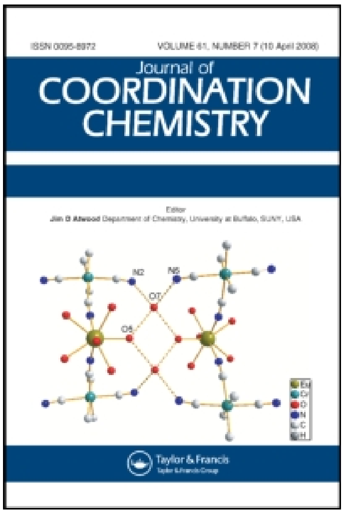

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Metal Complexes of Saccharin with the *N*-(2-hydroxyethyl)-ethylenediamine Ligand: Synthesis, Characterization and Spectroscopic Examination. Crystal Structures of *trans*- *Bis*(Saccharinato)*Bis*{*N*-(2-hydroxyethyl)-Ethylenediamine} copper(II) and Cadmium(II)

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METAL COMPLEXES OF SACCHARIN WITH THE *N*-(2-HYDROXYETHYL)-ETHYLENEDIAMINE LIGAND: SYNTHESIS, CHARACTERIZATION AND SPECTROSCOPIC EXAMINATION. CRYSTAL STRUCTURES OF *TRANS*-*BIS*(SACCHARINATO)*BIS*{*N*-(2-HYDROXYETHYL)-ETHYLENEDIAMINE} COPPER(II) AND CADMIUM(II)

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The novel transition metal saccharinato complexes of *N*-(2-hydroxyethyl)-ethylendiamine (HydEt-en) have been synthesized and characterized by elemental analyses, magnetic moments, UV–Vis and IR spectra. Coordination behaviour of HydEt-en has been studied. The Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) form mononuclear complexes, while the Fe(II) and Co(II) complexes are dimeric. The crystal structures of the $[Cu(sac)_2(HydEt\text{-}en)_2]$ and $[Cd(sac)_2(HydEt\text{-}en)_2]$ complexes, where sac is the deprotonated form of saccharin, were determined by x-ray diffraction. The metal ions are octahedrally coordinated by these ligands. The amine ligand acts as a bidentate N-donor ligand and its ethanol group is not involved in coordination. The sac ions coordinate through the deprotonated N as a monodentate ligand. The NH and OH groups of the amine ligand are involved in intra- and intermolecular hydrogen bonding with the carbonyl and sulphonyl oxygens of the sac ions to form a three-dimensional infinite network.

Keywords: Saccharin complexes; (2-hydroxyethyl)-ethylenediamine complexes; Crystal structures

INTRODUCTION

The water soluble alkali and alkaline earth salts of saccharin (*o*-sulphobenzimide) are widely used as a non-caloric artificial sweetener and food additive [1]. Research on synthesis and structural analysis of metal–saccharin complexes has been active in the

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last two decades, because of their potential effectiveness in biological systems and the suspected carcinogenic nature of saccharin [2,3]. Saccharin in its deprotonated form (sac) interacts with trace elements in the human body and readily forms complexes with a large number of metal ions. Nowadays it is generally recognized as safe in the United States [4]. The importance of sac may lie in its potential use as an antidote for metal poisoning [5].

Aqua complexes of sac with transition metals were reported by Kamenar–Jovanovski [6]. Haider *et al.* [7,8] and Cotton *et al.* [9,10] while Zhang [11] studied inner-transition metal saccharinates. Synthesis, structural and thermal characterization of mixed-ligand metal complexes of sac with mono and bidentate N-donor ligands such as pyridine [12–15], imidazole [16–18], phenanthroline [19–21] appeared in the literature recently. As part of our study on the synthesis, spectral and thermal analysis of transition metal complexes of sac with bidentate N-donor ligands [22–25], we describe in this paper, the preparation and spectroscopic identification of some novel metal–sac complexes containing *N*-(2-hydroxyethyl)ethylenediamine (HydEt-en), together with the single crystal x-ray structure of the Cu(II) and Cd(II) complex. To our knowledge, no metal complexes of HydEt-en have been reported in the literature.

