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Syntheses of mixed chelate copper(II) complexes containing β-ketoaminato and diamine ligands: Solvatochromism study

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ABSTRACT

Three new mixed-chelate Cu(II) complexes incorporating *N,N,N′,N′*-tetramethylenediamine (tmen) or *N,N*-dimethyl,*N′*-benzyl-ethylenediamine (dmben) as diamine chelate and a β-ketoaminato such as 4-amino-3-penten-2-onato (APO) or 3-amino-3-phenyl-2-buten-1-onato (APBO) with the general formula [Cu(β-ketoamine)(diamine)]ClO_4 were prepared and characterized. Their solvatochromic properties were studied by visible spectroscopy. X-ray crystal analysis confirmed that copper (II) ion in [Cu(APO)(tmen)]ClO_4 and[Cu(APBO)(tmen)]ClO_4 is almost in a square planar environment. Structure of [Cu(APO)(dmben)]ClO_4 was investigated by DFT calculation. The solvent-dependent visible spectroscopic absorption maxima, ν_{max}, were analyzed using stepwise multiple linear regression (SMLR) method to find the best model explaining the observed positive solvatochromism. The analysis demonstrated that among different solvent parameters, donor number (DN) is a dominant factor responsible for the shift in the d–d absorption band of the complexes to the lower wavenumber with increasing its values. The importance of steric effect in the diamine ligand and more delocalization of pi-bands in the β-ketoamine on the spectral and SMLR measurements are discussed.

1. Introduction

Through the past decade, chromotropism behaviors of inorganic complexes have been interested and investigated by many researchers [1–3]. Chromotropism means the reversible color transformation of the materials due to the surrounding physical and chemical conditions such as temperature (thermochromism), solvent (solvatochromism), pressure (piezochromism), light (photochromism) and electro-redox reaction (electrochromism) [4]. This phenomenon has many applications in thermo-sensitive, imaging, photo-switching and sensor materials [5,6]. One of the most attractive applications in inorganic chemistry is the use of solvatochromism behavior of complexes in Lewis acid–base indicators [7]. The origin of solvatochromism phenomena in metal complexes are classified into two general types [8,9]; in the first type, metal complexes in solution are interacted by solvent molecules in a direct fashion due to the direct attachment of the solvent molecules onto metal center and by indirect interactions between solvent molecules and ligands in the second type. In copper(II) and nickel(II) complexes with square planar structures the first type solvatochromism often observed while coordinatively saturated complexes are examples of the second type. Although there are a vast collection of solvatochromic complexes and compounds, a certain class of complexes such as mixed-chelate complexes of copper(II) exhibit considerable color change over a wide range of solvent used [1,10,11]. This is due to presence of strong John–Teller effect in these complexes, the d–d transition of copper(II) can be shifted because of the interactions of the solvent molecules with the axial sites of the copper center. Although there are many reports for syntheses and solvatochromic properties of mixed-chelate copper(II) complexes derived by β-diketones and diamines [12–15], based on our knowledge, such investigations have not been employed on synthesis and solvatochromism of mixed-chelate complex containing β-ketoaminato. By now, only some reports are available in literature concerning preparation of bis(β-ketoaminato) complexes and their properties and applications [16–20]. Therefore, the solvatochromism of this class of mixed-chelate complexes is still unexplored. In this report we synthesized and characterized three new mixed-chelate copper(II) complexes with a general formula [Cu(β-ketoamine)(diamine)]ClO_4 shown in Fig. 1, where β-ketoamine is 4-amino-3-penten-2-onato (APO) or 3-amino-3-phenyl-2-buten-1-onato (APBO) and diamine stands for *N,N*-dimethyl,*N′*-benzylethylenediamine (dmben) or *N,N,N′,N′*-tetramethylethylenediamine (tmen). Furthermore, solvatochromism behaviors of the mixed-chelate complexes in a number of organic solvents have been investigated. The effects of substitutions attached to the diamine and β-ketoaminato ligands on the solvatochromism of these complexes have been examined. There

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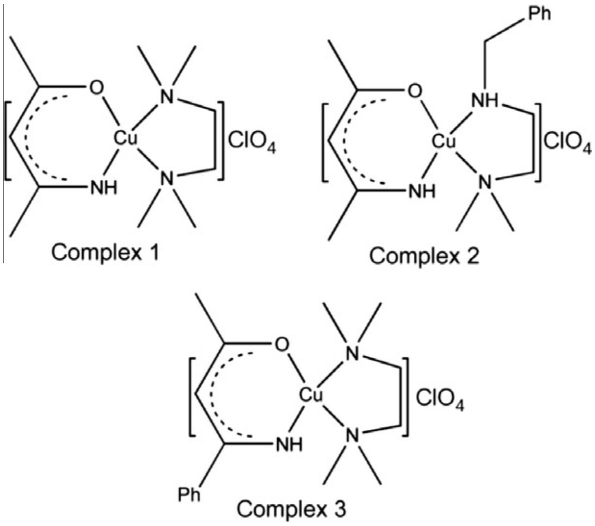

