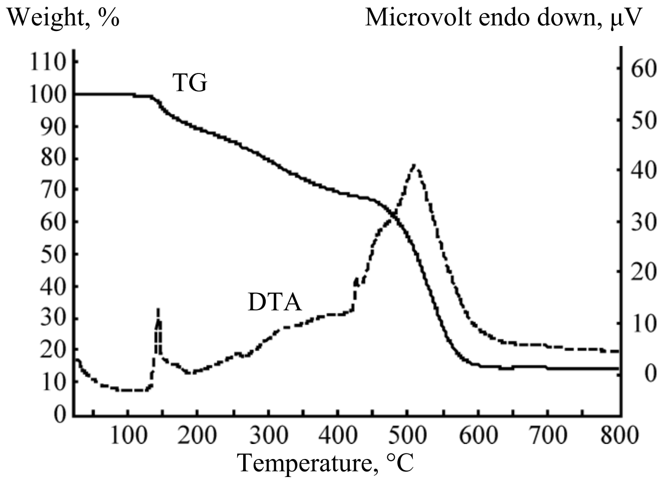


Fig. 2. TG and DTA curves of [Cu(HL')Cl]Cl.

was shifted towards lower frequency. The shift was attributed to the withdrawal of electron density from the oxime nitrogen atom due to coordination. The (–C–N–) band of the heterocyclic ring disappeared as a result of the complexation and formation of the chain from within the complex. The appearance of new bands at 3323–3279 and 1612 cm^{-1} for the Cu(II) complex provided conclusive evidence of the (–NH_2) and (C=N_{imine}) stretching vibrations of the amine and second azomethine group.

^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of ETQX exhibited three singlets at δ = 10.59, 2.57, and 5.65 ppm, that disappeared upon the addition of D_2O and were assigned to the proton of the oxime group, the NH proton adjacent to the CH_2 group and the other NH proton, respectively.

The ^{13}C NMR spectrum of PDO exhibited the carbonyl group signal at δ = 199.79 ppm, which was not observed in the spectrum of ETQX. ETQX spectrum contained a signal of the quaternary carbon atom of the heterocyclic ring at δ = 72.11 ppm indicating formation the 1,2,3,4-tetrahydroquinazoline ring [4–6, 11–15].

Table 2. Protonation constants (log *K* ± σ) of protonated ETQX at *T* = 25°C in *I* = 0.1 M KCl (σ is a standard deviation)

Equilibria	log *K*
$L^- + H^+ \leftrightarrow HL$	9.41 ± 0.01
$HL + H^+ \leftrightarrow H_2L^+$	8.99 ± 0.10
$H_2L^+ + H^+ \leftrightarrow H_3L^{2+}$	2.70 ± 0.20

Thermal analyses (Table 1). ETQX was stable up to 168°C and then decomposed into two separate temperature regions. Decomposition completed at 607°C (Fig. 1). The DTA curve demonstrated an endothermic peak at ca 159°C, without weight loss in the TG curve, indicating the melting point of the ligand.

TG-DTA curves for the Cu(II) complex are presented in Fig. 2. The thermal decomposition results were in good agreement with the theoretical formula based on the elemental analysis and AAS. The complex [Cu(HL')Cl]Cl was stable at temperature up to 113°C. Decomposition was observed in the temperature range 113–616°C in three steps, as indicated by the exothermic DTA peaks at 146, 261, 314, and 509°C. The resulting decomposition product, Cu, was

Scheme 1. The protonation equilibria of ETQX.

