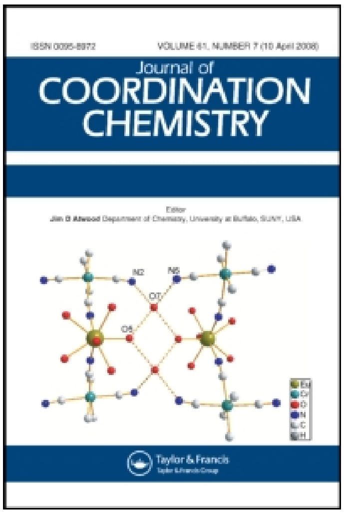

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Synthesis, Characterization and Spectral Studies of Triethanolamine Complexes of Metal Saccharinates. Crystal Structures of $[Co(TEA)_2](SAC)_2$ AND $[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2(CH_3OH)$

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SYNTHESIS, CHARACTERIZATION AND SPECTRAL STUDIES OF TRIETHANOLAMINE COMPLEXES OF METAL SACCHARINATES. CRYSTAL STRUCTURES OF $[Co(TEA)_2](SAC)_2$ AND $[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2(CH_3OH)$

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The novel transition metal saccharinate complexes of triethanolamine (TEA) have been synthesized and characterized by elemental analyses, magnetic moments, UV–Vis and IR spectra. Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) form mononuclear complexes of $[M(TEA)_2](SAC)_2$, where SAC is the saccharinate ion, while the Cu(II) complex is dimeric. The TEA ligand acts as a tridentate N,O,O'-donor ligand and one ethanol group is not involved in coordination. The SAC ion does not coordinate to the metal ions and is present as the counter-ion in the Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes, but coordinates to the Cu(II) ion as a monodentate ligand. The crystal structures of the $[Co(TEA)_2](SAC)_2$ and $[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2(CH_3OH)$ complexes were determined by single crystal x-ray diffraction. The Co(II) ion has a distorted octahedral coordination by two TEA ligands. The Cu(II) complex crystallizes as a dimethanol solvate and has doubly alkoxo-bridged centrosymmetric dimeric molecules involving two tridentate triethanolaminate (deprotonated TEA) and two monodentate SAC ligands. The geometry of each Cu(II) ion is a distorted square pyramid. Both crystal structures are stabilized by hydrogen bonds to form a three-dimensional network.

Keywords: Saccharin complexes; Triethanolamine complexes; Crystal structures

INTRODUCTION

Triethanolamine (TEA) readily forms complexes with all the metal ions and its simple transition metal complexes were synthesized by Sen and Dotson [1], and Brannon *et al.* [2] TEA behaves as a tri (N,O,O') [1,2] or tetradentate (N,O,O',O'') [3] ligand. The ethanol groups of the TEA ligand contain three hydroxyl protons that may dissociate and in some cases, it loses one of the ethanolic hydrogens to give the triethanolaminate,

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which also behaves as a ligand similar to the neutral TEA molecule. Homo- and heterobimetallic ethanolaminate derivatives of a number of metals have been reported recently [4–7].

The water soluble alkali and alkaline earth salts of saccharin (*o*-sulphobenzimide) are widely used as non-caloric artificial sweetener and food additive [8]. Saccharin in its deprotonated form (SAC) interacts with metal ions to form stable compounds in which SAC acts as a *N*-donor monodentate ligand or a counter-ion, depending on the presence of other ligands [9–14]. In recent years, we have studied the synthesis, spectral, thermal and crystallographic characterization of metal–SAC complexes with various amine ligands [15–19] and metal-TEA complexes [20–24]. As a part of our ongoing research, in this paper, we describe the preparation and spectroscopic characterization of some novel TEA complexes of metal saccharinates. The single crystal x-ray structures of the Co(II) and Cu(II) complexes are also reported.

