

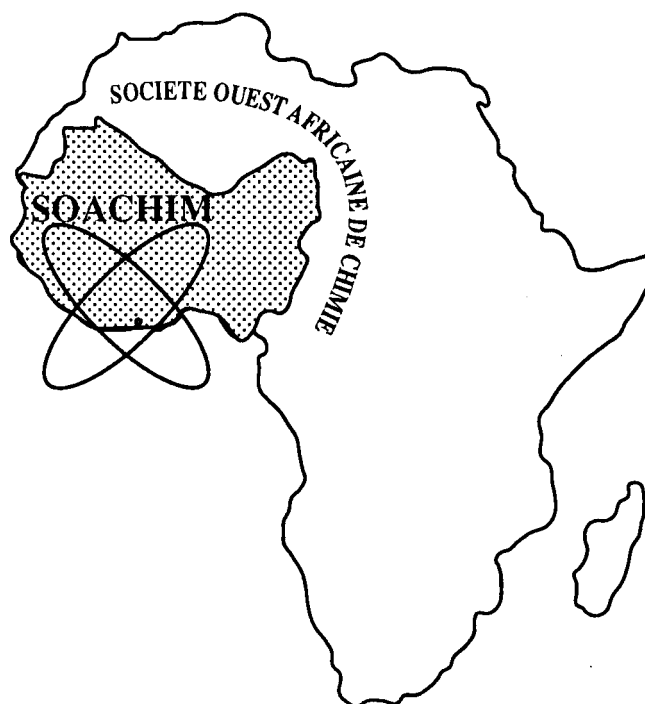
Cadmium and copper complexes derived from a chloranilic acid: spectroscopic study and crystal structure by X-rays diffraction

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Cadmium and copper complexes derived from a chloranilic acid: spectroscopic study and crystal structure by X-rays diffraction

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Abstract: Two complexes of cadmium and copper(II) derived from chloranilic acid were synthesized and characterized by spectroscopic studies and conductivity measurement. The structures of these compounds were determined by single crystal X-ray diffraction. The results show a one dimensional structure polymer complex of Cd(II) with formulated as $0.5(\text{C}_{12}\text{Cd}_2\text{Cl}_8\text{O}_8) \cdot 2(\text{C}_4\text{H}_{12}\text{N})$. It crystallizes in the monoclinic space group C2/c with cell dimensions, $a = 16.1954 (3) \text{ \AA}$, $b = 9.7018 (2) \text{ \AA}$, $c = 14.3440(3) \text{ \AA}$, $\beta = 105.563 (2)^\circ$. The mononuclear Cu(II) of formula $0.5(\text{C}_{12}\text{H}_2\text{Cl}_4\text{O}_9\text{Cu}) \cdot \text{C}_4\text{H}_{12}\text{N}$ complex crystallizes in the monoclinic space group P2₁/c with cell dimensions, $a = 11.3033 (7) \text{ \AA}$, $b = 10.2529 (4) \text{ \AA}$, $c = 23.0069 (16) \text{ \AA}$, $\beta = 92.098 (5)^\circ$. Extended supra-molecular assemblages are generated in both cases by hydrogen bonds.

Keywords: Cadmium(II); Copper(II); Chloranilate; X-rays; Crystal structure.

Complexes du cadmium et du cuivre dérivés de l'acide chloranilique: étude spectroscopique et détermination structurale par diffraction de rayons X

Résumé: Deux complexes de cadmium et de cuivre(II) dérivés de l'acide chloranilique ont été synthétisés et caractérisés par des études spectroscopiques et des mesures de conductivité. Les structures de ces composés ont été déterminées par diffraction des rayons X sur monocristaux. Les résultats montrent un complexe polymère à structure unidimensionnelle de Cd(II) avec la formule $0.5(\text{C}_{12}\text{Cd}_2\text{Cl}_8\text{O}_8) \cdot 2(\text{C}_4\text{H}_{12}\text{N})$. Il cristallise dans le groupe d'espace monoclinique C2/c de dimensions cellulaires $a = 16,1954 (3) \text{ \AA}$, $b = 9,7018 (2) \text{ \AA}$, $c = 14,3440 (3) \text{ \AA}$, $\beta = 105,563 (2)^\circ$. Le complexe mononucléaire Cu(II) de formule $0.5(\text{C}_{12}\text{H}_2\text{Cl}_4\text{O}_9\text{Cu}) \cdot \text{C}_4\text{H}_{12}\text{N}$ cristallise dans le groupe d'espace monoclinique P2₁/c de dimensions cellulaires, $a = 11,3033 (7) \text{ \AA}$, $b = 10,2529 (4) \text{ \AA}$, $c = 23,0069 (16) \text{ \AA}$, $\beta = 92,098 (5)^\circ$. Des assemblages supra-moléculaires étendus sont générés dans les deux cas par des liaisons hydrogène.