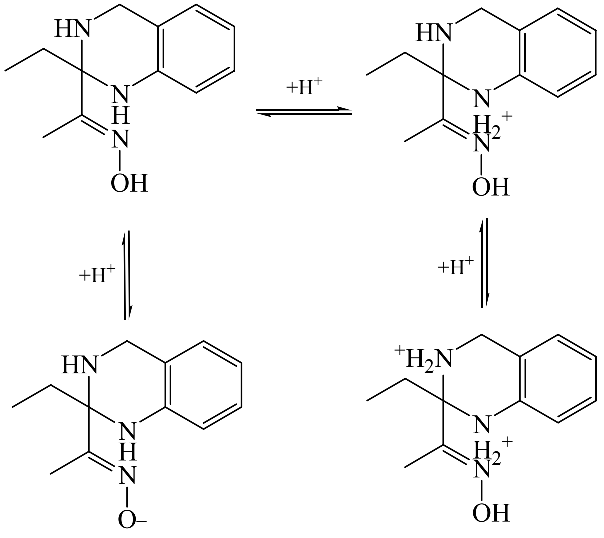


Table 3. Stability constants (log β ± σ) of Cu(II) complex of ETQX at $T = 25°C$ in $I = 0.1$ M KCl (σ is a standard deviation)

Equilibria	β	log β
$Cu^{2+} + L^- \leftrightarrow CuL^+$	$\beta_{CuL^+} = \frac{[CuL^+]}{[Cu^{2+}][L^-]}$	13.2 ± 0.1
$Cu^{2+} + L^- + H^+ \leftrightarrow CuLH^{2+}$	$\beta_{CuLH^{2+}} = \frac{[CuLH^{2+}]}{[Cu^{2+}][L^-][H^+]}$	18.7 ± 0.2
$CuL^+ + H^+ \leftrightarrow CuLH^{2+}$	$\beta_{CuLH^+} = \frac{[CuLH^+]}{[H^+][CuL^+]}$	5.5 ± 0.2
$CuL^+ + H_2O \leftrightarrow CuL(OH) + H^+$	$\beta_{CuLH_{-1}} = \frac{[CuL(OH)][H^+]}{[CuL^+]}$	5.7 ± 0.6

formed upon removal of the organic ligand and halogens which demonstrated that the organic ligand acted as a reducing agent during thermal decomposition.

Protonation constants of the ligand. The protonation constants of the synthesised ligand (Scheme 1) were determined potentiometrically in an aqueous medium at 25°C in $I = 0.1$ M KCl. Two inflection points were observed in the titration curve of protonated ETQX (Fig. 3). In the two buffer zones along the inflection point, the number of titrated protons was three per ligand. For protonated ETQX, the first two protons were released from the $(N^1)H_2^+$ and $(N^3)H_2^+$ groups of the heterocyclic ring, and the third proton was released from the group N=O–H. Herein, the lone ligand is indicated as HL, where the proton preceding L is the oxime group proton. The lone ligand had one deprotonable oxime group proton. The protonation constants of protonated ETQX were calculated from potentiometric data by the BEST software program and are presented in Table 2.

Stability constants of the Cu(II)–ETQX complexes. Potentiometric titrations of the Cu(II)–ETQX system were performed at 25°C in 0.1 M KCl ionic medium. Initially, the solid ligand and the excess HCl solution were added to a potentiometric cell followed by addition of Cu(II) solutions with mole ratios of 1 : 1 and 1 : 2. The observed curves were shifted towards the lower pH region compared to the titration curve of protonated ETQX itself (Fig. 3, curves *2* and *3*). Three inflection points were observed at $m = 2$, $m = 3$, and $m = 4$ on the titration curves of the 1 : 1 and 1 : 2 Cu(II)–ETQX systems, where m is number of moles of