EXPERIMENTAL

Materials and Instrumentation

TEA [$N(CH_2CH_2OH)_3$], [alternatively named tris(2-hydroxyethyl)amine], sodium saccharinate dihydrate, and all metal salts were purchased from Merck. 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 10^{-3} M DMF solutions 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. Elemental analyses (C, H and N) were carried out at the TUBITAK Marmara Research Centre. Melting points were determined using a Rigaku TG8110 thermal analyzer 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, $[M(SAC)_2(H_2O)_4]\cdot 2H_2O$ (M = Mn, Co, Ni, Cu, Zn, Cd and Hg) were prepared according to the conventional methods described in the literature [10–13]. The *bis*(saccharinato) Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes (1.0 mmol) were dissolved in the methanol–isopropanol mixture (1 : 1) (40 mL) with stirring at 60°C and then cooled to room temperature. The TEA ligand (2.0 mmol) was added to the solution of the metal complexes with continuous stirring for *ca.* 60 min at room temperature. The resulting solutions were left to stand at room temperature and evaporate slowly over a few days for crystallization. The crystals of the metal complexes were collected by suction filtration, washed with acetone and dried in air. Attempts to prepare the Fe(II) complex failed due to oxidation in air. Table I lists analytical data together with the melting points and colors of the complexes.

TABLE I Analytical data for TEA complexes of metal saccharinates

Complexes	*Color*	*M.p.* (°C)	*Fw.*	*Anal. (Calcd. and Found) (%)*			*Yield (%)*
				C	*H*	*N*	
$[Mn(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Mn$	Yellow-brown	188	717.68	43.5 43.0	5.3 5.9	7.8 7.2	74
$[Co(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Co$	Pale-pink	181	721.67	43.3 42.8	5.3 5.5	7.8 7.5	87
$[Ni(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Ni$	Blue	216	721.45	43.3 43.1	5.3 5.6	7.8 7.4	85
$[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2CH_3OH$[a] $C_{28}H_{44}N_4O_{14}S_2Cu_2$	Green	125	851.87	39.5 39.5	5.2 5.3	6.6 6.3	77
$[Zn(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Zn$	White	90	728.11	42.9 43.2	5.3 5.5	7.7 7.3	80
$[Cd(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Cd$	White	209	775.15	40.3 40.0	4.9 5.5	7.2 6.9	74
$[Hg(TEA)_2](SAC)_2$ $C_{26}H_{38}N_4O_{12}S_2Hg$	White	112	863.33	36.2 35.8	4.4 4.6	6.5 5.9	67

[a] Each TEA is monoanionic due to deprotonation of its hydroxyl hydrogen

X-ray Structure Determination and Refinement

Suitable crystals of the manganese and copper complexes were mounted on a glass fiber and x-ray diffraction data for both complexes were recorded on a BRUKER SMART 1000CCD area detector. The determination of unit cell and the data collection were performed with MoK_α radiation ($\lambda = 0.71069$). The data were collected at a temperature of 298 ± 2 K to a maximum θ value of 27.62° and 27.51° for the Co(II) complex and the Cu(II) complex, respectively. 7993 reflections were collected for the Co(II) complex, while 8924 reflections were recorded for the Cu(II) complex. An absorption correction was applied to both complexes. The structures were solved by direct methods [25] and refined by a full-matrix least-squares procedure [26] on F^2. Molecular drawings were obtained using ORTEPIII [27]. The details of data collection, refinement and crystallographic data are summarized in Table II.