EXPERIMENTAL

Materials and Instrumentation

Sodium saccharinate dihydrate and all metal salts were purchased from Merck, while *N*-(2-hydroxyethyl)-ethylenediamine. ($NH_2CH_2CH_2NHCH_2CH_2OH$) (HydEt-en) [alternatively named 2-(2-aminoethylamino)ethanol] was obtained from Aldrich. All other analytical grade chemicals and solvents were purchased commercially and used without further purification.

Electronic spectra were measured on a Unicam UV2 spectrophotometer in 2×10^{-4} M aqueous solutions of the ligand, Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes and in 2×10^{-4} M acetone solutions of the Mn(II) complex in the 200–800 nm range. IR spectra were recorded on a Mattson FTIR spectrophotometer as KBr pellets. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy magnetic balance according to the Evans method. The elemental analyses (C, H, N and S contents) were performed on a Vario EL Elemental Analyser. Melting points and water contents were determined using a Rigaku TG8110 thermal analyser with a heating rate of 10°C min^{-1} in a dynamic nitrogen atmosphere.

Preparation of 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 = Mn, Fe, Co, Ni, Cu, Zn, Cd and Hg) were prepared according to conventional methods [6–19], The *bis*(saccharinato)tetraaqua Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes (1.0 mmol) were dissolved in H_2O (25 mL) with stirring on a water bath at 80°C and then cooled to room temperature. The amine ligand (2.0 mmol) dissolved in H_2O

TABLE I Analytical data for metal complexes

Complexes	*Color*	*M.p. (°C)*[a]	*Fw.*	*Anal. (Calcd. and Found) (%)*				*Yield (%)*
				C	*H*	*N*	*S*	
[Mn(sac)$_2$(HydEt-en)$_2$]	Pale-brown	154	627.34	42.1	5.1	13.4	10.2	85
$C_{22}H_{32}N_6O_8S_2Mn$				42.0	5.2	13.1	10.0	
[Fe$_2$(sac)$_2$(HydEt-en)$_2$] ·3H$_2$O[b]	Brown	80[a]	736.10	35.9	4.9	11.4	8.7	62
$C_{22}H_{36}N_6O_{11}S_2Fe_2$				35.6	4.9	11.3	8.4	
[Co$_2$(sac)$_2$ (HydEt-en)$_2$]·2H$_2$O[b]	Dark-brown	162	724.26	36.5	4.7	11.6	8.8	67
$C_{22}H_{34}N_6O_{10}S_2Co_2$				36.9	4.9	11.7	9.2	
[Ni(sac)$_2$(HydEt-en)$_2$]	Pale-violet	216	631.11	41.9	5.1	13.3	10.2	76
$C_{22}H_{32}N_6O_8S_2Ni$				41.6	5.2	13.3	9.7	
[Cu(sac)$_2$(HydEt-en)$_2$]	Blue	180	635.94	41.6	5.0	13.2	10.2	83
$C_{22}H_{32}N_6O_8S_2Cu$				41.5	5.0	13.2	10.3	
[Zn(sac)$_2$(HydEt-en)$_2$]	White	192	637.77	41.4	5.0	13.2	10.0	78
$C_{22}H_{32}N_6O_8S_2Zn$				41.3	4.9	13.1	10.2	
[Cd(sac)$_2$(HydEt-en)$_2$]	White	227	684.80	38.6	4.8	12.3	9.4	65
$C_{22}H_{32}N_6O_8S_2Cd$				37.8	4.6	12.0	9.1	
[Hg(sac)$_2$(HydEt-en)$_2$]	White	157	772.99	34.18	4.1	10.9	8.3	61
$C_{22}H_{32}N_6O_8S_2Hg$				34.25	4.2	10.8	8.1	

[a]Decomposition point, [b]Each HydEt-en is anionic due to deprotonation of its ethanolic hydrogen.

(10 mL) was added to the solutions of the metal complexes with continuous stirring for *ca.* 30 min at room temperature. Because of decomposition of the original Mn(II), Fe(II) and Hg(II) saccharinates during dissolution in water, their metal complexes were prepared in 1-butanol using the same procedure. 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. Table I lists analytical data together with the decomposition points and colors of the complexes.

