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Spectra-structure relationship: Synthesis, characterization of copper(II) complexes with ibuprofenate, *o*-methoxybenzoate, *p*-ethoxybenzoate and single crystal X-ray structure determination of [*trans*-Cu(en)₂(H₂O)₂](L)₂ where en = ethylenediammine, L = *o*-methoxybenzoate/*p*-ethoxybenzoate

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ABSTRACT

To investigate the spectra–structure relationship, three new copper(II) complex salts of composition $[trans-Cu(en)_2(H_2O)_2](L_1)_2$ 2H₂O(1), $[trans-Cu(en)_2(H_2O)_2](L_2)_2(2)$ and $[trans-Cu(en)_2(H_2O)_2](L_3)_2$ (3) (where L₁ = ibuprofenate, L₂ = o-methoxybenzoate and L₃ = p-ethoxybenzoate) were obtained when ethylenediamine was added to 'Cu(L)₂' (L = L₁/L₂/L₃) in methanol–water solution. The intermediate 'Cu(L)₂' salts were prepared by reaction of copper sulphate with sodium salt of ibuprofen, o-methoxybenzoic acid or p-ethoxybenzoic acid, respectively, in aqueous medium in 1:2 molar ratio. The newly synthesized complex salts have been characterized by elemental analyses, spectroscopic techniques (UV/visible and IR), magnetic moment determinations and conductance measurements. X-ray structure determination revealed an ionic structure consisting of one $[trans-Cu(en)_2(H_2O)_2]^{2+}$, two $(C_9H_8O_3)^-$ ions in **3**. In these complex salts central metal ion copper(II) is coordinated by four nitrogen atoms, originating from two chelating ethylenediamine ligands and two oxygen atoms of two coordinated water molecules, showing distorted octahedral geometry around copper metal ion. Both of these structurally correlated octahedral $[trans-Co(en)_2(H_2O)_2]^{2+}$ species have shown absorption at $\lambda_{max} \approx 540$ nm in the UV/visible spectrum.

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1. Introduction

Copper is one of the trace elements essential to the healthy life of many plants and animals usually occurring as the part of prosthetic group of oxidizing enzymes (e.g. ascorbic acid oxidase, tyrosinase, laccase, monoamine oxidase, cytochrome oxidase and galactose oxidase). These oxidases, high molecular weight proteins containing 0.03–0.05% of copper, play a vital role in biological oxidation and reduction processes [1]. Copper containing proteins/enzymes (cytochrome *c* and superoxide dismutase) are involved in important biochemical functions like reduction of oxygen and destruction of harmful superoxide anion, and the disease associated with copper deficiency is anaemia and copper accumulation is Wilson's disease. Antiseptic properties of copper(II) salts and bis-copper(II)-3,5-diisopropyl salicylate as a promising radiation recovery agent [1b] for application in nuclear warfare and cancer patients are also noteworthy for providing impetus to the chemistry of copper(II) complexes.

A thematic issue on biomimetic inorganic chemistry [2] has recently appeared in literature, which contains extensive study of copper complexes. Besides this, a large number of papers on copper complexes continue to appear in almost all the top journals of inorganic chemistry. Cu(hfac)₂ (hfac = hexafluoroacetylacetonate) is widely used in the synthesis of molecular magnets [3-4]. Replacement of the native mononuclear type I copper ion in cuperedoxins with other metals has been utilized for decades to facilitate the investigation of this key family of metalloproteins [5]. Furthermore, inorganic chemistry of copper(II) is very fascinating because of a number of reasons such as (i) copper(II) exhibits a variety of coordination numbers from 4 to 8 with associated geometries, (ii) copper(II) complexes are liable to Jahn-Teller distortion, (iii) the anionic ligand may be non-coordinated or coordinated and (iv) it is one of the constituent metal ions in most of the superconductors. In the last decade, several reports have focused on the construction of copper(II) complexes with cyclodextrin derivatives [6–9] which find applications as chiral recognition receptors.