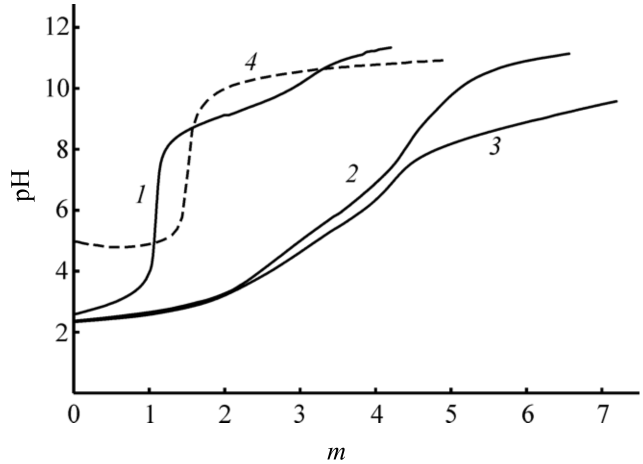


Fig. 3. Potentiometric titration curves for the Cu(II)-ETQX system at 25°C in $I = 0.1$ M KCl. (*1*) ETQX, (*2*) Cu(II) : ETQX (1 : 1), (*3*) Cu(II) : ETQX (1 : 2), and (*4*) Cu(II).

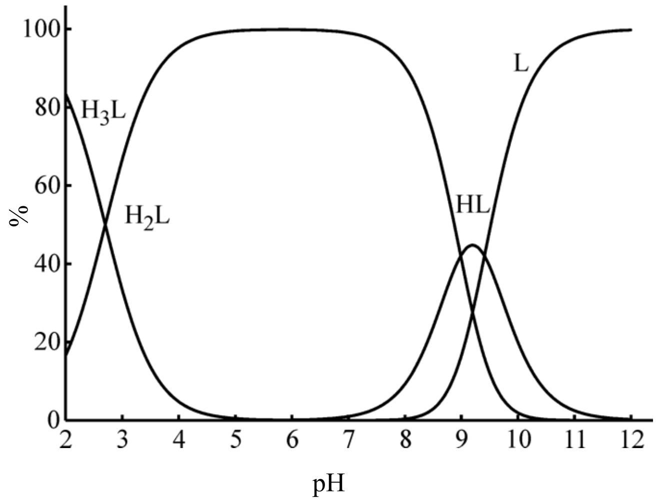


Fig. 4. Distribution of species as a function of pH for the protonated ETQX (H_3L^{2+}) system at 25°C in 0.1 M KCl.

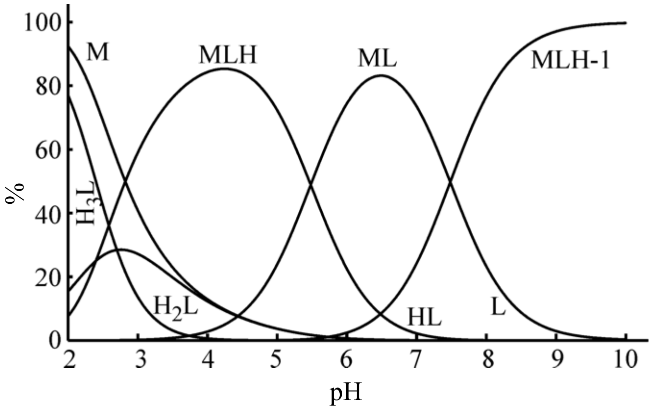


Fig. 5. Distribution of species as a function of pH for the Cu(II)–ETQX system, in the ratio 1 : 1 at 25°C and in 0.1 M KCl.

a base added per mole of metal. Experimental data indicated that, in the $m = 0.0–3.0$ buffer zone the CuL complex formed between Cu(II) and ETQX.

The stability constants of the complexes that formed in the Cu(II)–ETQX systems (1 : 1 and 1 : 2) were calculated by the BEST computer program (Table 3). The potentiometric titration curves of the Cu(II)–ETQX systems were shifted towards the lower pH region compared to that of the ligand and showed the titration of a total of three protons, indicating that one ligand binded to the metal ions.

Distribution diagram. The concentration distribution curves of the protonated ETQX system (in the absence of metal) are shown in Fig. 4. In this system, as the H_3L^{2+} concentration decreased, H_2L^+ reached the maximum concentration 100% in pH range ca 4.8–7.0. At pH 9.1, HL reached the maximum of ca 40%. L^- started to form at pH ca 8.0 and reached the concentration 100 % at pH 11.5 in the same system.

