A dimeric copper coumarin complex: synthesis and crystal structure of [{Cu(4-methyl-7-(salicylideneamino)coumarin)_2}_2]

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Abstract: A binuclear copper complex [{Cu(L)_2}_2], C_{68}H_{48}Cu_2N_4O_{12}C (where L is 4-methyl-7- (salicylideneamino)coumarin), has been synthesized and characterized using elemental analysis, molar conductance measurements, and infrared, ultraviolet and ESR spectroscopy. The molecular structure of title compound, determined by single-crystal X-ray diffraction studies, reveals that the two symmetric Cu(L)_2 units are associated into a dimer by rather long Cu...O bonds. The Cu(II) ions are bridged via the phenolic oxygen of one of the monomers and have distorted trigonal bipyramidal conformation geometry. Within each monomer the two methylsubstituted coumarin skeletons are trans to one another, but adopt a parallel arrangement with respect to the other monomer. Only half of the complex molecule can be found in the asymmetric unit, Z' = 0.5, the other half is generated by the symmetry centre.

Keywords: Coumarin • Schiff base • Copper(II) complex • Crystal structure • ESR

1. Introduction

Interest in coumarin chemistry has flourished for many years, largely as a result of the wide spread use of coumarin derivatives. Apart from the medicinal, biological and pharmacological applications coumarins are also used as sweeteners, fixatives of perfumes, additives in food and cosmetics, odor stabilizers in tobacco and odor maskers in paints and rubber [1].

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. 2-Hydroxy Schiff base ligands and their complexes derived from the reaction of derivatives of salicylaldehyde with amines have been studied extensively for their various crystallographic, structural and magnetic properties [2]. Although Schiff bases containing coumarin moiety have been used in a variety of enzymes [3], little attention has been given to their metal binding properties and the structural features of their complexes.

Synthesis, crystal structure and spectroscopic properties of 4-methyl coumarin skeleton fused to 2-hydroxyphenyl ring via an azomethine linkage (HL) have been reported previously [4]. The title compound [{Cu(L)_2}_2], (1) (Scheme 1), was synthesized and characterized as part of our systematic studies of coordination ability of Schiff bases containing coumarin moiety. The copper complex was chosen because of the important biological role that copper, an essential trace element, plays in all living organisms [5-7].

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2. Experimental Procedures

2.1. Materials
Chemicals and solvents were purchased from Sigma-Aldrich Company Ltd. and used without further purification.

2.2. Synthesis of [{Cu(L)2}2]

\[
\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O} \quad (0.04 \text{ g}, \ 0.2 \text{ mmol}) \text{ dissolved in} \ 20 \text{ ml} \ \text{of ethanol was added to a warm solution of 4-methyl-7-(salicylideneamino)coumarin} \ (0.05 \text{ g}, \ 0.2 \text{ mmol}) \ \text{in} \ 20 \text{ ml} \ \text{of ethanol. The mixture was stirred for} \ 10 \text{ min at room temperature and then refluxed for} \ 1 \text{ h. The green solid complex that precipitated was filtered off, washed several times with ethanol and with diethylether, and air-dried. Yield: 60\% (0.08 g, 0.06 mmol) based on HL, m.p > 573 K with decomposition. UV/Vis, } \lambda \text{(nm) in DMSO (10}^{-3} \text{ M): 250, 300, 319, 695. Elemental analysis calculated for C}_{68}\text{H}_{48}\text{Cu}_{2}\text{N}_{4}\text{O}_{12}\text{C: 65.85, N 4.52, H 3.90%; found: C 65.73, N 4.98, H 3.87%. Metal analysis (Cu) (calculated: 10.25, found: 10.60%), molar conductance (} \Omega^{-1} \text{ cm}^2\text{ mol}^{-1} \text{): 4.24. IR (} \nu \text{ cm}^{-1} \text{): 3446 (O-H), 1715 (C=O), 1606 (C= N), 1590 (C=C), 1230 (C-O).}
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2.3. Physical measurements

Infrared spectra of solids were recorded as KBr discs on a JASCO FT/IR 460 plus Fourier - Transform Spectrometer. Electronic absorption spectra were recorded on a JASCO V-530 UV/Vis Spectrophotometer. Elemental analysis (C, H and N) was performed on Element Analyzer 2400, Pekin Elmer, while metals analysis was determined by atomic absorption. X-band powder ESR spectra were recorded on a JEOL/JES-FA100 SERIES electron spin resonance spectrometer at ambient temperature.

