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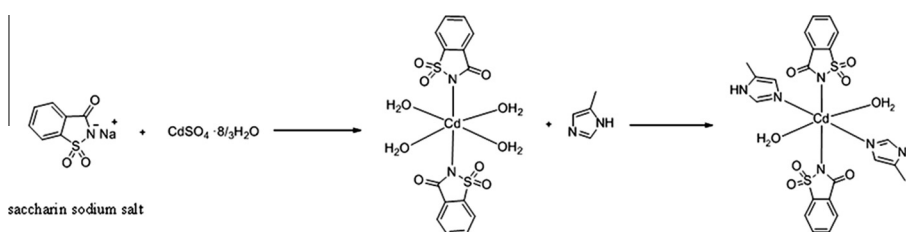
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journal homepage: www.elsevier.com/locate/saaSynthesis, crystal structure, spectroscopic, fluorescent, thermal properties and EPR spectra of doped Cu^{2+} ions in $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_2(\text{meim})_2]$ single crystalM. Fidan ^{a,*}, F. Semerci ^{b,c}, E. Şahin ^{c,d}, O.Z. Yeşilel ^b, R. Tapramaz ^e, Y. Şahin ^a^a Department of Physics, Faculty of Sciences, Ataturk University, 25240 Erzurum, Turkey^b Department of Chemistry, Faculty of Arts and Sciences, Eskişehir Osmangazi University, Eskişehir, Turkey^c Department of Chemistry, Faculty of Arts and Sciences, Kırklareli University, Kırklareli, Turkey^d Department of Chemistry, Faculty of Sciences, Ataturk University, 25240 Erzurum, Turkey^e Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

HIGHLIGHTS

- ▶ The crystal structure of the synthesized $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_2(\text{meim})_2]$ (complex **1**) was determined.
- ▶ Spectral and thermal analysis data of complex **1** was agreed with the crystal structure.
- ▶ Magnetic properties of complex **1** and its structural change occurred with temperature were studied with EPR spectroscopy.
- ▶ Both TGA and EPR spectra was found discoverable changes around 140 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

The crystal structures of the six-coordinate complexes $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_2(\text{meim})_2]$ (complex **1**) formed by reaction of 4-methylimidazole (meim) with $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ (saccharinate = sac), was synthesized and characterized by elemental analysis, infrared (IR) and electron paramagnetic resonance (EPR) spectroscopy, thermal analysis and X-ray single crystal diffraction. X-ray diffraction analysis revealed that complex **1** crystallized in the monoclinic crystal system with space group $P2_1/c$. The Cd(II) center was six-coordinated with four nitrogen atoms from two sac and two 4-meim ligands, two oxygen atoms from two aqua ligands. Spectral and thermal analysis data for complex **1** was in agreement with the crystal structures. In addition complex **1** displayed blue fluorescent emission in the solid state at room temperature. Single crystal EPR spectra at room temperature are resolved and have exhibited that two different Cu^{2+} complexes were located in different chemical environments which contained two magnetically non-equivalent Cu^{2+} sites. In low temperature EPR spectra down to 110 °C did show no considerable change. At higher temperatures, however, both thermo gravimetric analyses (TGA) and EPR spectra showed detectable changes around 140 °C; the causes and the mechanisms of changes are discussed.

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Introduction

Recently, many novel coordination compounds with unique structures have attracted significant attention not only owing to their intriguing variety of architectures, but also because of their

potential applications in materials with luminescent and optical properties [1,2]. Saccharin (o-sulfobenzimide; Hsac) and its salts have been known as sweeteners for many years [3]. Structural properties of sodium saccharinate salt has been attracting the attentions of crystal engineering [4,5]. The coordination chemistry of saccharinate anion is drawing attention, not only because of its interesting and polyfunctional ligand leading to a wide range of coordination modes, forming complexes from mononuclear to

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polynuclear structures but also its photoluminescence properties with d^{10} metal ions [6,7]. Luminescent metal-organic compounds can be prepared by combination of aromatic or conjugated organic units with d^{10} metal ions [8]. In addition to metal ions and ligands, the presence of non-covalent interactions such as hydrogen bonds and aromatic interactions are important for luminescence properties of coordination compounds [9]. Recently, it was found that number of silver(I)-saccharinate coordination compound were luminescent at room temperature [7,10–13]. Luminescence studies of other d^{10} metal ion such as Cd(II) and Zn(II)-saccharinate complexes are rare. In former researches, imidazole-derivative ligands were successfully used to synthesize some certain coordination compounds, whose photoluminescence properties have been examined [14].