Fig. 1. The three complexes used in this study.

are some empirical scales due to nature of solute–solvent interaction such as Dimroth and Reichardt's ET(30), Kosower's Z, Kamlet and Taft's α, β, π*, dielectric constant, ε and Gutman's donor, DN and acceptor numbers, AN [21–26]. While ET(30) is used widely in organic compounds [27], DN and AN have spread use for transition metal complexes [3]. Utilization of some statistical software like SPSS has been interested recently by researches to find an optimized model to describe the relation between ν_{max} in absorption spectra of complexes in solution and the solvent's polarity scales [1,10,11]. In this study, correlation between maximum wavenumber of the complexes and solvent parameters (DN, AN, ET(30), α, β, π*) was studied using multiple linear regression (MLR) method.

2. Experimental

2.1. Materials and methods

N,N-dimethyl,*N′*-benzyl-ethylenediamine [28], APO [29] and the complexes of $[Cu_2(OH)_2(tmen)_2](ClO_4)_2$, $[Cu_2(OH)_2(dmben)_2](ClO_4)_2$ [30] and $[Cu(APO)_2]$ [31], were prepared according to published procedures. All solvents were spectral-grade and all other reagents were used as received. All the samples were dried to constant weight under a high vacuum prior to analysis. *Caution: perchlorate salts are potentially explosive and should be handled with appropriate care.* Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on 1.00×10^{-3} M samples in selected solvents. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument. The electronic absorption spectra were measured using a Braic2100 model UV–Vis spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400DRX Spectrometer. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer. The following solvents were used for solvatochromic study: dichloromethane (DCM), nitromethane (NM), nitrobenzene (NB), benzonitrile (BN), acetonitrile (AN), propionitrile (PN), acetone (Ac), tetrahydrofuran (THF), ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pyridine (Py) and hexamethylphosphorictriamide (HMPA).

Table 1
Crystal data and structure refinement for the complex of **1** and **3**.

Compound	$[Cu(APO)(tmen)]ClO_4$, 1	$[Cu(APBO)(tmen)]ClO_4$, 3
Formula	$C_{44}H_{96}Cl_4Cu_4N_{12}O_{20}$	$C_{16}H_{26}ClCuN_3O_5$
Formula weight	1509.29	439.39
Color	dark blue	dark blue
T (K)	296(2)	296(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	*P*21/c	*P*bca
Crystal size (mm)	0.45 × 0.26 × 0.16	0.49 × 0.21 × 0.14
Unit cell dimensions		
a (Å)	15.8361(7)	15.0967(5)
b (Å)	30.3950(12)	15.7021(5)
c (Å)	15.2061(7)	16.8468(6)
β (°)	106.291(2)	90
V (Å^3)	7015.4(5)	3993.5(2)
Z	4	8
Calculated density (Mg/m^3)	1.427	1.462
$F(000)$	3152	1832
θ (°)	1.34–27.00	2.23–27.00
Index ranges	$-20 \leqslant h \leqslant 20$, $-38 \leqslant k \leqslant 38$, $-18 \leqslant 19$	$-19 \leqslant h \leqslant 19$, $-20 \leqslant k \leqslant 20$, $-21 \leqslant 21$
Reflections collected	197186	190140
Independent reflections R_{int}	15342 (0.0558)	4361 (0.0272)
Completeness to 2 θ = 27.00 (%)	100.0	100.0
Absorption correction	multi-scan	multi-scan
Data/restraints/parameters	15342/6/811	4361/0/276
Final R indices[a]$[I > 2\sigma(I)]$[b]	$R_1 = 0.0533$, $wR_2 = 0.1441$	$R_1 = 0.0331$, wR2 = 0.0892
Goodness-of-fit on F^2[c]	1.036	1.072
R indices (all data)	$R_1 = 0.1010$, $wR_2 = 0.1815$	$R_1 = 0.0404$, $wR_2 = 0.1061$
Largest difference in peak and hole (e Å^{-3})	0.830 and −0.556	0.381 and −0.496

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR = [(\sum[F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]$½.
[c] $S = \sum[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]$½.