2.4 Structure determination

Single crystals of 1 were grown by slow evaporation from chloroform/DMSO (1:3 by volume). The data for the complex were collected at 173(2) K. Data collection: COLLECT [8]; cell refinement: HKL DENZO and SCALEPACK [9]; data reduction: HKL SCALEPACK

Table 1. Crystal data and structure refinement for [{Cu(L)2}2](1).

| Property | Value |
|----------|-------|
| Empirical formula | C_{68}H_{48}Cu_{2}N_{4}O_{12} |
| Formula weight | 1240.18 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P1 (No.2) |
| Unit cell dimensions | a = 8.9665(2) Å, b = 12.2603(5) Å, c = 13.6356(5) Å, α = 103.516(2)°, β = 102.353(2)°, γ = 105.048(2)° |
| Volume | 1345.95(8) Å³ |
| Z | 1 |
| Z' | 0.5 |
| Density (calculated) | 1.53 Mg/m³ |
| Absorption coefficient | 0.87 mm⁻¹ |
| F(000) | 638 |
| Crystal size | 0.30 x 0.05 x 0.01 mm³ |
| Independent reflections | 5270 [R(int) = 0.068] |
| Reflections with I>2σ(I) | 3996 |
| Refinement method | Full-matrix least-squares on F² |
| Goodness-of-fit on F² | 1.010 |
| Final R indices [I>2σ(I)] | R1 = 0.045, wR2 = 0.085 |
| R indices (all data) | R1 = 0.071, wR2 = 0.095 |
| Largest diff. peak and hole | 0.30 and -0.37 e.Å⁻³ |

Table 2. Selected bond lengths (Å) and bond angles (º) for the complex [{Cu1(L1)2}]; estimated standard deviation are shown in parentheses.

| Bond/ Angle | Value/ (°) |
|-------------|-----------|
| Cu-O(1)    | 1.885(2)  |
| O(1)-Cu-N(1) | 91.06(9) |
| O(4)-Cu-N(1) | 90.0(9) |
| O(4)-Cu-N(2) | 94.08(9) |
| Cu-O(4)    | 1.914(2)  |
| Cu-N(1)    | 2.038(2)  |
| N(1)-Cu-N(2) | 89.68(9) |
| N(2)-Cu-O(4) | 89.68(9) |

Scheme 1. Synthesis of dimeric copper coumarin complex.
3. Results and Discussion

The complex, dark green in colour, is stable at ambient temperature, is insoluble in water, slightly soluble in ethanol, methanol and chloroform and very soluble in DMF and DMSO. The negligibly low molar conductance values in 1·10^{-4} M DMSO solution suggest non-electrolyte behavior [13].

3.1 Single crystal X-ray diffraction study of [{Cu (L)2}2] (1)

Fig. 1 shows the ORTEP-3 view of the complex with carbon, oxygen and nitrogen atoms numbered as shown and with hydrogen atoms omitted. Lactone oxygen atoms have been found not to participate in coordination of the Cu(II) centres. The structure is made up of centrosymmetric binuclear units. The two coumarin skeletons in the asymmetric unit are nearly parallel to each other with an angle of 11.24°. According to the procedure described by Addison et al., the shape of the polyhedra can be considered as a distorted trigonal-bipyramidal since the τ values \( \tau = (\theta_1 - \theta_2)/60° \) where \( \theta_1 \) and \( \theta_2 \) are the largest angles in the coordination sphere \( \tau = 0.60 \) for the Cu atom. (\( \tau \) equals to 1 for trigonal-bipyramidal \( D_{3h} \) and 0 for square-based-pyramidal \( C_{4v} \) geometries) (Table 2) [14].

In the distorted trigonal bipyramid three short bonds occupy the basal positions, two of them from the phenolic oxygen atoms, and one from the azomethine nitrogen atom; the Cu atom in the apical position is coordinated by a phenolic oxygen atom of the other monomer, with a bond length of 2.291 (2) Å, and by an azomethine nitrogen atom with a bond length of 2.071(2). The Cu-O bond length of the bridging phenolic oxygen Cu-O(4)’ is longer than the non-bridging one [1.885(2) and 1.914(2)]. The two Cu atoms are separated by about 3.313 Å. Such data are in good agreement with those reported for salicylate dimers [3.168(1)-3.265(4)] [15].

The bond lengths of the O(3)-C(16) and O(6)-C(33) bonds of the carbonyl groups of terminal units are 1.220(4) and 1.208(4) Å respectively, similar to that found in HL [C=O is 1.2119(15) Å] [4], indicating that the length of the carbonyl bond is not affected by coordination. Electron localization was also found at the short C(14)-C(15) and C(31)-C(32) bond with a length of 1.347(4) and 1.344(4) respectively [16]. The C=N bonds are longer than that found in the free ligand [they are 1.297(4) and 1.304(4) Å in 1, while the bond length of C=N in HL is 1.2882(16) Å, this elongation confirms that the azomethine nitrogen atom is the second coordination site in HL.

Molecules of 1 pack to form layers involving an extensive network of C–H···O interactions (Table 3).