In this paper, we report the synthesis, structure; luminescent properties and EPR of new Cd(II) saccharinate complex. The crystal structures of this complex will be presented and discussed. The relevance between the structures and the luminescence properties of the complex is discussed in detail.

Experimental

Aqueous solution of the $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (2 mmol, 20 mL) was added to an aqueous solution of NaSac (4 mmol, 20 mL). After stirring for 30 min, precipitates were filtered and washed with methanol to yield the compound $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [15]. An aqueous solution of 4-methylimidazole (4-meim) 4 mmol, 20 mL was added into aqueous solutions of the above compound (2 mmol, 20 mL), under stirring, and the mixture was allowed to stand at room temperature. After a few days, well-formed crystals were selected for X-ray studies. Anal. Calc. for $\text{C}_{22}\text{H}_{24}\text{N}_6\text{O}_8\text{S}_2\text{Cd}$: C, 39.03; H, 3.57; N, 12.41% Found: C, 39.26; H, 3.48; N, 12.77%. IR (KBr): ν (cm^{-1}) 3549 (br), 3292(vs), 3207(m), 3136(m) 3082(sh), 3024(m), 2960(w), 2922(w), 1642(vs), 1616(sh), 1585(s), 1502(m), 1458(m), 1340(m) 1265(vs), 1112 (s), 1051(m), 1147(vs), 956(m), 804(w), 752(s), 681(m), 650(m), 605(m), 536(w).

Results and discussion

FT-IR investigation

IR data for the title complex is shown in Table 1 and compared with those of sodium saccharinate monohydrate [16]. The absorption bands between 3673 and 3434 cm^{-1} are characteristic of $\nu(\text{OH})$ vibrations of aqua ligands. The series of overlapping bands in 3300–2150 cm^{-1} region of the solid-state spectrum were assumed to be characteristic of 4-methylimidazole ligands [17]. The relatively weak absorption bands between 3162 and 2787 cm^{-1} are assigned to the $\nu(\text{CH})$ vibrations. In complex 1, the carbonyl O atom of the sac ligand did not participate in metal bonding and appeared as two sharp bands at 1641 and 1616 cm^{-1} . The asymmetric and symmetric stretchings bands of the SO_2 group in the spectra of complex 1 were observed as two strong IR bands at approximately ca. 1265 (accompanied with a shoulder around 1286 cm^{-1}) and 1148 cm^{-1} , respectively. In the complex, $\nu(\text{CO})$ carbonyl and $\nu(\text{SO}_2)$ sulphonyl vibrations remained unchanged or shifted slightly to higher frequencies compared with that of its sodium salt. This situation in the stretching modes of $\nu(\text{CO})$ and $\nu(\text{SO}_2)$ elucidate that carbonyl and sulphonyl oxygens in complex 1 did not involve in the coordination. The absorption bands around 1585 and 1458 cm^{-1} are assumed to be corresponding to the $\nu(\text{C}-\text{C})$ vibrations of the aromatic rings, respectively. The IR bands at 1340 and 956 cm^{-1} are assigned to the symmetric and antisymmetric stretching of C–N–S groups, respectively.

Table 1
Selected IR spectroscopic data^a for $\text{Na}(\text{sac}) \cdot \text{H}_2\text{O}$ and $[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_2(4\text{-meim})_2]$.