The concentration distributions of the complex species in the Cu(II)–ETQX systems could be obtained using the SPE software (Fig. 5). In the Cu(II)–ETQX systems, the $CuHL^{2+}$ complex started to form at pH ca 2 and reached the maximum concentration ca 86% within pH range 4–4.5. For the same system, at pH ca 6.5, the concentration of the CuL^+ complex was ca 85%, whereas the $CuLH_{-1}$ complex reached its maximum concentration over a rather basic region for Cu(II)–ETQX systems.

In the distribution diagrams of the Cu(II)–ETQX systems, $CuLH^+$ complex appeared at an acidic pH and in a higher ratio indicating that nitrogen atoms of the imine groups were coordinated to Cu(II) ions.

EXPERIMENTAL

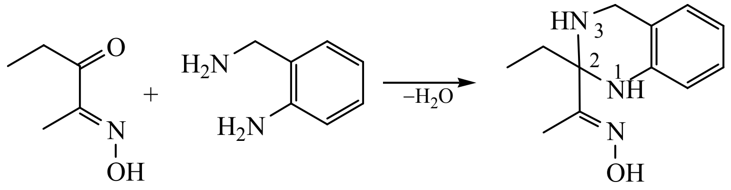
Materials and preparation of the solutions. All chemicals were provided by Merck, Aldrich and Sigma Chemical Co. and were used without further purification.

A copper(II) chloride solution was prepared by dissolving copper(II) chloride (99.9%) in concentrated HCl to prevent hydrolysis. The stock solution of copper(II) chloride was standardised complexometrically by Na_2EDTA [25]. The excess acid in the copper(II) stock solution was determined by potentiometric titrations as described previously [26–29]. A carbonate-free KOH solution (0.1 M) was standardised potentiometrically against potassium hydrogen phthalate standard [30, 31]. A hydrochloric acid solution (0.1 M) was prepared and standardised by titration (KOH). KCl used as a background electrolyte, was a Merck p.a. reagent. The ionic strength of all solutions was adjusted to 0.1 M by the addition of KCl. All solutions were prepared with analytical-grade water ($R = 18$ MΩ) in grade A glassware.

Synthesis of 2,3-pentanedione monoxime (PDO). PDO was carried out in accordance with the method presented in [32]. The structure of PDO was deduced from its FT-IR and NMR spectral data. FT-IR (KBr pellet), ν_{max}, cm^{-1}: 3326 (O–H); 2982, 2942 ($C–H_{alifatic}$); 1671 (C=O); 1015 (N–O). ^1H NMR spectra (DMSO-d_6), δ, ppm, *J,* Hz: 12.22 s (–OH, 1H, disappeared upon addition of D_2O); 2.40 q ($–CH_2–$, $J = 7.2$, 2H); 1.79 s ($–CH_3$, 3H); 0.96 t ($–CH_2–C\underline{H}_3$, $J = 7.2$, 3H). ^{13}C NMR spectrum (DMSO-d_6) δ, ppm: 199.79 (C=O); 154.93 ($C=N_{oxime}$); 30.13 ($–CH_2–$); 8.66 ($–CH_3$); 8.53 ($CH_2–\underline{C}H_3$).

Synthesis of ETQX. A solution of 2-aminobenzylamine (2-ABA) (20.0 mmol, 2.44 g) in 10 mL of absolute ethanol was added dropwise to a solution of PDO (20.0 mmol, 2.30 g) in 10 mL of absolute ethanol. The reaction mixture was stirred for 2 h at room temperature and stored for few days at room temperature. The white crystalline product was filtered, washed with cold ethanol and dried in air (Scheme 2). mp 159°C (DTA_{max}). Calculated, %: C 65.73; H 7.81; N 19.16. $C_{12}H_{17}N_3O$ (218.3 g/mol). Found, %: C 65.91; H 7.77; N 19.19. FT-IR (KBr pellet), ν_{max}, cm^{-1}: 3393, 3280 sh (N–H); 2877 br (O–H···N); 1606 s, sh ($C=N_{oxime}$); 885 m (N–O). UV-Vis (methanol), λ_{max}, nm ($\varepsilon \times 10^4$ M^{-1} cm^{-1}): 300 (0.24); 245 (0.99); 208 (3.00). ^1H NMR spectrum (DMSO-d_6) δ, ppm, *J,* Hz: 10.59 s (–OH, 1H, disappeared upon addition of D_2O); 6.82 d.t (H_{Ar}, $J = 8.0$, 1.6, 1H), 6.70

Scheme 2. Synthesis of ETQX.