X-ray Structure Determination and Refinement

Suitable crystals of the copper and cadmium complexes were mounted on a glass fiber and X-ray diffraction data for both complexes were recorded on a BRUKER SMART 1000 CCD area detector; crystals of other complexes were not adequate for the structural analysis. The determination of unit cell and the data collection were performed with MoK_{α} radiation ($\lambda = 0.71073$). The data were collected at a temperature of 143 ± 2 K to a maximum θ value of 28.29° and 30.51° for the Cu(II) complex and the Cd(II) complex, respectively. 49 682 reflections were collected for the Cu(II) complex, while 28 847 reflections were recorded for the Cd(II) complex. Absorption correction was applied to both complexes. The structures were solved by direct methods [26] and refined by a full-matrix least-squares procedure on F^2. The details of data collection, refinement and crystallographic data are summarized in Table II.

TABLE II Crystallographic data for [Cu(sac)$_2$(HydEt-en)$_2$] and [Cd(sac)$_2$(HydEt-en)$_2$]

Empirical formula	$C_{22}H_{32}N_6O_8S_2Cu$	$C_{22}H_{32}N_6O_8S_2Cd$
Fw	636.19	685.06
Temperature (K)	143(2)	143(2)
Radiation	MoK$_\alpha$, 0.71073 Å	MoK$_\alpha$, 0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	*P*21/*c*	*P*1
Cell dimensions		
a (Å)	23.406(3)	11.0107(10)
b (Å)	7.6819(10)	11.2093(10)
c (Å)	15.9109(10)	11.8222(10)
α (°)	90	86.899(39)
β (°)	109.280(3)	68.259(3)
γ (°)	90	80.621(3)
V (Å^3)	2700.4(5)	1337.2(2)
Z	4	2
D_{calcd} (mg cm^{-3})	1.562	1.701
μ (mm^{-1})	1.021	1.031
F(000)	1320	700
θ range (°)	0.92–28.29	1.84–30.51
Reflections collected	49 682	28 847
Independent reflections	6694 [R(int) = 0.0271]	15267 [R(int) = 0.0249]
Absorption correction	Semi-empirical from equivalents	Multiple scans (SADABS)
Goodness-of-fit	0.997	1.041
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0283$, $wR2 = 0.0757$	$R1 = 0.0258$, $wR2 = 0.0669$
R indices (all data)	$R1 = 0.0375$, $wR2 = 0.0809$	$R1 = 0.0280$, $wR2 = 0.0686$
Largest diff. peak and hole (e Å^3)	0441 and − 0.390	0.844 and − 0.814

RESULTS AND DISCUSSION

Synthesis

Synthesis of [M(sac)$_2$(L)$_2$] complexes is straight-forward by treatment of the aqua complexes of metal–sac with appropriate ligand in solution, since the aqua ligands are labile and readily displaced by neutral ligands. The metal–sac complexes of HydEt-en were synthesized by direct reaction of the ligand with the aqua metal–sac. In the starting metal–sac complexes, the M(II) ions are octahedral with a centrosymmetric arrangement of two saccharinate nitrogen atoms in *trans* positions and four water molecules [6–10]. Thus, the addition of the neutral amine ligand to the solution of the starting complexes resulted in the substitution of the aqua ligands, as followed by a sharp color change, and the formation of *bis*(saccharinato) *bis*(amine)M(II).