Complexation behaviour of carboxylate ligands becomes significant as many of the non-steroidal drugs like ibuprofen sodium (A) and diclofenac sodium (B) contain carboxylate group (as shown in Scheme 1). Carboxylates are versatile ligands, which can exhibit a

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varity of coordination modes [10] and it is essential to have control over the binding of the carboxylate groups to metal ions in a specific manner. A guick and efficient characterization is possible if the spectral behaviour (especially the UV absorption) becomes characteristic feature for a specific coordination mode of a complexing ligand. That is, a positive correlation is attainable through spectra-structure relationship. In this regard, it is worth mentioning that, all the three complex salts reported in this paper showed a maximum UV absorption (λ_{max}) around 540 nm. A detailed structural study is essential to establish a complete relationship between the spectral properties and the specific coordination modes of L₁ to L₃. Thus, in continuation of our interest in Cu(II) complexes [11], this paper reports the synthesis and characterization of *trans*-diaguabis(ethylenediamine)copper(II) with L₁, L₂, and L_3 , where L_1 = ibuprofenate, L_2 = *o*-methoxybenzoate, L_3 = *p*-ethoxybenzoate, and single crystal X-ray structures of trans-diaquabis(ethylenediamine)copper(II)o-methoxybenzoate and diaquabis(ethylenediamine)copper(II)p-ethoxybenzoate.

2. Experimental

2.1. Material

Analytical grade reagents were used throughout this work without any further purification.

2.2. Instruments

Carbon, Hydrogen and Nitrogen were estimated micro-analytically by automatic Perkin-Elmer 2400 CHN elemental analyzer and copper was determined gravimetrically by standard method [12]. FT-IR spectra were recorded as KBr pellets on Perkin-Elmer Spectrum RXFT-IR system. UV/visible spectra were recorded in H₂O using HITACHI 330 Spectrometer. Conductance measurements were performed on Pico Conductivity Meter (Model CNO4091201, Lab, India) in aqueous medium at 25 °C by using double distilled water. The specifications of apparatus used for magnetic measurements were as: pole face diameter, 10.2 cm; pole gap, 4.0 cm; current, 7.0 A; magnetic field, 6 kG.

2.3. Synthesis

2.3.1. Synthesis of $Cu(en)_2(L_1)_2(H_2O)_2$

0.5 g (0.0020 mol) of CuSO₄·5H₂O was dissolved in 20 ml of water taken in a beaker. In another beaker 0.160 g (0.0040 mol) of sodium hydroxide and 0.826 g (0.0040 mol) of lbuprofen were dissolved in minimum amount (20 ml) of water. When both solutions were mixed, a light ocean blue coloured precipitated product was obtained, which was filtered through fine filter paper and washed with cold water and alcohol. The product obtained was dried in air. The precipitated product was suspended in water-methanol mixture and ethylenediamine was added to this solution drop wise till colour of the solution changed to dark blue. The solution was allowed to evaporate slowly at room temperature. After

one week, blue coloured crystalline product was obtained. The newly synthesized complex salt was sparingly soluble in water, soluble in methanol and dichloromethane but insoluble in acetone. The complex salt decomposed at 348 K. Anal. Calcd. $Cu(en)_2(L_1)_2(-H_2O)_2$: C 57.18%, H 8.57%, N 8.89%, O 15.25%, Cu 10.08%; Found: C 56.91%, H 8.07%, N 8.03%, O 14.87%, Cu 9.04%.

2.3.2. Synthesis of $Cu(en)_2(L_2)_2(H_2O)_2$

CuSO₄·5H₂O (0.5 g 0.0020 mol) was dissolved in 20 ml of water. In another beaker 0.159 g (0.0040 mol) of sodium hydroxide and 0.664 g (0.0040 mol) of *o*-methoxybenzoic acid were dissolved in minimum amount (20 ml) of water. On mixing two solutions, dark blue coloured precipitated product was obtained. The dark blue coloured product was dissolved in water–methanol solution and then ethylenediamine was added to the solution drop wise till colour of solution changed to dark blue. The solution was allowed to evaporate slowly at room temperature, after six days, blue coloured crystals were obtained. The newly synthesized complex salt was freely soluble in water and ethanol but insoluble in chloroform. The complex salt decomposed at 465 K. Anal. Calcd. Cu(en)₂(L₂)₂(H₂O)₂: C 46.02%; H 5.75%, N 10.73%, O 24.54%, Cu 12.17%; Found: C 45.48%, H 6.02%, N 11.01%, O 23.13%, Cu 11.03%.