PDO 2-ABA ETQX

d (1H, J = 7.2), 6.56 d.d (H_{Ar}, J = 6.8, 1.2, 1H), 6.39 d.t (H_{Ar}, J = 8.0, 1.2, 1H); 5.65 s (N^1H, 1H); 2.57 s (N^3H, 1H); 3.62 d ($-CH_2-N$, J = 16.4, 1H), 3.49 d (J = 16.4, 1H); 1.66–1.54 m ($-CH_2-$, 2H); 1.75 s ($-CH_3$, 3H), 0.82 t, (J = 7.6, 3H). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 157.22 ($C{=}N_{oxime}$); 144.66, 126.78, 125.65, 120.66, 115.68, 114.69 (C_{Ar}); 72.11 ($^{Alkyl}{>}C{<}$); 42.72 ($-CH_2-N$); 31.90 ($-CH_2^-$); 9.89 ($H_3\underline{C}-C{=}N$); 7.83 ($-CH_3$). LC–MS (methanol) m/z: 219.8 $[HL]^+$.

Synthesis of [Cu(HL')Cl]Cl. A solution of $CuCl_2\cdot 2H_2O$ (1.00 mmol, 0.17 g) in ethanol (5 mL) was added dropwise to a solution of ETQX (1.00 mmol, 0.22 g) in ethanol (10 mL) upon stirring at room temperature followed by stirred for 3 h at room temperature. The precipitated dark-green-coloured complex was named filtered off, washed with cold water and ethanol repeatedly and dried at room temperature. The complex was bis{3-(2-amino-benzylimino)-pentan-2-one oxime}copper(II) chloride (Fig. 6). mp: 146°C (DTA_{max}, decomp.). Calculates, %: C 40.74; H 4.84; N 11.88; Cu 17.96. $C_{12}H_{17}N_3OCl_2Cu$ (353.8 g/mol). Found, %: C 40.82; H, 4.43; N 12.25; Cu 17.81. FT-IR (KBr pellet), ν_{max}, cm^{-1}: 3323, 3279 sh (N–H); 3201 (O–H); 1612 m ($C{=}N_{imine}$); 1593 m ($C{=}N_{oxime}$); 898 w (N–O). UV-Vis (methanol), λ_{max}, nm ($\varepsilon \times 10^4\,M^{-1}\,cm^{-1}$): 619 (0.017); 316 (1.05); 237 (1.48); 206 (2.72). μ_{eff} = 1.73 BM. Molar conductance (methanol), Λ_M, $\Omega^{-1}\,cm^2\,mol^{-1}$ = 96.

Equipments. Potentiometric titrations were carried out in double-wall glass vessel in inert atmosphere (nitrogen gas) using a Schott TitroLine Alpha Plus automatic titrator equipped with a Schott combined pH electrode at (25 ± 0.1)°C using a VWR 11405. The titrator was connected to a computer, and automatic titrations were performed using a suitable computer program to control titrant delivery.

Molar conductivity of the Cu(II) complex was measured by using a WTW model inoLab 730 conductivity meter.

Magnetic susceptibility measurements were performed at room temperature with a Sherwood Scientific MK1 model magnetic susceptibility balance.

C, H and N microanalyses, metal analysis and mass spectroscopy were carried out at the Technical and Scientific Research Council of Turkey, TUBITAK Bursa Test and Analysis Laboratory.

UV-Vis spectra were registered in the methanol solution (10^{-4} M) of the compounds with ATI-Unicam UV2 spectrophotometer over the range of 800–200 nm.