The new complexes were obtained in good yields and the elemental analyses conformed to their proposed formula (see Table I). The results clearly indicate that Mn(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) form mononuclear complexes, while the Fe(II) and Co(II) complexes are dimeric. Dimeric compositions require deprotonation of the ethanolic groups of the amine ligands in order to compensate for the positive charges of metal ions. The ethanolate group participates in coordination, usually resulting in the formation of dimeric structures with alkoxo-bridges between the coordinated metal ions as reported for the metal complexes of ethanolamines [27,28]. The Fe(II) and Co(II) complexes contain three and two molecules of water, respectively, as determined by TG (mass loss for the iron complex, calcd. 7.33% and found 7.32%; mass loss for the cobalt complex, calcd. 4.97% and found 4.63%). Dimeric structures of these complexes were also evidenced by determining their metal contents (the iron content, calcd. 15.17% and found 15.48%; the cobalt content, calcd. 16.27% and found 16.46%), and the percentage of iron (15.56%) and cobalt (16.31%) in the residues formed at 900°C in the complete decomposition under nitrogen atmosphere. The higher metal content suggests binuclear structures of the Fe(II) and Co(II) complexes.

All the metal complexes except the Co(II) complex are non-hygroscopic and stable in air, but the Co(II) complex is highly hygroscopic. The Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) are very soluble in water, while the Fe(II) complex is slightly soluble in water, acetone and ethanol. The Mn(II) complex is also soluble in water, but air-oxidized during dissolution. All the metal complexes except for the Fe(II) complex exhibit sharp melting points as determined by DTA, but the Fe(II) complex does not have a melting point and decomposes at 80°C.

Spectroscopic and Magnetic Properties

The λ_{max} values of the different absorption bands displayed by the complexes are given in Table III, together with the ε_{max} values. The amine ligand does not exhibit an electronic transition in the UV–Vis region and therefore, the bands mainly around 265 nm in the UV region are due to intraligand transitions of sac [8,23]. The extremely intense magnitude of the band with ε_{max} value over 3200 L mol^{-1} cm^{-1} is very remarkable. The Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes show broad bands with very low intensity in the range 350–800 nm, which are assigned to *d–d* transitions of octahedral coordination [29]. The additional shoulder at 737 nm in the spectra of the Cu(II) complex clearly indicates the presence of the Jahn–Teller effect due to the non-equivalent C–N bonds with different lengths [30]. The Zn(II), Cd(II) and Hg(II) complexes display only transitions of sac in the UV region.

The effective magnetic moments of the complexes at room temperature are listed in Table III. The metal complexes show a high-spin configuration. The magnetic moments agree well with the octahedral geometry around the metal ions and the calculated values of the spin-only magnetic moments.

Selected IR data are summarized in Table IV. A strong and broad band centred at 3325 cm^{-1} in the spectrum of the free amine is assigned to ν(OH) of the ethanol

TABLE III Electronic spectral data and magnetic moments of complexes

Complexes	λ_{max} (nm)/ε (L mol^{-1} cm^{-1})				μ_{eff} (BM) *Found (calcd.)*[a]
[Mn(sac)$_2$(HydEt-en)$_2$]	266 (6265)	470 (25)	727 (12)		5.66 (5.92)
[Fe$_2$(sac)$_2$(HydEt-en)$_2$] · 3H$_2$O	266 (7095)	365 (1820)	741 (68)		4.76 (5.19)
[Co$_2$(sac)$_2$(HydEt-en)$_2$] · 2H$_2$O	272 (7065)	482 (169)	749 (57)		3.75 (3.87)
[Ni(sac)$_2$(HydEt-en)$_2$]	267 (4475)	350 (104)	563 (58)	764 (58)	2.73 (2.83)
[Cu(sac)$_2$(HydEt-en)$_2$]	262 (7055)	581 (126)	737 (84)		1.5 (1.73)
[Zn(sac)$_2$(HydEt-en)$_2$]	266 (3845)				Dia.
[Cd(sac)$_2$(HydEt-en)$_2$]	266 (3690)				Dia.
[Hg(sac)$_2$(HydEt-en)$_2$]	264 (3220)				Dia.

[a] Spin-only values.

