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Solvato- and thermochromism study in oxalato-bridged dinuclear copper(II) complexes of bidentate diamine ligands

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Two new oxalato complexes of the formula $[Cu_2(L)_2(\mu\text{-ox})(MeOH)_2](ClO_4)_2$ (**1**) and $[Cu_2(L)_2(\mu\text{-ox})](NO_3)_2$ (**2**), where ox = oxalato and L = *N,N′*-dibenzylethane-1,2-diamine, were prepared and characterized by elemental analysis, IR and UV–vis spectroscopies and molar conductance measurements. The crystal structure of compound **1** was determined by single-crystal X-ray analysis. The compounds are solvatochromic and their solvatochromism was studied with different solvent parameter models using the stepwise multiple linear regression (SMLR) method with SPSS/PC software. It was demonstrated that the donor power of the solvent plays the most important role in the observed positive solvatochromism of the compounds. The complexes show irreversible thermochromism in solution due to the substitution of the weakly coordinated counter ions and coordinated solvents by solvent molecules.

1. Introduction

Bridged dinuclear and polynuclear copper(II) complexes have been the subject of current attention for chemists due to their ability to communicate electronic interactions between paramagnetic centers separated by connectors. It has been demonstrated that among the various types of bridging ligands, the oxalate anion ($C_2O_4^{2-}$) is an outstanding ligand for metal ions because it is a good chelating agent of 3d ions and also a good transmitter of magnetic and electronic interactions. The oxalato ligand can yield complexes having several kinds of nuclearity, for example mononuclear [1,2], homodinuclear [3–5], heterodinuclear [6], homotrinuclear [7–12] and heterotrinuclear [13] complexes.

Chromotropism is the change in color of a substance due to the physical and chemical properties of its ambient surrounding medium, such as temperature, solvent, pH and ion. Chromotropism properties of inorganic compounds have been studied during the past four decades [14–17]. This phenomenon has many applications in thermo-sensitive, imaging, photo-switching sensor materials [18,19], pollutant sensor [20] and as Lewis acid-base indicators [15]. Among the metal complexes whose color changes are due to d–d transitions, the copper(II) ion can be an excellent candidate due to its diverse coordination numbers, various geometrical structures and the presence of a strong Jahn–Teller effect. Mixed-chelate copper(II) complexes containing β-diketonate and diamine ligands have exhibited notable solvatochromism properties [21,22,14]. However, these complexes suffer from low color intensity because their colors originate from the d–d transitions of the copper(II) ions. Thus, the preparation of complexes with higher molar absorptivity values is extremely desirable. In this regard, mixed-chelate oxalato-bridged dinuclear complexes, as shown in Fig. 1, were synthesized and their chromotropism properties were studied. It was expected that the dinuclear copper(II) complexes would show higher molar absorptivity in comparison with their analogous mononuclear complexes.

2. Experimental

2.1. Materials

The diamine ligand was prepared according to a published procedure [23,24]. All chemicals were of reagent grade quality. The solvents used in the solvatochromism study were spectral-grade, purchased from commercial sources and used as received. These solvents are as follows: 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).

Caution! Perchlorate salts are potentially explosive and should be handled with appropriate care.

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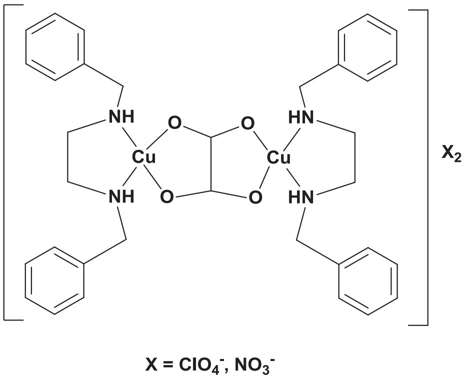

Fig. 1. The complexes used in this study.

2.2. Physical measurements

Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on concentrations of 1.00×10^{-3}, 2.00×10^{-4}, 3.00×10^{-4} and 5.00×10^{-4} M of samples in the selected solvents. Then for each solvent, a curve was plotted by drawing the molar conductance versus the concentration of the sample. The curve was then extrapolated to an infinitely dilute solution to obtain the molar conductance value. Infrared spectra were recorded using KBr disks and a Bruker FT-IR instrument. The electronic absorption spectra were measured with a Braic2100 model UV–vis spectrophotometer using 1 cm quartz cells. 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.

