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Coordination versatility of 2,2′-(ethylenedioxy)bis(ethylamine) in new mono- and polynuclear metal(II) complexes of saccharinate: Synthesis, characterization and crystal structures

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ABSTRACT

The reaction of $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ (M = Ni^{II}, Cu^{II}, Cd^{II} and *sac* = saccharinate) with 2,2′-(ethylenedioxy)bis(ethylamine) (*edbea*) resulted in $[Ni(edbea)(sac)_2]\cdot 2H_2O$ (**1**) $[Cu(edbea)(sac)_2]$ (**2**), $[Cu(\mu\text{-}edbea)(sac)_2]_n$ (**3**) and $[Cd(edbea)_2](sac)_2$ (**4**), which have been characterized by elemental analyses, magnetic measurements, FT-IR and EPR (for **3**) spectroscopies, thermal analysis, magnetic properties (for **1** and **3**) and X-ray diffraction methods. The *edbea* ligand display different coordination modes in the present complexes. For example, **1** and **2** it acts a tridentate way, while it exhibits a μ-N/O bidentate bridging mode between the copper centers in **3**. On the other hand, the geometry of **4** eight-coordinated by two tetradentate *edbea* ligands is the bicapped trigonal prism structure in which *S*(°) value is the smallest. The *EPR* spectrum of **3** showed that the local geometry of Cu(II) ion has an elongated rhombic coordination. Complexes **1** and **3** exhibited a paramagnetic behavior as expected, but complex **1** displayed an antiferromagnetic interaction at low temperatures.

1. Introduction

Saccharin (*SacH*, 1,2-benzisothiazoline-3-(*2H*)one 1,1-dioxide or *o*-sulfobenzimide) is a well-known artificial sweetener and commercially available as the sodium salt, $Na(sac)\cdot 2H_2O$. Saccharin itself has a very low solubility in water. However, it deprotonates in water by loosing its acidic imine hydrogen and forms the saccharinate anion (*sac*).

The *sac* anion acts as an interesting polyfunctional ligand in coordination chemistry, since it has a three different donor groups such as the imino nitrogen, carbonyl oxygen and sulfonyl oxygen atoms. The first complexes of *sac* were the aqua complexes of the divalent transition metals ions with a composition of $[M(sac)_2(H_2O)_2]\cdot 2H_2O$ (M(II) = V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd) [1–8]. In these complexes, in addition to the coordination of four aqua ligands, two *sac* anions coordinate to the metal ions through the deprotonated nitrogen atoms in the *trans* positions of the coordination octahedron. It became a common practice to use $[M(sac)_2(H_2O)_4]\cdot 2H_2O$ as synthetic precursors for the synthesis of new mixed ligand metal complexes of *sac*, since the aqua ligands in these metal complexes are very labile and readily displaced by neutral ligands. The structural studies showed that *sac* exhibits different modes of coordination and forms metal complexes from mononuclear species to coordination polymers, due to its polyfunctional behavior and the studies in this field have been comprehensively reviewed by Baran and Yilmaz [9].

The coordination chemistry of the 2,2′-(ethylenedioxy)bis(ethylamine) ligand (*edbea*) has not been received much attention. Two studies on the Cu(II) complexes of macrocyclic ligands with the *edbea* backbone have appeared in the literature [10,11]. Moreover, Ni(II) and Cu(II) complexes containing the *edbea* ligand were reported by our group recently [12].

As part of our continued interest in the coordination chemistry of the *sac* ligand, herein we describe the synthesis and structural characterization of Ni(II) (**1**), Cu(II) (**2**, **3**), and Cd(II) (**4**) complexes of *sac* with the 2,2′-(ethylenedioxy)bis(ethylamine) ligand (*edbea*). The crystal and molecular structure of the Cu(II) and Cd(II) complexes, namely $[Cu(edbea)(sac)_2]$ (**2**), $[Cu(\mu\text{-}edbea)(sac)_2]_n$ (**3**) and $[Cd(edbea)_2](sac)_2$ (**4**), were determined by X-ray diffraction. In addition, magnetic and EPR of the complexes were reported.

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2. Experimental

2.1. Materials and instrumentation

All chemicals were purchased commercially and used as received. The elemental analyses (C, H, N and S contents) were carried out using a LECO, CHNS-932 elemental analyser. Electronic spectra of the complexes in MeOH were measured on a Jasco V-530 spectrophotometer in the 200–900 nm range. IR spectra were recorded on a Jasco FT/IR 430 FTIR spectrophotometer as KBr pellets. The *EPR* powder spectrum was recorded with JEOL FA300 X-band ESR spectrometer, with about 5 mW microwave power and 100 kHz magnetic field modulation. The 10–300 K magnetization measurements were carried out on a Quantum Design PPMS system. X–T graphs were recorded under the constant magnetic field of 5 kOe. Magnetic data were corrected for the diamagnetic contribution of the sample holder. Thermal analysis curves (TG, DTA and DTG) were obtained using a Perkin-Elmer Diamond thermal analyser in a flowing nitrogen atmosphere. A sample size of 5–10 mg and a heating rate of 10 °C min^{-1} were used.

2.2. Synthesis of the metal complexes

The following general procedure has been adopted for the preparation of the complexes. The divalent metal complexes of *sac*, $[M(sac)_2(H_2O)_2]\cdot 2H_2O$ (M = Ni, Cu and Cd) were prepared according to the conventional methods described in the literature [5]. $[M(sac)_2(H_2O)_2]\cdot 2H_2O$ (2.0 mmol) were dissolved in MeOH (25 mL) with stirring at a water bath of ca. 60 °C. A solution of the *edbea* ligand (2.0 mmol) in MeOH (10 mL) was added to the solutions of the aqua metal complexes with continuous stirring at ca. 60 °C for ca. 30 min. The resulting solutions were left to stand at room temperature and allowed to evaporate slowly over a few days for crystallization. The crystals of the metal complexes were collected by suction filtration, washed with water and dried in air. The visual examination of the crystals of the Cu(II) complex indicated that the crystals consist of two different crystals in shape and color. Most of the crystals were pale blue and the rest was dark blue in color. In the case of zinc(II), the co-precipitation of the complex with the starting compounds occurred and therefore, these complexes could not be obtained.