TABLE IV IR spectral data for the amine and metal complexes

Compounds	$\nu(OH)$	$\nu(NH)$	$\nu(CH)$	$\nu(C{=}O)$	$\delta(NH)$	$\delta(CH)$	$\nu_{asym}(SO_2)$	$\delta(C{=}O)$	$\nu_{sym}(SO_2)$	$\nu(CO)$	$\nu(MN)$
HydEt-en	3325 b	3218 m	2949 w	–	1616 s	1469 s	–	–	–	1067 s	–
$[Mn(sac)_2(HydEt\text{-}en)_2]$	3380 s	3299 m	2949 w	1656 vs	1580 s	1471 m	1265 vs	1156 vs	1123 s	1069 m	548 m
$[Fe_2(sac)_2(HydEt\text{-}en)_2] \cdot 3H_2O$	3407 s	3272 s	2949 w	1656 vs	1591 s	1460 m	1254 vs	1156 vs	1123 m	1047 w	537 m
$[Co_2(sac)_2(HydEt\text{-}en)_2] \cdot 2H_2O$	3488 s	3353 s	2949 sh	1634 vs	1580 vs	1471 s	1265 s	1156 vs	1123 s	1058 m	548 m
$[Ni(sac)_2(HydEt\text{-}en)_2]$	3380 s	3272 s	2948 w	1665 vs	1579 vs	1469 m	1262 vs	1164 vs	1128 s	1079 m	542 m
$[Cu(sac)_2(HydEt\text{-}en)_2]$	3515 s	3272 m	2976 w	1645 vs	1580 s	1460 m	1265 vs	1156 vs	1123 s	1058 m	537 m
$[Zn(sac)_2(HydEt\text{-}en)_2]$	3353 s	3245 s	2976 w	1626 vs	1580 s	1464 s	1267 vs	1162 vs	1123 s	1046 vs	536 m
$[Cd(sac)_2(HydEt\text{-}en)_2]$	3485 s	3352 m	2993 m	1652 vs	1579 s	1469 m	1286 vs	1152 vs	1127 s	1054 m	542 m
$[Hg(sac)_2(HydEt\text{-}en)_2]$	3568 b	3272 w	2949 w	1656 vs	1591 s	1460 m	1265 vs	1156 vs	1123 s	1058 m	548 m

group with a strong hydrogen bond. This band shifts to higher frequency in the complexes, probably due to weaker hydrogen bonding. The distinct medium bands in the range 3220–3352 cm^{-1} and 2868–2993 can be assigned to the NH and CH stretches of the amine ligand, respectively. The NH bands in the spectra of the complexes split into two separate bands due to non-equivalent coordination positions of the ligand to the metal ions. The ν(CO) vibrations of sac appear at *ca.* 1650 cm^{-1} as very strong bands for all complexes. The very strong bands at *ca.* 1470 and 1150 cm^{-1} correspond to the stretching vibrations of $\nu_{asym}(SO_2)$ and $\nu_{sym}(SO_2)$, respectively. Additional absorption bands at 1297 and 1293 cm^{-1} occurred in the spectra of the iron and cobalt complexes, respectively and may be attributed to bridging ligands to form a dimeric structure. The weak bands in the region 400–550 cm^{-1} are due to M–N stretching vibrations [31].

Description of the Crystal Structures

Selected bond distances and angles in the Cu(II) and Cd(II) complexes are listed in Tables V and VI, respectively. The molecular structures of these complexes are shown in Figs. 1 and 2, respectively.

The structure of both complexes consists of discrete neutral molecules in which the metal, located on a symmetry center, exhibits somewhat distorted octahedral geometry bonding two sac ions and two amine ligands. Each amine acts as a bidentate donor, *via* its two nitrogens (N, N) and the ethanolic group containing O does not participate in coordination. The amine molecules occupy *cis* positions of the equatorial plane, while the monodentate sac ions, through their deprotonated nitrogen, are positioned in the axial *trans* positions of the octahedron. The M–N$_{sac}$ bonds [2.5507(14) Å for the copper complex, and 2.412(4) and 2.525(5) Å for the cadmium, complex] are longer than the M–N$_{amine}$ bonds [2.0210(14) Å for the copper complex and 2.346(4) and 2.390(5) Å for the cadmium complex]. The Cu–N$_{amine}$ bonds are much shorter than those of the Cd–N$_{amine}$ bonds, indicating stronger interaction of the amine ligand

TABLE V Selected bond distances (Å) and angles (°) for [Cu(sac)$_2$(HydEt-en)$_2$][a]