2.3. Synthesis

2.3.1. Preparation of $[Cu_2(L)_2(ox)(MeOH)_2](ClO_4)_2$, $2[Cu_2(L)_2(ox)](ClO_4)_2{\cdot}2MeOH{\cdot}H_2O$, **1**

To a solution of the diamine ligand L (0.960 g, 4 mmol) in methanol (25 mL) was slowly added $Cu(ClO_4)_2{\cdot}6H_2O$ (1.480 g, 4 mmol) in methanol (10 mL). The resulting mixture was stirred for 1 h at room temperature. To this deep blue solution was then added $K_2C_2O_4{\cdot}H_2O$ (0.368, 2 mmol) in water (10 ml) under 2 h continuous stirring. The desired compound precipitated from the solution as a blue solid. The compound was recrystallized by diffusion of diethyl ether into a methanol solution and dried at room temperature. Yield: 2.14 g; 55%. *Anal.* Calc. for $C_{106}H_{138}N_{12}O_{41}Cu_6Cl_6$ (MW = 2830.28 g mol^{-1}): C, 44.98; H, 4.91; N, 5.94, Cu, 13.47. Found: C, 45.23; H, 4.75; N, 6.15 Cu, 13.40%. Selected IR data (ν/cm^{-1} KBr disk): 3451 (m, O–H str), 3243 (m, N–H str.), 1453 (m, CH_2–Ph str.), 1659 (vs CO_2 str), 1354 (w, OCO str), 1093 (s, Cl–O str.), 804 (w, OCO bend), 625 (m, Cl–O bend.).

2.3.2. Preparation of $[Cu_2(L)_2(ox)](NO_3)_2$, **2**

This compound was prepared according to the procedure used for **1**, except that copper(II) nitrate trihydrate was used instead of copper(II) perchlorate hexahydrate. A blue precipitate was obtained, recrystallized from acetonitrile and dried at room temperature. The yield was 45%. *Anal.* Calc. for $C_{34}H_{40}N_6O_{10}Cu_2$ (MW = 819.81 g mol^{-1}): C, 49.81; H, 4.92; N, 10.25, Cu, 15.5%. Found: C, 49.65; H, 5.15; N, 9.90, Cu, 15.36%. Selected IR data (ν/cm^{-1} KBr disk): 3429 (m, O–H str), 3165 (m, N–H str.), 1657 (vs CO_2 str), 1454 (m, CH_2–Ph str.), 1385 (s, N–O str), 801 (w, OCO bend).

2.4. X-ray structure

Crystals of **1** were obtained by diffusion of diethyl ether into a methanol solution at room temperature. X-ray data were collected at 150 K on a Bruker APEX2 CCD area-detector diffractometer (Mo Kα). Data collection, cell refinement, data reduction and absorption correction were performed using multi scan methods with Bruker software [25–27]. The structure was solved by the direct method using the program SHELXT 2014 [28]. The non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2 using SHELXL 2014 [29]. All hydrogen atoms were placed in calculated positions and refined as isotropic with the "riding-model" technique. The asymmetric unit contains one complete molecule in a general position and a second half molecule placed about the inversion center. The complex has some disorder. The disorder is related to one of the phenyl rings (C23–C29) and also the coordinated methanol molecule (O8) which appears in the major component and the solvent methanol which appears in the minor component.

2.5. SMLR analysis

In this work, a multivariate statistical method using the SPSS/PC software package was used in the classification and selection of solvents. Multiple regression is an extension of simple linear regression. It is used when the prediction of the value of a variable based on the value of two or more other variables is required. The variables that are expected to be predicted are called the dependent variables. The variables that are utilized to predict the values of the dependent variables are called the independent variables. The multiple linear regression equation is shown in Eq. (1).

$$Y = b_o + b_1X_1 + b_2X_2 + \cdots + b_pX_p \qquad (1)$$

where Y is the predicted or expected value of the dependent variable (λ_{max} in this report), X_1 through to X_p are distinct independent

Table 1
Summarized crystallographic data of **1**.

Empirical formula	$C_{106}H_{138}Cl_6N_{12}O_{41}Cu_6$
M (g mol^{-1})	2827.37
T (K)	150(2)
λ	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	11.3939(11)
b (Å)	17.0959(17)
c (Å)	17.1154(17)
α (°)	106.571(3)
β (°)	96.378(3)
α (°)	99.760(3)
V (Å^3)	3104.0(5)
Z	3
D_{calc} (kg m^{-3})	1.513
μ (mm^{-1})	1.225
Index ranges	$-14 \le h \le 14$ $-22 \le k \le 22$ $-22 \le l \le 22$
$F(000)$	1460
Crystal size (mm)	0.180 × 0.160 × 0.060
Reflections collected/unique (R_{int})	78,436/14,530 (0.0843)
Completeness to theta = 25.242	100.0%
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	14530/3/777
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0420, wR_2 = 0.0897
R indices (all data)	R_1 = 0.0979, wR_2 = 0.1067
Goodness-of-fit (GoF)	0.999
Largest difference peak and hole (e Å^{-3})	0.633 and −0.599

$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 15.8676P]$.
$P = (F_o^2 + 2F_c^2)/3$.
$S = \sum[w(F_o{}^2 - F_c{}^2)^2/(N_{obs} - N_{param})]^{1/2}$.