Mots-clés: Cadmium(II); Cuivre(II); Chloranilate; Rayons X; Structure cristalline.

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1. Introduction

In recent year many investigations in coordination chemistry were deal to fine new materials with exceptional properties [1-3]. On this field polymeric structures are largely studied [4-6]. These compounds are often valuable materials for the development of novel properties that can be used in areas such as magnetism [3, 7], luminescence [8]. The derivatives of chloranilic acid are precursors of interest in the preparation of coordination compounds in the form of polymers. For the chloranilic acid derivatives, the chelating effect of the dianion and the position of the donor sites which give it the possibility of acting as a bridge make it an excellent candidate for the preparation of polymeric compounds [7, 9-11]. In addition, the derivatives of the chloranilate ion have a delocalized π system associated with a plane geometry that gives them the possibility of playing a role in magnetic [3] and redox properties [12, 13] of the compound. In this paper, we describe the synthesis of a polymeric complex of cadmium and a mononuclear complex of copper which are well characterized by spectroscopic and X-ray diffraction technics.

2. Experimental

2.1. Starting materials and Instrumentations

Commercially available methanol, chloranilic acid, triethylammonium hydroxide, and cadmiumchloride were purchased from Aldrich and used without further purification. The IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum Two spectrophotometer (4000–400 cm^{-1}). Fluorescence spectrum were recorded on a Perkin Elmer LS-55 spectrofluorimeter at room temperature (298 K). The molar conductance of 10^{-3} M solution of the metal complex in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Emission spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. Samples in adequate solvent solutions were placed in 1 cm path length

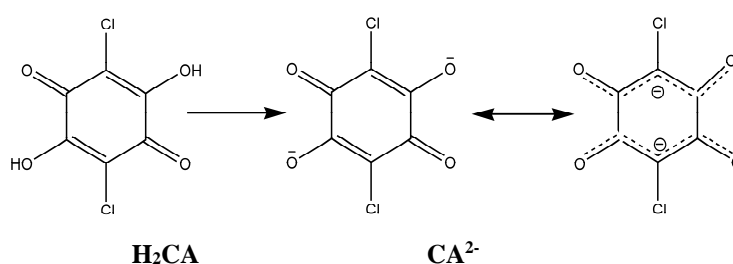
quartz cuvettes for room temperature measurements.

2.2. Synthesis of the Complexes

In a round bottom flask, 1.737 mmol (0.2 g) of L-proline was dissolved in 5 mL of methanol. 1.737 mmol (0.633 g) of trimethylammonium hydroxide was added. The resulting colorless solution was stirring during 15 minutes before to add 10 mL of methanolic solution of 0.868 mmol of CdCl_2 or $\text{CuCl}_2 \cdot 3\text{H}_2\text{O}$. The mixture was continuously stirred 30 minutes at room temperature, 10 mL of methanolic solution of 0.434 mmol (0.090 g) of chloranilic acid (H_2CA) was added dropwise. A purple precipitate appears immediately. After 30 mn the precipitate was recovered by filtration and the filtrate was left to evaporation. After two weeks of slow evaporation the filtrate gives purple crystals suitable for X-ray diffraction.

2.3. Crystal Structure Determination and Refinement

Crystals suitable for X-diffraction, of the reported compounds, were grown by slow evaporation of MeOH solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table I. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [20]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [21]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using *ORTEP-3* [22].



Scheme 1

Table I: Crystal data and Details of Structure Determination for Cd(II) and Cu(II) complexes