Cu1–N1	2.0210(14)	S111–O111	1.4466(14)
Cu1–N1#1	2.0210(14)	S111–O112	1.4438(14)
Cu1–N2	2.0562(13)	C111–O110	1.2340(19)
Cu2–N2#1	2.0562(13)	C111–N111	1.365(2)
Cu1–N111	2.5507(14)	C111–C117	1.503(2)
Cu1–N121#1	2.5507(14)	C112–C117	1.381(2)
N1–C1	1.480(2)	C112–C113	1.382(2)
C1–C2	1.504(3)	C113–C114	1.396(2)
C2–N2	1.494(2)	C114–C115	1.397(3)
N2–C3	1.477(2)	C115–C116	1.389(3)
C3–C4	1.517(2)	C116–C117	1.389(2)
C4–O1	1.412(2)	C112–S111	1.7604(16)
N111–S111	1.6113(14)		
N1–H01A···O110#1	2.9839(19)	N2–H02···O112#1	3.113(2)
N1–H01B···O112#3	3.0862(19)		
N1–Cu1-N2	87.93(6)	N1–Cu1–N2#1	95.07(6)
N1–Cu1–N111	92.35(5)	N111–Cu1–N111#1	180.0
N1–Cu1–N111#1	87.65(5)	N1–Cu1–N1#1	180.0

[a] Symmetry transformations used to generate equivalent atoms:
#1 $-x, -y+1, -z+1$; #2 $-x+1, -y, -z+1$; #3 $-x, -y+2, -z+1$; #4 $x, y-1, z$.

TABLE VI Selected bond lengths (Å) and angles (°) for $[Cd(sac)_2(HydEt\text{-}en)_2]^a$

Cd1–N1	2.350(5)	N111–C111	1.343(5)
Cd1–N2	2.346(4)	S111–O111	1.468(4)
Cd1–N3	2.390(5)	S111–O112	1.446(4)
Cd1–N4	2.351(5)	C111–O110	1.258(4)
Cd1–N111	2.525(5)	C111–C112	1.514(5)
Cd1–N121	2.412(4)	C112–C113	1.415(5)
N1–C1	1.470(6)	C113–C114	1.353(6)
C1–C2	1.578(6)	C114–C115	1.411(5)
C2–N2	1.479(7)	C115–C116	1.421(5)
N1–C3	1.529(6)	C116–C117	1.368(6)
C3–C4	1.466(6)	C117–S111	1.771(4)
C4–O1	1.479(6)	C112–C117	1.391(5)
N111–S111	1.613(4)		
N1–H1···O111	3.219(6)	N2–H22···O140#1	2.915(5)
N2–H21···O110	3.003(6)	O1–H01···O130	2.786(6)
O2–H02···O122	2.778(6)	O3–H03···O131	2.811(6)
N1–Cd1–N2	77.38(14)	N1–Cd1–N3	172.46(14)
N1–Cd1–N4	102.10(16)	N2–Cd1–N4	174.52(17)
N1–Cd1–N111	86.74(16)	N111–Cd1–N121	176.40(18)
N1–Cd1–N121	96.28(15)		

[a] Symmetry transformations used to generate equivalent atoms:
#1 $x, y-1, z+1$; #2 $x, y, z+1$; #3 $x, y, z-1$; #4 $x, y+1, z-1$.

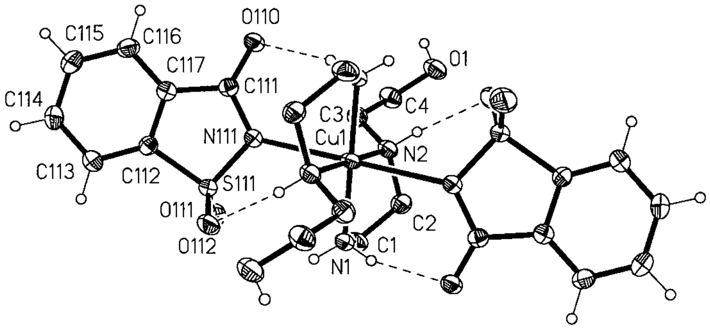

FIGURE 1 A view of $[Cu(sac)_2(HydEt\text{-}en)_2]$ showing the atomic numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and the CH_2 hydrogens of the HydEt-en ligand have been omitted for clarity.