2.3.3. Synthesis of $Cu(en)_2(L_3)_2(H_2O)_2$

Copper sulphate pentahydrate (0.5 g, 0.0020 mol) was dissolved in 20 ml water taken in a beaker. In another beaker 0.159 g (0.004 mol) of sodium hydroxide and 0.664 g (0.004 mol) of *p*-ethoxybenzoic acid were dissolved in minimum amount of water. When both the solutions were mixed, light blue coloured precipitated product was obtained. The product was suspended in water-methanol solution. Ethylenediamine was added drop wise to the solution till colour changed to dark blue. Blue coloured crystals appeared after one week from the solution when it was allowed to evaporate slowly at room temperature. The newly synthesized complex salt was freely soluble in water and methanol but insoluble in dichloromethane. The complex salt decomposed at 483 K. Anal. Calcd. Cu(en)₂(L₃)₂(H₂O)₂: C 48.04%, H 6.91%, N 10.19%, O 23.29%, Cu 11.56%; Found: C, 47.09, H 6.41%, N 11.17%, O 22.43%, Cu 11.03%.

2.4. X-ray crystallography

Good single crystals of **2** and **3** suitable for X-ray diffraction studies were grown from aqueous solution by slow evaporation method. X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). Intensities were corrected for Lorentz, polarization and absorption effects [13]. Crystal data, data collection and refinement parameters are summarized in Table 1 and selected bond length and angles are reported in Table 2. The structure was solved by direct methods with the SIR97 program [14] and refined by full-matrix least squares using the SHELXL-97 program [15]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically; hydrogen atoms were found in the Difference Fourier map and refined isotropically. All other calculations were performed using the programs WinGX [16] and PARST [17].

3. Results and discussion

3.1. Synthesis

The intermediate 'Cu[L]₂' salts were obtained when copper sulphate pentahydrate was reacted with sodium salt of ibuprofen, *o*-methoxybenzoic acid and *p*-ethoxybenzoic acid, respectively, in 1:2 molar ratio in aqueous medium. In all cases light blue coloured precipitated product was obtained.

Crystal data, data collection and refinement parameters of complex salts **2** and **3**.

Crystal data	2	3
Chemical formula	(CuC ₄ H ₂₀ N ₄ O ₂).2(C ₈ H ₇ O ₃)	$(CuC_4H_{20}N_4O_2).2(C_9H_9O_3)$
M _r	522.05	550.10
Cell setting, space group	Triclinic, P1	Monoclinic, C2/c
a, b, c (Å)	8.0780(2), 11.8304(3), 12.7560(3)	34.5702(7), 7.1682(2), 10.5284(2)
α, β, γ (°)	81.0440(12), 81.1030(12), 82.8840(9)	94.6070(11)
V (Å ³)	1183.45(5)	2600.57 (10)
Ζ	2	4
$D_x ({ m Mg}{ m m}^{-3})$	1.465	1.405
Crystal form, colour	Needle, violet	Plate, blue
Crystal size (mm)	$0.35 \times 0.12 \times 0.09$	$0.45 \times 0.40 \times 0.09$
No. of measured, independent and observed reflections	19596, 5683, 4201	15369, 3120, 2427
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R _{int}	0.056	0.050
θ_{\max} (°)	28.0	28.0
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.115, 1.04	0.048, 0.135, 1.05
No. of reflections/No. of parameters	5683/435	3120/237
Weighting scheme	Calculated $w = 1/[\sigma_2(F_o^2) + (0.0646P)^2 + 0.1245P]$ where	Calculated $w = 1/[\sigma_2(F_o^2) + (0.0583P)^2 + 4.9054P]$ where
	$P = (F_o^2 + 2F_c^2)/3$	$P = (F_o^2 + 2F_c^2)/3$
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (e Å ⁻³)	0.36, -0.56	0.28, -0.34

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Selected bond lengths and angles (Å and $^\circ)$