Chemical formula	0.5(C ₁₂ Cd ₂ Cl ₈ O ₈)·2(C ₄ H ₁₂ N)	0.5(C ₁₂ H ₂ Cl ₄ CuO ₉)·C ₄ H ₁₂ N
Mr	538.58	328.61
Crystal system, space group	Monoclinic, C2/c	Monoclinic, P21/c
Temperature (K)	293	293
<i>a</i> (Å)	16.1954 (3)	11.3033 (7)
<i>b</i> (Å)	9.7018 (2)	10.2529 (4)
<i>c</i> (Å)	14.3440 (3)	23.0069 (16)
β (°)	105.563 (2)	92.098 (5)
<i>V</i> (Å ³)	2171.16 (8)	2664.5 (3)
<i>Z</i>	4	8
<i>D</i> _{cal} (g cm ⁻³)	1.648	1.638
F(000)	1080	1328
Radiation type	Mo Kα	Mo Kα
μ (mm ⁻¹)	1.52	2.05
θ _{max} (°)	28.383	26.297
<i>h, k, l</i> ranges	-19 ≤ <i>h</i> ≤ 20, -12 ≤ <i>k</i> ≤ 12, -18 ≤ <i>l</i> ≤ 18	-14 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 12, -28 ≤ <i>l</i> ≤ 28
Crystal size (mm)	0.50 × 0.16 × 0.03	0.25 × 0.2 × 0.15
Measured reflections	15416	43703
Independent reflections	2428	5297
[<i>I</i> > 2σ(<i>I</i>)] reflections	2232	4153
Parameters/restraints	118/0	334/0
<i>R</i> _{int}	0.023	0.032
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.027	0.041
<i>wR</i> ₂	0.069	0.125
Goodness-of-Fit	1.06	1.06
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.58, -0.48	1.07, -0.58

3. Results and discussion

3.1. General study

The IR spectrum of the cadmium complex shows two main bands pointed respectively at 1482 cm⁻¹ and 1553 cm⁻¹ which are characteristic of a chloranilate ion close to D_{2h} symmetry [17]. These values are smaller than those found for the free chloranilic acid ligand which exhibits characteristic bands at 1667 cm⁻¹ and 1631 cm⁻¹. The shift is indicative of a bis-chelating chlorinate ion. This coordination mode is confirmed by the X-ray diffraction structure. The IR spectrum of the Cu(II) complex exhibits a medium intensity bands at 1482 cm⁻¹ and 1553 cm⁻¹ which are characteristic of a

coordinated chloranilate group. Another band pointed at 1612 cm⁻¹ is indicative of the presence of free C=O function [18]. These facts show that the chloranilate anion is coordinated on one side the other face remaining free. Additional bands at 3450 cm⁻¹ and 837 cm⁻¹ are observed and are attributed to the -OH of the coordinated water molecule [19]. Both spectra revealed a band at 948 cm⁻¹ attributed to the tetraethyl ammonium cation [20]. The molar conductivity of the two complexes are measured for a freshly prepared solution of complex in DMF and after two weeks. The values of 45 Ω⁻¹.cm².mol⁻¹ for the Cd(II) complex is indicative of electrolyte of type 1:1 [21]. The Cu(II) complex shows values of

147 $\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ which is characteristic of a 2:1^[21] electrolyse in DMF. The UV-Vis spectrum of the copper(II) complex is recorded in DMF solution in the range of 200–1000 nm. The band pointed at 340 nm is attributed to the intraligand $n\rightarrow\pi^*$ transitions of the C=O chromophore. The d-d transitions are very low energy due the Jahn-Teller effect^[22]. The magnetic moment value of 1.64 μ_B is in the range expected for a mononuclear copper(II) complex^[23].

3.2. Description of crystals structures

3.2.1. Cd complex

The X-ray structural determination of the cadmium compound reveals a polymeric structure which crystallizes in the monoclinic system in the space group $C2/c$. The structure of the compound is formulated as $0.5[\text{Cd}_2\text{Cl}_2(\text{CA})_2]\cdot 2(\text{NEt}_4)$ and the ORTEP drawn is showed in Figure 1a. In the structure, the cadmium(II) ions are linked in a bidentate fashion to two chloranilate molecules ligand via two oxygen atoms per ligand and two chloride anions. Selected bond lengths and angles are listed in Table II. The chloranilate ligand acts as *bis*-chelating bridging unit between two cadmium (II) ions. Two cations of triethylammonium are present per cadmium atom. The metal centre is hexacoordinated. Each Cd(II) cation in the