$[Ni(edbea)(sac)_2]\cdot 4H_2O$ (**1**). A turquoise solid. Yield: 31%. *Anal.* Calc. for $C_{20}H_{32}S_2O_{12}N_4Ni$: C, 37.34; H, 5.01; N, 8.71; S, 9.97. Found: C, 36.87; H, 5.02; N, 7.82; S, 9.03%. Selected IR bands (cm^{-1}, KBr pellet): 3480sbr (νOH), 3325m, 3275m (νNH), 1627vs (νC=O), 1259vs ($\nu_{asym}SO_2$), 1155vs ($\nu_{sym}SO_2$), 1350m (ν_{sym}CNS), 952s (ν_{asym}CNS). UV–Vis in MeOH, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 231 (1387), 241 (1449), 252 (1401), 263 (1365), 280 (1311), 384 (37), 638 (23), 757 (17).

$[Cu(edbea)(sac)_2]$ (**2**). Dark blue crystals. Yield: 4%. *Anal.* Calc. for $C_{20}H_{24}S_2O_8N_4Cu$: C, 41.70; H, 4.20; N, 9.73; S, 11.13. Found: C, 41.90; H, 4.17; N, 9.97; S, 11.43%. Selected IR bands (cm^{-1}, KBr pellet): 3315sb, 3268 m (νNH), 1670vs, 1647vs (νC=O), 1286vs ($\nu_{asym}SO_2$), 1151vs ($\nu_{sym}SO_2$), 1332 m (ν_{sym}CNS), 960vs (ν_{asym}CNS). UV–Vis in MeOH, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 216 (1346), 236 (1393), 259 (836), 660 (18), 746 (19).

$[Cu(\mu\text{-}edbea)(sac)_2]_n$ (**3**). Pale blue crystals. Yield: 34%. *Anal.* Calc. for $C_{20}H_{24}S_2O_8N_4Cu$: C, 41.70; H, 4.20; N, 9.73; S, 11.13. Found: C, 41.90; H, 4.17; N, 9.97; S, 11.43%. Selected IR bands (cm^{-1}, KBr pellet): 3311s (νNH), 1654vs (νC=O), 1282vs, 1247 ($\nu_{asym}SO_2$), 1145vs ($\nu_{sym}SO_2$), 1326m (ν_{sym}CNS), 950s (ν_{asym}CNS). UV–Vis in MeOH, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 216 (1346), 236 (1393), 259 (836), 660 (18), 746 (19).

$[Cd(edbea)_2](sac)_2$ (**4**). Colorless crystals. Yield: 47%. *Anal.* Calc. for $C_{26}H_{40}S_2O_{10}N_6Cd$: C, 40.39; H, 5.21; N, 10.87; S, 8.29. Found: C, 40.12; H, 5.08; N, 10.83; S, 8.07%. Selected IR bands (cm^{-1}, KBr pellet): 3346m, 3303m, 3263m (νNH), 1644vs (νC=O), 1282vs, 1261 ($\nu_{asym}SO_2$), 1149vs ($\nu_{sym}SO_2$), 1335m (ν_{sym}CNS), 949s (ν_{asym}CNS).

2.3. X-ray crystallography

Intensity data for complexes of the complexes **2**, **3** and **4** were collected using a Rigaku R-AXIS RAPID-S diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 program [13]. All non-hydrogen atoms were found from the difference Fourier map and refined anisotropically. The CH hydrogen atoms were included using a riding model. The details of data collection, refinement and crystallographic data are summarized in Table 1.

Table 1
Crystallographic data and structure refinement for complexes **2**–**4**.

Complex	**2**	**3**	**4**
Formula	$C_{20}H_{24}CuN_4O_8S_2$	$C_{20}H_{24}CuN_4O_8S_2$	$C_{26}H_{40}CdN_6O_{10}S_2$
M	576.12	576.12	773.16
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$
a (Å)	8.2751(3)	7.4434(8)	14.8430(4)
b (Å)	11.9225(5)	7.9047(9)	25.3500(8)
c (Å)	12.3407(5)	11.4650(5)	18.7070(7)
α (°)	108.355(5)	100.021(5)	90
β (°)	93.969(5)	100.781(5)	107.797(3)
γ (°)	94.168(5)	113.868(5)	90
V ($Å^3$)	1147.0(10)	582.1(6)	6702.0(4)
Z	2	2	8
D_{calc} (g cm^{-3})	1.668	1.643	1.533
μ (mm^{-1})	1.190	1.173	0.837
F(000)	594	297	3184
θ Range (°)	2.07–26.41	2.93–26.42	2.16–26.50
Index range	$-9 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 15$	$-9 \leqslant h \leqslant 9$, $-9 \leqslant k \leqslant 9$, $-14 \leqslant l \leqslant 14$	$-18 \leqslant h \leqslant 18$, $-31 \leqslant k \leqslant 31$, $-19 \leqslant l \leqslant 23$
Reflections collected	25335	12893	39280
Data/parameters	4704/316	2389/160	13649/811
Goodness-of fit (GOF) on F^2	1.020	0.992	1.036
R_1 [$I > 2\sigma$]	0.0588	0.0692	0.0924
wR_2	0.1540	0.1700	0.2355