Complex salt 2			
Cation			
Cu1-01	2.634(2)	Cu1-N4	2.007(2)
Cu1-02	2.709(2)	Cu1–N3	2.003(2)
Cu1-N2	2.009(2)	Cu1–N1	2.004(2)
N1-Cu1-N2	84.81(9)	N2-Cu1-N3	95.09(9)
N1-Cu1-N4	95.04(9)	N3-Cu1-N4	85.05(9)
Anion			
03-C5	1.260(3)	04-C5	1.235(3)
06-C13	1.252(4)	07-C13	1.240(3)
C5–C6	1.504(3)	$C-C_{ring}$ (av.)	1.386(4)
C11-05	1.375(3)	C5-C12	1.421(3)
C13-C14	1.514(3)	08-C19	1.375(3)
08-C20	1.419(3)		
O3-C5-C6	116.7(2)	04-C5-C6	118.5(2)
03-C5-03	124.8(2)	C11-O5-C12	107.8(2)
C19-08-C20	118.5(2)	O6-C13-O7	125.6(2)
06-C13-C14	118.5(2)	07-C13-C14	113.9(2)
Complex salt 3			
Cation			
Cu1-01	2.553(2)	Cu1–N1	2.016(2)
Cu1–N2	2.021(2)		
N1-Cu1-N2	84.70(10)	01-Cu1-N2	89.34(9)
01-Cu1-N1	90.93(9)		
Anion			
02-C9	1.253(4)	O3–C9	1.253(3)
C3-C9	1.512(3)	C6-04	1.373(3)
04-C10	1.434(3)	C-C _{ring} (av.)	1.387(4)
02-C9-03	124.4(2)	02-C3-C9	117.8(2)
O3-C9-C3	117.8(2)	C6-O4-C10	117.3(3)

$$\mathsf{CuSO}_4 + 2\mathsf{NaL} \xrightarrow{\mathsf{H}_2\mathsf{O}} \mathsf{Cu}[\mathsf{L}]_2 + \mathsf{Na}_2\mathsf{SO}_4 \tag{1}$$

where L = ibuprofenate, *o*-methoxybenzoate, *p*-ethoxybenzoate.

The precipitated products were filtered, washed with water followed by alcohol and dried 'Cu[L]₂' salts were separately dissolved/ suspended in water-methanol solution. To these solutions ethylenediamine was added drop wise with continuous stirring until dark blue solutions resulted, which when allowed to evaporate at room temperature, gave the dark blue micro-crystalline solid/single crystals, in accordance with Eq. (2).

$$Cu(L)_2 + 2en \stackrel{H_2O-MeOH}{\rightarrow} Cu(en)_2(L)_2(H_2O)_2 \tag{2}$$



Fig. 1. Probable structures of copper(II) complexes: $[Cu(en)_2(H_2O)_2](L_1)_2$ (A) or $[Cu(en)_2(L)_2]\cdot 2H_2O$ (B).

The elemental analyses corresponded to the composition of the complex salts consistent with either of the two structural formulae $[Cu(en)_2(H_2O)_2](L_1)_2$ or $[Cu(en)_2(L)_2]\cdot 2H_2O$, they may have cis or trans conformations depending upon the position of ligands with respect to each other (as shown in Fig. 1).

3.2. Molar conductance

Conductance measurements were carried out at 25 °C in aqueous medium and plots of Λ (molar conductance) versus $C^{1/2}$ (square root of concentration) were drawn. When the concentration was extrapolated to zero, it gave $\Lambda_o = 248$, 238 and 258 Sm² mol⁻¹ for Cu(en)₂(H₂O)₂(lbf)₂, Cu(en)₂(H₂O)₂(*o*-methoxybenzoate)₂ and Cu(en)₂(H₂O)₂(*p*-ethoxybenzoate)₂. These values fall in the range for 1:2 electrolytes [18], which was confirmed by single crystal X-ray structure in the case of **2** and **3**.

3.3. Spectroscopy

Infrared spectra of the newly synthesized complex salts **1–3** have been recorded in the region 4000–400 cm⁻¹ and tentative assignments have been made on the basis of earlier reports in literature [19]. The bands in the region, 443–461 cm⁻¹ are assigned to v(Cu-N), 535–541 cm⁻¹ are assigned to v(Cu-O), 1606–1624 cm⁻¹ are assigned to v(C=C), and 1570–1590 cm⁻¹ are assigned to $v_s(NH_2)$. The IR bands due to $v_{as}(OCO)$, $v_s(OCO)$ are observed in the region 1528–1555 and 1381–1394 cm⁻¹. In complex salts **2** and **3** IR bands at 1236 and 1254 cm⁻¹ are assigned to v(C=O). The IR bands in the region 3030–3160 cm⁻¹ showed the presence of unsaturation in the complex salts due to the v(=C-H) stretching. The bands in the region 3267–3265 cm⁻¹ are characteristic of antisymmetric stretching vibrations of N–H bond of



Fig. 2. UV/visible spectra of complex salt 1, 2 and 3. (λ_{max} = 544, 546 and 542, respectively).

ethylenediamine molecules attached to copper metal ion. The value of \triangle obtained by subtracting $v_{as}(OCO)$ and $v_s(OCO)$, falls in the region of 160–170 cm⁻¹ which corresponded to ionic carboxylates [19b].