3.2. Infrared and electronic spectra of the complex

In the IR spectrum, the OH stretching vibration of the complex is recorded around 3446 cm^{-1}, which is attributed to intermolecular hydrogen bonding. The characteristic absorption of the C=N stretching vibration is shifted from 1639 cm^{-1} in HL [4] to 1606 cm^{-1} in 1, confirming coordination via the azomethine nitrogen atom. The sharp, strong peak at 1715 cm^{-1} assigned to C=O remains unchanged compared to HL, thus excluding possibility of coordination of the ligand by the lactone oxygen in Cu(II) complex. The UV–Vis absorption spectrum of the complex in DMSO showed absorption bands at 319 and 300 nm assigned to the combination of LMCT / π-π* transitions of the benzene and coumarin rings and azomethine linkage. A d–d transitions of Cu^{2+} ion were recorded at 695 nm. [15]

**Table 3.** C–H···O interactions geometry (Å, °)

| D-H···A | D-H   | H···A | D-A   | D-H···A | Symmetry codes |
|--------|-------|-------|-------|--------|----------------|
| C(7)–H(7)···O(3) | 0.95  | 2.45  | 3.365(3) | 163  | [1-x,2-y,1-z] |
| C(22)–H(22)···O(6) | 0.95  | 2.48  | 3.261(4) | 140  | [1+x,1+y,1+z] |
| C(26)–H(26)···O(1) | 0.95  | 2.52  | 2.836(4) | 100  | [intra] |
| C(30)–H(30)···O(3) | 0.95  | 2.60  | 3.509(4) | 160  | [x,-1+y,z] |
4. Conclusions

Crystal structure determination of \([\{Cu(4-Methyl-7-(salicylideneamino)coumarin)2\}_2]\) complex indicates that the ligand moiety HL bonds to the copper(II) centers in a bidentate fashion, through phenolic oxygen and azomethine nitrogen, and that the oxygen of the lactone carbonyl does not participate in coordination. Distorted trigonal bipyramidal geometry of the complex was determined by single crystal X-ray diffraction study and by solid state ESR measurements at room temperature.

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Supplementary data

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 621125. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

\[\alpha^2 = \frac{A_j}{0.036 \text{ cm}^{-1}} + \frac{(g_j - 2.0023)}{3/7 (g_j - 2.0023) + 0.04} \]

The value of \(\alpha^2\) (0.5227) indicates the covalence in bonding between Cu(II) and the ligand [21].

In axial symmetry the g-values are related by the expression \(G = \frac{g_{\perp} - 2}{g_{\parallel} - 2} = 0.225\) where the G value is less than 2 suggesting exchange interaction of Cu-Cu in the complex. [18-22], which is in good agreement with the single crystal x-ray diffraction study. In axial symmetry the g-values are related through the expression \(G = \frac{g_{\perp} - 2}{g_{\parallel} - 2} = 0.225\) where the G value of less than 2 suggests exchange interaction of Cu-Cu in the complex [18-22]. This is in good agreement with the single crystal x-ray diffraction study performed on the title complex.
References

[1] Y.K. Tyagi et al., Eur. J. Med. Chem. 40, 413 (2005) and references cited therein.
[2] A.A. Khandar, S.A. Hosseini-Yazdi, S.A. Zare, Inorg. Chim. Acta 358, 3211 (2005)
[3] R.E. Smith, F.A. Dolbeares, United States Patent 4155916, 1979.22.05
[4] E.S. Aazam, A. Fawazy, P.B. Hitchcock, Acta Crystlogr. E 62, o4285 (2006), DOI:10.1107/S1600536806034519
[5] P. Lemoine, B.J. et al., Inorg. Biochem. 89, 18 (2002)
[6] L.G. Zhu, S. Kitagawa, H. Miyasaka, H.C. Chang, Inorg. Chim. Acta 355, 121 (2003)
[7] Y. Wang, N. Okabe, Acta Crystlogr. E 60, m1434 (2004), DOI:10.1107/S1600536804022615
[8] Nonius. COLLECT. Nonius BV, Delft, The Netherlands (2000)
[9] Z. Otwinowski, W. Minor, Method enzymol, Macromolecular Crystallography, Part A 176, 307 (1997)
[10] G.M. Sheldrick, SHELXS97 and SHELXL97. University of Göttingen, Germany, (1997)
[11] L.J. Farrugia, J. Appl. Cryst. 30, 565 (1997)
[12] L.J. Farrugia, J. Appl. Cryst. 32, 837 (1999)
[13] W.J. Geary, Coord. Chem. Rev. 7, 81 (1971)
[14] A.W. Addison, T.N. Rao, J. Reedijk, J. Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. 7, 1349 (1984)
[15] N. Palanisami, G. Prabusankar, R. Murugavel, Inorg. Chem. Commun. 9, 1002 (2006)
[16] I. Fujii, Y. Mano, N. Hirayama, Anal. Sci. 21, x7 (2005)
[17] B.J. Hathaway, A.A.G. Tomlinson, Coord. Chem. Rev. 5, 143 (1970)
[18] J.E. Wertz, J.R. Bolton, Electron Spin Resonance (McGraw Hill Book Company, New York, 1972)
[19] M.S. Masoud, E.A. Khalil, A.M. Hafez, A.F. El-Husseiny, Spectrochim Acta A 61, 989 (2005)
[20] D. Kivelson, R. Neiman, J. Chem. Phys. 35, 149 (1961)
[21] D.K. Johnson, H.J. Stoklosa, J.R. Wasson, G.L. Seebach, J. Inorg. Nucl. Chem. 37, 1397 (1975)
[22] A.A. El Bindary, Spectrochim Acta A 57, 49 (2001)