Assignment(cm^{-1})	$\text{Na}(\text{sac}) \cdot \text{H}_2\text{O}$ [16]	$[\text{Cd}(\text{sac})_2(\text{H}_2\text{O})_2(4\text{-meim})_2]$
$\nu(\text{OH})$	3333 (br); 3264 (br)	3549 (br),
$\nu(\text{NH})$	–	3292 (vs), 3207 (m), 3136 (m)
$\nu(\text{CH})$	3080 (vw), 3050 (w), 3012 (vw)	3082 (sh), 3024 (m), 2960 (w), 2922 (w)
$\nu(\text{CO})$	1642 (vs); 1629 (sh)	1642 (vs), 1616 (sh)
$\nu(\text{CC})$	1590 (s); 1555(vw);1460 (m)	1585 (s), 1502 (m), 1458 (m)
$\nu_s(\text{CNS})$	1336 (m)	1340 (m)
$\nu_{as}(\text{SO}_2)$	1258 (vs)	1265 (vs), 1286 (sh)
$\delta(\text{CH})$	1165 (sh); 1118 (s); 1051(m)	1112 (s), 1051 (m)
$\nu_s(\text{SO}_2)$	1150 (vs)	1148 (vs)
$\nu_{as}(\text{CNS})$	950 (m)	956 (m)
$\delta(\text{CO})$	794 (w)	804 (w)
$\delta(\text{SO}_2)$	610 (m)	681 (m), 650 (m), 605 (m)
$\delta(\text{CNS})$	543 (w)	536 (w)

^a sac, saccharinate; as, asymmetric; s, symmetric; vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; vw, very weak; br, broad.

Crystal structures

The crystal analysis of complex 1 revealed that it was a mononuclear complex consisting of one Cd(II) ion, two sac, two aqua and two 4-meim ligands (Fig. 1). The crystal data and the structure refinement parameters are provided in Table 2 for complex 1. The complex 1 crystallized in the monoclinic crystal system space group $P2_1/c$. As shown in Fig. 1, the Cd(II) was six-coordinated with four nitrogen atoms from two sac and two 4-meim ligands, and two oxygen atoms from two aqua ligands. The Cd(II) ion exhibited a distorted octahedral geometry, in which two 4-meim and two aqua ligands were located in the equatorial plane and the axial sites were occupied by two sac ligands (Fig. 1). The Cd–N2 and

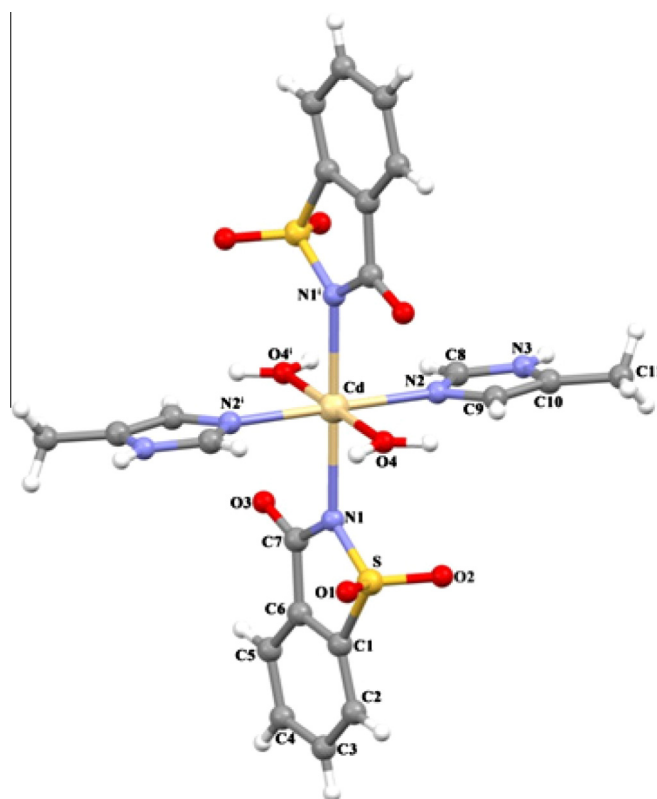


Fig. 1. The molecular structure of complex 1 showing the atom numbering scheme.

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