The electronic spectra of the newly synthesized complex salts have been recorded in H₂O. The solution state UV/visible absorption spectrum of Cu(en)₂(H₂O)₂(L)₂ complex salts **1–3** showed strong absorption around 540 nm (as shown in Fig. 2) due to the d–d transitions typical of octahedral low spin copper(II). These values of λ_{max} observed for title complex salts are comparable [20] with those of complex salt containing [*trans*-Cu(en)₂(H₂O)₂]²⁺ cation. In our earlier studies of copper(II) complexes with sulphonates and *p*-nitrobenzoate, the λ_{max} values around 540 nm were observed where [*trans*-Cu(en)₂(H₂O)₂](anion)₂ type complex salts were formed. Therefore, the composition of complex salts corresponded to probable structural formula **(A)** (Fig. 1). [Cu(en)₂(H₂O)₂](L)₂.

For a particular metal ion, the magnitude of the ligand field splitting parameter for octahedral complexes, Δ_0 , depends on the nature of the ligand. It is to be stressed that these complexes can only be considered as approximately octahedral because of the Jahn–Teller distortion expected for a d⁹ ion. This distortion has been clearly demonstrated for [Cu(en)₂X₂] complexes in the solid state [21].

3.4. Magnetic measurements

Copper in +2 oxidation state has spin only magnetic moment of 1.73 BM but due to spin orbit coupling, higher values are often ob-



Fig. 3. ORTEPIII view and atom numbering scheme for **2**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn as dashed lines.



Fig. 4. ORTEPIII view and atom numbering scheme for **3**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are drawn as dashed lines.

served. Normally those copper(II) compounds having ionic or weak covalent bonds have moments at room temperature in the range 1.9–2.2 B.M. Compared to 1.72–1.82 BM for those having strong covalent bonds [22]. The Gouy's method has been used for the measurement of magnetic susceptibilities of the complex salts at room temperature and the values observed are 1.96, 1.92, 1.95 BM for complex salts **1**, **2** and **3**, respectively. The values observed for title complex salts corresponded to the ionic nature of the complexes.

4. Crystal structure

4.1. Coordination geometry and bonding

The structure of the copper(II) complex salts **2** and **3** were unambiguously established by single crystal X-ray crystallography.

Table 3

Hydrogen bonding parameters (Å, $^\circ)$ of ${\bf 2}$ and ${\bf 3}$

Hydrogen bond	D-H	DA	HA	D-H.A
Complex salt 2				
N1-H2…06	0.93(4)	3.107(3)	2.30(3)	146(3)
N3-H1…O3	0.83(4)	2.998(3)	2.26(3)	149(3)
N4-H19…O6	0.77(4)	3.004(3)	2.32(3)	147(3)
01-H33…03	0.78(5)	2.794(3)	2.04(5)	162(4)
02-H32…06	0.74(5)	2.743(3)	2.05(5)	155(5)
N1-H3…O1 ⁱ	0.78(3)	3.240(3)	2.54(3)	151(3)
01-H31…04 ⁱⁱ	0.80(4)	2.957(3)	2.19(4)	159(4)
N4-H22…O4 ⁱⁱ	0.85(3)	2.954(3)	2.12(3)	164(3)
02-H27…07 ⁱⁱⁱ	0.84(4)	2.724(3)	1.94(4)	153(4)
N2–H23…O7 ⁱⁱⁱ	0.83(3)	2.912(3)	2.16(3)	151(3)
Complex salt 3				
01-H7…02	0.93(4)	2.781(3)	1.86(4)	167(4)
N1-H2…O3	0.91(4)	3.005(3)	2.14(4)	160(3)
N1–H3…O2 ^{iv}	0.95(3)	3.170(3)	2.36(3)	143(3)
01–H8…03 ^v	0.82(4)	2.770(3)	1.97(4)	166(4)
N2-H15…O2 ^{vi}	0.99(4)	3.021(3)	2.11(4)	151(3)
N2-H14…O3 ^{vii}	0.90(4)	3.148(3)	2.35(4)	147(3)

Symmetry codes: (i) -x - 1, 1 - y, -z; (ii) -x, 1 - y, -z; (iii) -x - 1, -y, -z; (iv) x, -y-1, z-1/2; (v) 1/2-x, -y-3/2, -z; (vi) x, y + 1, z; (vii) x, -y-1, z + 1/2.