polymeric structure shows a distorted octahedral geometry. The equatorial plane around each Cd(II) cation is formed by two oxygen atoms from one chloranilate ligand, one oxygen atom of the second chloranilate ligand and one terminal chlorine atom. The axial positions are occupied by one oxygen atom from the second chloranilate ligand and one terminal Cl atom. In the equatorial plane, the *cisoid* angles are in the range of 70.34(6)–99.52(5)° while the *transoid* angles are 155.68(10)° and 166.17(5)°, respectively. These observations are indicative of a distorted environment from an ideal octahedral geometry. Two type of Cd-O distances are revealed with different values of 2.2937(17) Å and 2.3722(18) Å respectively. The two Cd-Cl distances are equal with value of 2.5040(7) Å. This value is slightly lower than the value reported in Cd(II) complexes with a terminal Cl^[24]. The CA^{2-} anions act as bridges and connect two cadmium cations in an on-ending fashion. In this polymeric structure, the Cd...Cd separation is 8.452 Å. The crystal lattice consists in a superposition of layers parallel to *c* axis and the distance of Cd...Cd interlayers is 8.439 Å. Intramolecular hydrogen bonds involving the CH of the tetraethylammonium cation as donor and a coordinated O atom of the chlorinate group (C-H...O) or a coordinated chloro atom as acceptors (C-H...Cl) were observed (Figure 1b).

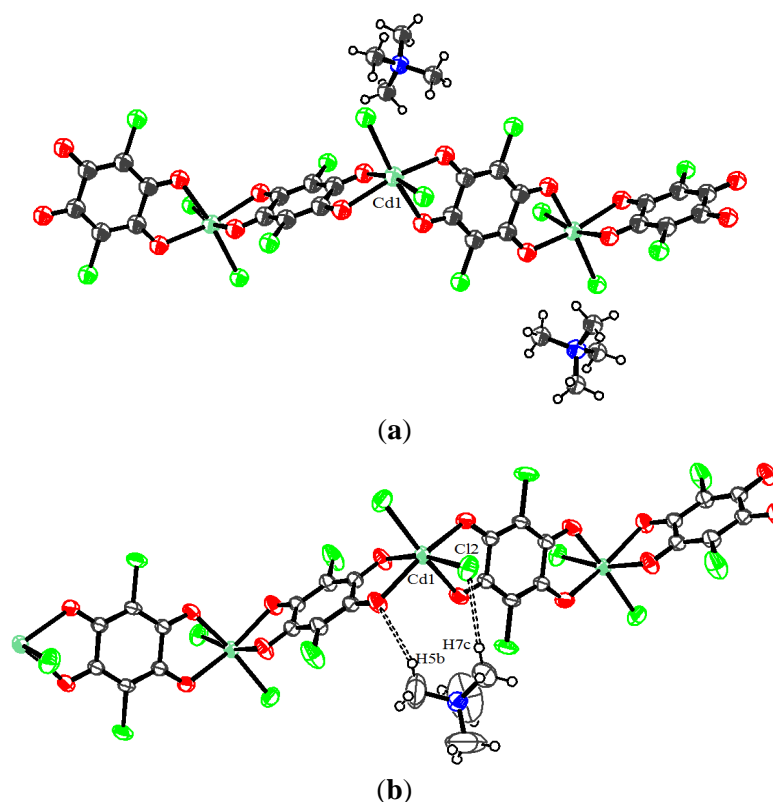


Figure 1: (a) ORTEP representation of the structure of the Cd(II) complex; (b) Intramolecular C-H...O hydrogen bonds are shown as dashed lines.

Table II. Selected interatomic distances (Å) and angles (°)

Cd1—Cl2	2.5040 (7)	Cu01—O006	1.935(2)
Cd1—Cl2 ⁱ	2.5040 (7)	Cu01—O007	1.949(2)
Cd1—O1 ⁱ	2.2937 (17)	Cu01—O008	1.935(2)
Cd1—O1	2.2937 (17)	Cu01—O00B	2.266(3)
Cd1—O2 ⁱⁱ	2.3722 (18)	Cu01—O009	1.927(2)
Cd1—O2 ⁱⁱⁱ	2.3722 (18)	O006—Cu01—O009	167.74(9)
O1—Cd1—O1 ⁱ	155.70 (10)	O006—Cu01—O00B	96.37(9)
O2 ⁱⁱⁱ —Cd1—Cl2 ⁱ	166.18 (5)	O007—Cu01—O008	164.09(9)
O1 ⁱ —Cd1—Cl2 ⁱ	99.52 (5)	O007—Cu01—O009	94.22(9)
O2 ⁱⁱ —Cd1—Cl2	166.18 (5)	O007—Cu01—O00B	100.99(9)
O2 ⁱⁱⁱ —Cd1—Cl2	90.28 (5)	O008—Cu01—O009	84.05(9)
O2 ⁱⁱ —Cd1—Cl2 ⁱ	90.28 (5)	O008—Cu01—O00B	94.91(9)
O2 ⁱⁱ —Cd1—O1 ⁱ	90.90 (6)	O009—Cu01—O00B	95.89(9)
O2 ⁱⁱⁱ —Cd1—O1	90.90 (6)		