with the Cu(II) ions, with respect to the Cd(II) ions. The M–N_{sac} distances of the both complexes are close to each other. The Cu-N_{sac} bond [2.5507(13) Å] is significantly longer than those found in $[Cu(sac)_2(bpy)_2sac \cdot 2H_2O$, [2.030(5)]; [32] $[CuH_2O)(bpy)_2(sac)_2]$, [2.032(2)] [14] and the Cd–N_{sac} distance is also longer than those found in the $[Cu_2(sac)_4(im)_4]$ dimer [2.208(5) and 2.323(5) Å] [18]. Since all Cu(II) ions lie on crystallographic inversion centers, the *trans* angles in the Cu(II) complex are 180°, while the cis ones are in the range 87.65(5) to 95.07(6)°. However, the interaxial angles in the Cd(II) complex are between 172.46(14)–176(18)° and 77.38(14)–102.10(16)°. It is evident that Jahn–Teller distortion may be responsible for the observed distorted octahedral geometry around the Cu(II) center, as also observed in the electronic spectra of the Cu(II) complex.

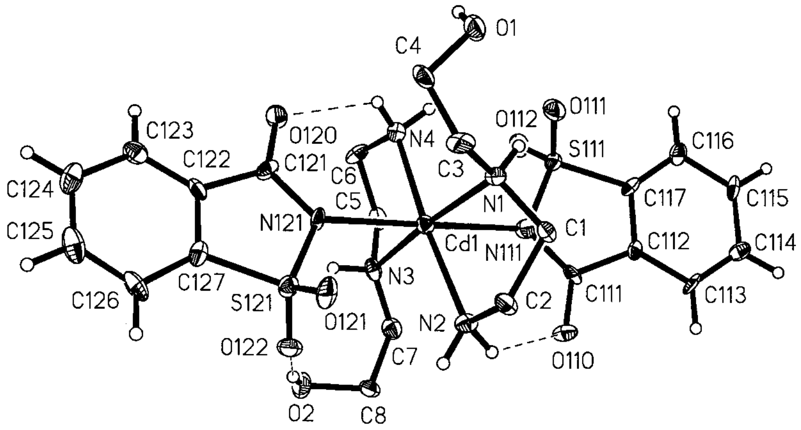

FIGURE 2 A view of $[Cd(sac)_2(HydEt\text{-}en)_2]$ showing the atomic numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level and the CH_2 hydrogens of the HydEt-en ligand have been omitted for clarity.

Both sac ions are essentially planar and the dihedral angles between the planes of the *trans* sac ions are 0 and 166° for the Cu(II) and Cd(II) complexes, respectively. The bond distances and angles within the sac ions are virtually identical to those found in free sac [33]. The hydrogen atoms of the NH and free OH groups participate in the intra- and intermolecular hydrogen bonding with the sac ions. The NH and OH hydrogens form intramolecular hydrogen bonding with the carbonyl oxygen and the sulfonyl oxygen within the same molecule, respectively, while the NH hydrogens participate in the intermolecular hydrogen bonding with the carbonyl oxygens of the adjacent molecules. The individual molecules are thus linked by hydrogen bonds to form a three-dimensional infinite network.

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Supplementary Material

Crystallographic data (atomic coordinates, atomic displacement parameters and bond geometries) for the structures reported in the paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material with a deposition number CCDC 147301 for the copper complex and CCDC 147300 for the cadmium complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

References

[1] L.O. Nabors and C.G. Robert (1991). *Alternative Sweeteners*, 2nd Edn. Marcel Dekker, New York.
[2] I.C. Munro, C.A. Modie, D. Krewski and H.C. Grice (1957). *Toxicol. Appl. Pharmacol.*, **32**, 513.
[3] M.J. Allen, E. Bayland, C.E. Dukes, E.S. Horning and J.G. Watson (1957). *Br. J. Cancer*, **11**, 212.