Fig. 5. Hydrogen bonding arrangement in the crystal of 2.



Fig. 6. Unit cell packing diagram for 2(a) and 3(b) (view along b axis).

In **2**, the asymmetric unit contains one *p*-ethoxybenzoate anion and a half of the $[trans-Cu(en)_2(H_2O)_2]^{2+}$ cation, while in **3**, the cation lies on an inversion center. ORTEPIII [23] view of the complex salts 2 and 3 are shown in Figs. 3 and 4. In both the complex cations, two chelating ethylenediamine molecules coordinated with copper metal ion and the slightly distorted octahedral coordination is completed by two water O atoms in axial positions (Figs. 3 and 4). The values of T parameter [24] (indicating the degree of tetragonal distortion about the Cu(II) atom) in the complex salts 2 and 3 are 0.75 and 0.79 which are within the range 0.76-0.84 reported for such complex salts [25]. A comparison of T parameter and structural parameters of the present complex salts with those of other related Cu(II) complexes showed a substantial agreement for bond lengths and angles (given in Table S1 in Supplementary material). The C-O distances in the carboxylate anions of the two complex salts (Table 2) are very similar and are typical of delocalized bonds. Hydrogen-bonding parameters are reported in Table 3.

4.2. Packing

In both crystals, the packing architecture is mainly controlled by the formation of O–H…O hydrogen bonds, involving O–H groups of the coordinated water molecules as donors and the oxygen atoms of the carboxylate anions as acceptors. The structures are made more robust by additional N-H--O interactions. The H-bonding parameters are reported in Table 3. The O…O contact distances, on average 2.80(9) and 2.789(1) Å for 2 and 3, respectively, are longer than expected for Charge Assisted Hydrogen Bonds, that are usually in the range 2.45–2.65 Å [26], due to the fact that the donor atoms are involved in the formation of the additional N-H...O bonds. Taking into consideration only the strongest interactions, the hydrogen-bond pattern can be described in terms of graph-set approach [27]. In both cases there is the formation, by symmetry, of the same $R_4^4(12)$ motif (R = ring) shown in Fig. 5, which, in turn, leads to two $C_2^2(8)$ chains running, in both structures, along the *b* axis. The hydrogen bond links in the crystal lattice resulted the separate columns formation by the cations and the anions (Fig. 6), the only difference between the two structures being the mutual orientation of the benzoate derivatives, i.e. the carboxylate anions are arranged in the herringbone pattern in **2** while in **3** they are disposed in a parallel way.

5. Conclusions

Copper(II)arylcarboxylates react with ethylenediamine (en) in water–methanol solution to form dark blue coloured crystalline ionic solids in which two en molecules displace four water molecules from the coordination sphere of the hexaaqua copper(II) complex (in general). On the basis of physico-chemical data available ($\lambda_{max} \approx 540$), the trans octahedral ionic structure, predicted in the solution state, has been confirmed by single-crystal X-ray structure determinations of [*trans*-Cu(en)₂(H₂O)₂](L)₂: **2**, **3** in the solid state. Probably, the same is true for ibuprofenato complex salt **1** also.

Thus, we have shown that the electronic spectrum may be used to (i) predict the formation of ionic [*trans*-Cu(en)₂(H₂O)₂]²⁺and aryl carboxylates anions in solution which may be confirmed by the solid state X-ray structure determination of the single crystals (obtained after evaporation of solution at room temperature) and (ii) complex salts are anhydrous and their formation is unaffected by the substitution on the benzene ring. Further studies are in progress to establish this spectra–structure relationship for other copper(II) aryl carboxylate complex salts in the presence of ethylenediamine ligand.

Appendix A. Supplementary data

Crystallographic data for complex salts **2** and **3** have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 691637 and CCDC 691638. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2008.08.003.

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