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

3.2.2. Cu complex

The X-ray structural determination of the copper compound reveals a mononuclear Cu(II) complex which crystallizes in the monoclinic system with the space group $P2_1/C$. An ORTEP view of the compound formulated as $0.5[\text{Cu}(\text{CA})_2(\text{H}_2\text{O})_2] \cdot 2(\text{NEt}_4)$ is shown in Figure 2a. Selected bond lengths and angles are listed in Table II. In the mononuclear Copper(II) complex the Cu(II) ion is linked to two ligand molecules via two oxygen atoms and one water molecule resulting in a pentacoordinated metal ion. The coordination environment around the Cu(II) center is best described as a distorted square pyramidal geometry. The basal plan is occupied by chloranilate oxygen atoms O1, O4, O5 and O8 with angle values significantly different of the ideal value of 90° and 180° (O-Cu-O = $94.46(9)^\circ$, O-Cu-O = $84.06(9)^\circ$, O-Cu-O = $94.21(9)^\circ$ and O-Cu-O = $83.86(9)^\circ$; O-Cu-O = $167.73(10)^\circ$ and O-Cu-O = $164.11(11)^\circ$). The sum of the subtended angles is 356.59° . The apical position is occupied by Ow with angles values with the atoms in the base plane in the range [$94.91(11)$ -

$100.98(10)^\circ$] severely deviated from the ideal value of 90° . The oxygen atom of the chloranilate group are strongly linked to the Cu(II) ion with the shortest distance values in the range [$1.927(2)$ - $1.949(2)$ Å]. These values are comparable to those found for related complexes ^[25]. The Cu-O_w distance is the longest with value of $2.266(3)$ Å which is longer than the value found for a similar complex ^[26]. The coordination environment around the second Cu(II) center is best described as a distorted square pyramidal geometry. The Addison parameter ^[27] τ ($\tau = (\alpha - \beta) / 60$, α and β are the largest angles around the metal center; $\tau = 0$ is indicative of a perfect square pyramidal geometry and $\tau = 1$ is indicative of a perfect trigonal bipyramidal geometry) can be used for determining the environment around the Cu(II). For this complex the τ value of 0.06 support the distorted square pyramidal geometry. In this compound, there is intermolecular hydrogen bonds involving the OH of the coordinated water molecules donor and a free O atom of the chlorinate group as acceptor (O-H...O) (Figure 2b).