^1H NMR and ^{13}C NMR spectra were recorded at 25°C on a Varian Mercury Plus 400 MHz spectrometer in DMSO-d_6.

FT-IR spectra were recorded over the 4000–400 cm^{-1} region with a Thermo-Nicolet 6700 Fourier-Transform Infrared Spectrometer by using KBr pellets.

Thermal analysis curves (TG and DTA) were registered using a Seiko Exstar 6200 thermal analyser in a dry-air atmosphere at the heating rate of 10°C/min for ETQX and at the heating rate of 5°C/min for the Cu(II) complex over the temperature range of 25–800°C using platinum crucibles.

Potentiometric titration. Potentiometric titrations were carried out in calibrated potentiometric cells. The standardised HCl solution was titrated with a KOH solution. Based on the titration data accumulated in the acidic region, the following equation was established:

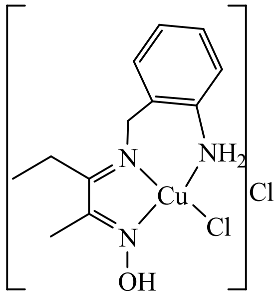


Fig. 6. Suggested structure of Cu(II) complex.

$$E, \text{mV} = E^0_{\text{cell}} + S\log [\text{H}^+] + E_\text{j},$$

where E^0_{cell} is the standard potential of the cell, S is the electrode slope and E_j is the liquid junction potential, which depends only on the ionic strength. When the potential values were measured for the ligand or metal + ligand solutions, pH values were calculated from the potential value using the above equation. From the titration data obtained in the basic region, K_w values were calculated from several separate [H^+] and [OH^-] measurements in 0.1 M KCl [25, 33]. The daily calculated K_w values were obtained between 13.60 and 13.70.

The ionic strength of the solutions was kept constant (0.1 M) using KCl solution, and the total volume of 50 mL was used for each titration. The potentiometric measurements were performed by titrating 50 mL of the titrant solution with the standard KOH solution until the formation of slightly insoluble species was traced. The overall experimental procedure involved the potentiometric titrations of the following solutions:

(a) 5 mL 0.1 M HCl + 5 mL 1 M KCl (for cell calibration);

(b) solution from (a) + 0.1 mmol ETQX + 0.2 mmol HCl (for the determination of the protonation constants of ETQX);

(c) solution from (b) + 0.1 mmol Cu(II) (for the determination of the stability constant of the ML complex);

(d) solution from (b) + 0.05 mmol Cu(II) (for the determination of the stability constants of the ML_2 complexes);

(e) solution from (a) + 0.1 mmol Cu(II) [for a pH range over which hydrolysis of the Cu(II) ion occurs].

Data processing. Computations of the protonation constants of the ligand and the stability constants of the binary complexes of Cu(II) based on potentiometric data were carried out using the BEST [33], software program which was used to minimise the standard deviation of the fit (σ_{fit}) between the observed and calculated pH values for the overall titration data. The protonation and stability constants were obtained as the average values of least three titrations. The potentiometric results were analysed using the SPE software program [33] and the distributions of species were drawn for ETQX and Cu(II)–ETQX systems.

CONCLUSIONS

The ligand ETQX was synthesised by the condensation of PDO with 2-aminobenzylamine (2-ABA). The FT-IR and NMR spectra of ETQX indicated that the ligand remained in the ring form. In FT-IR spectra of the Cu(II) complex of ETQX, the stretching vibration band was caused by the imine group that indicate the ligand conversion to the chain form in the Cu(II) complex and coordination to the metal ion in the chain fprm. In light of the foregoing discussion, we have proposed a square-planar geometry for the Cu(II) complex [Cu(HL')Cl]Cl.

Computer refinement of the titration data indicated the presence of CuL^+, CuLH^{2+} and CuLH_{-1} species in the binary complex systems.

Based on the physicochemical and spectral data discussed above it was assumed that the ligand behaved as an NNN tridentate coordinating with amine, imine and oxime nitrogen atoms.

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