[4] J. Anderson and B. Deskins (1995). *The Nutrition Bible*, William Morrow and Company.
[5] E.W. Ainscough, E.N. Baker and A.M. Brodie (1990). *Inorg. Chim. Acta*, **172**, 185.
[6] B. Kamenar and G. Jovanovski (1982). *Cryst. Struct. Commun.*, **11**, 257.
[7] Z. Haider, K.M.A. Malik, K.J. Ahmed, H. Hess, H. Riffel and M.B. Hursthouse (1983). *Inorg. Chim. Acta.*, **72**, 21.
[8] Z. Haider, K.M.A. Malik and K.J. Ahmed (1985). *Inorg. Synth.*, **23**, 47.
[9] F.A. Cotton, G.E. Lewis, C.A. Murillo, W. Schwotzer and G. Valle (1984). *Inorg. Chem.*, **23**, 4038.
[10] F.A. Cotton, E. Libby, C.A. Murillo and G. Valle (1990). *Inorg. Synth.*, **27**, 306.
[11] Y. Zhang (1998). *Spect. Lett.*, **31**, 1609.
[12] A.D. Magri, G. Dascenzo, S.N. Cesaro and E. Chiacchierini (1980). *Thermochim. Acta*, **36**, 279.
[13] O.V. Quinzani, S. Tarulli, O.E. Piro, E.J. Baran and E.E. Castellano (1997). *Z. Naurforsch* B. **52**, 183.
[14] G. Jovanovski, P. Naumov. O. Grupce and B. Kaitner (1998). *Eur. J. Solid State Inorg. Chem.*, **35**, 231.
[15] O.V. Quinzani, S. Tarulli, C. Marcos, S.G. Granda and E.J. Baran (1999). *Z Anorg. Allg. Chem.*, **625**, 1848.
[16] L. Jianmin, Z. Yugeng, L. Wenbin, L. Shixiong and H. Jinling (1992). *Polyhedron*, **11**, 419.
[17] Z. Yugeng, L. Jianmin, L. Wenbin, L. Shixiong and H. Jinling (1992). *J. Crystallogr. Spectrosc. Res.*, **22**, 433.
[18] Li Jianmin, Ke Yanxiong, W. Quanming and Wu Xintao (1997). *Cryst. Res. Technol.*, **32**, 481.
[19] Z. Yugeng, Li Jianmin, W. Jing, Wu Xingtao and Du Shaowu (1994). *Cryst. Res. Technol.*, **29**, 975.
[20] R.M.K. Deng, C. Bilton, K.B. Dillon and J.A.K. Howard (2000). *Acta Cryst.*, **C56**, 142.
[21] E.J. Baran, C.C. Wagner, M. Rossi and F. Caruso (2000). *Z. Anorg. Allg. Chem.*, **626**, 701.
[22] H. Icbudak and V.T. Yilmaz (1997). *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 1571.
[23] V.T. Yilmaz, Y. Topcu and F. Yilmaz (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 409.
[24] V.T. Yilmaz (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 621.
[25] H. Icbudak, T.K. Yazicilar and V.T. Yilmaz (1999). *Thermochim. Acta.*, **335**, 93.
[26] G.M. Sheldrick (1990). *Acta Cryst.*, **A46**, 467.
[27] M.B. Hursthouse, K.J. Izod, M.A. Mazid and P. Thornton (1990), *Polyhedron*, **9**, 530.
[28] J. Madarasz, P. Bombiez, M. Czugler and G. Pokol (2000). *Polyhedron*, **19**, 457.
[29] A.B. Lever (1968). *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam.
[30] J.D. Lee (1991). *Concise Inorganic Chemistry*. Chapman and Hall, London.
[31] K. Nakamoto (1978). *Infrared and Raman spectra of Inorganic and Coordination Compounds*. Wiley, New York.
[32] A. Hergold-Brundic, O. Grupce and G. Jovanovski (1991). *Acta Cryst.*, **C47**, 2659.
[33] Y. Okaya (1969). *Acta Cryst.*, **B25**, 2257.