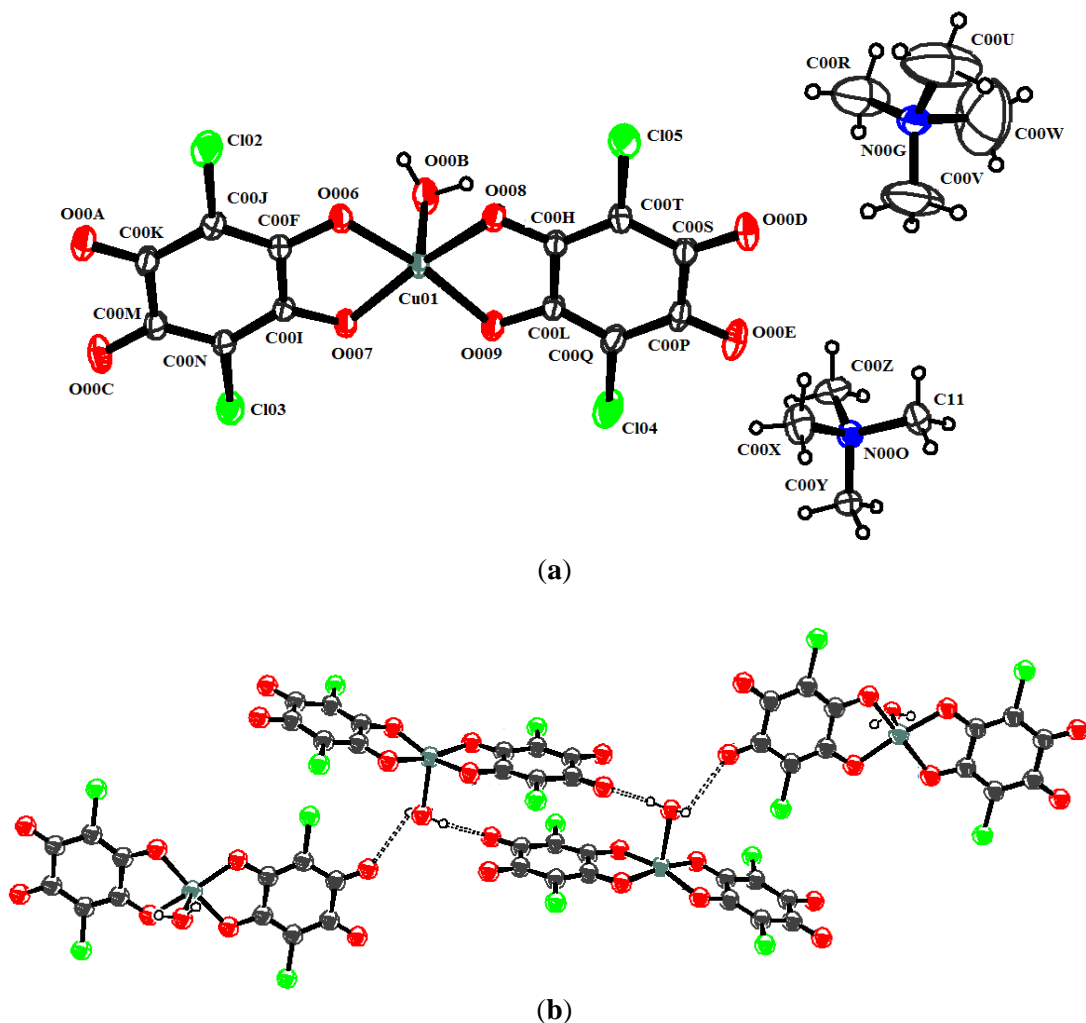


Figure 2: (a) ORTEP representation of the structure of the Cu(II) complex; (b) Intermolecular O–H···O hydrogen bonds are shown as dashed lines.

3.3. Fluorescence properties

The complex of cadmium in DMF, on exciting at 250 nm, exhibits fluorescence at 422 nm. This may be assigned as intra-ligand ($\pi-\pi^*$) fluorescence. When increasing the concentration from 0.25 mg/mL to 0.5 mg/mL, a significant enhancement of the fluorescence appears. From 0.5 mg/mL to 1 mg/mL no enhancement of the fluorescence intensity is observed (Figure 3). No shift of λ_{em} is observed on increasing the concentration. The fluorescence intensity is only concentration dependent in this case in the range [0 - 0.5 mg/mL]. The DMF solvent have a good coordination ability through his oxygen atom and can link to the Cd(II) ion. The direct consequence of this strong electron-donor ability is the enhancement of the fluorescence as reported in the literature [28].

4. Conclusion

Chloranilic acid used as ligand allowed to synthesize a large number of complexes with

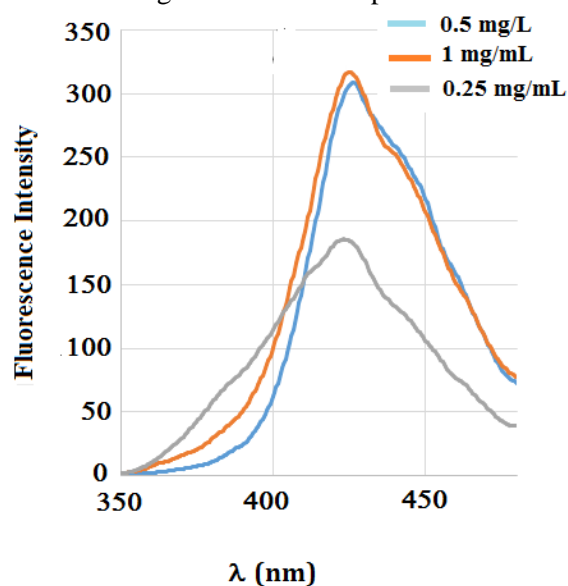


Figure 3: Fluorescence spectra of the complex recorded at room temperature in DMF at different concentration.

original structures as well with transition metal ions as with lanthanides. The polytopic nature of the chloranilate dianion, having potentially four coordination sites, can be controlled to accommodate ions of different sizes. In this work, we report the synthesis of complexes of cadmium(II) and copper(II) and their characterizations by spectroscopic analysis and X-ray diffraction technic. In the cadmium complex the metal center is in a severely distorted octahedral geometry while in the copper complex the geometry around the metal center is a square pyramidal. The Cd(II) compound have luminescent property which is concentration dependent.

5. Supporting information

CCDC-1913603 and 1913604 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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