RESULTS AND DISCUSSION

Synthesis and General Properties

Mixed-ligand complexes of SAC are prepared by reaction of an appropriate ligand with the tetraaquabis(saccharinato)metal(II) complexes in solution, since the aqua ligands are labile and readily displaced by neutral ligands. The TEA complexes of the metal saccharinates were synthesized by the direct reaction of the neutral ligand with the corresponding aqua metal complex of SAC. Thus, addition of the bulky TEA ligand to the solution of the aqua complexes resulted in substitution of both the aqua and SAC ligands, and the formation of the metal complexes of $[M(TEA)_2](SAC)_2$, where M is Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Hg(II). The molar ratio of M : TEA in the complexes is 1 : 2 and SAC is present as a counter ion. In the case of the Cu(II) complex, the TEA ligand was ionized during the complexation and converted to the triethanolaminate monoanion. This resulted in the formation of a dimeric

TABLE II Crystallographic data for $[Co(TEA)_2](SAC)_2$ and $[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2CH_3OH$

	$[Co(TEA)_2](SAC)_2$	$[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2CH_3OH$
Empirical formula	$C_{26}H_{38}N_4O_{12}S_2Co$	$C_{28}H_{44}N_4O_{14}S_2Cu_2$
Fw	721.65	851.87
Temperature (K)	298 (2)	298 (2)
Radiation	MoK_α, 0.71069 Å	MoK_α, 0.71069 Å
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Cell dimensions		
a (Å)	7.9729 (4)	8.2025 (4)
b (Å)	9.0475 (4)	10.3657 (5)
c (Å)	11.9712 (6)	10.6638 (5)
α (°)	74.046 (1)	102.512 (1)
β (°)	86.465 (1)	99.414 (1)
γ (°)	65.628 (1)	94.473 (1)
V (Å)	754.97 (6)	867.15 (7)
Z	1	1
D_{calcd} (Mg m^{-3})	1.597	1.631
μ (mm^{-1})	0.777	1.419
F(000)	377	442
θ range (°)	1.77–27.62	1.99 to 27.51
Index ranges	$-10 \leq h \leq 9$; $-11 \leq k \leq 11$; $-15 \leq l \leq 15$	$-10 \leq h \leq 10$; $-13 \leq k \leq 13$; $-13 \leq l \leq 13$
Reflections collected	7998	8924
Independent reflections	3485 [*R*(int) = 0.0202]	3971 [*R*(int) = 0.0274]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Goodness-of-fit	1.080	1.002
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0302$, $wR2 = 0.0819$	$R1 = 0.0369$, $wR2 = 0.0958$
R indices (all data)	$R1 = 0.0396$, $wR2 = 0.0856$	$R1 = 0.0509$, $wR2 = 0.1024$
Largest diff. Peak and hole (e Å^3)	0.341 and -0.304	0.984 and -0.385

Cu(II) complex containing the deprotonated TEA and SAC ligands. The molar ratio of Cu : TEA : SAC in the dimeric complex is 2 : 2 : 2. Dimeric compositions are usually achieved by alkoxo-bridges, and require deprotonation of one of the ethanolic groups of the ethanolamine ligands, in order to compensate for the positive charges of metal ions [28–30]. The complexes were obtained in good yields and the elemental analyses conformed to their proposed formulas (See Table I). All the metal complexes are non-hygroscopic and stable in air. They are very soluble in DMF and DMSO, and sparingly soluble in warm *n*-butanol, and the methanol–isopropanol mixture (1 : 1). Dissolution of the complexes in water occurs with decomposition.

Spectroscopic and Magnetic Properties

The λ_{max} values of the different absorption bands displayed by the complexes are listed in Table III, together with the ε_{max} values. The TEA ligand exhibits two relatively sharp bands in the UV region at *ca.* 235 and 250 nm. The band around 300 nm is due to intra-ligand transitions of SAC [11]. The intense magnitude of the transition band of SAC is very noticeable compared to those of TEA. The metal complexes show broad bands with very low intensity in the range 400–800 nm, which are assigned to *d–d* transitions of octahedral coordination [31]. The Zn(II), Cd(II) and Hg(II) complexes display only transitions of TEA and SAC in the UV region.

TABLE III Electronic spectral data and magnetic moments of complexes

Complexes	λ_{max}(nm)/ε M^{-} cm^{-1}			μ_{eff} *(BM) Found (calcd.)*[a]
	TEA	*SAC*	*d–d*	
$[Mn(TEA)_2](SAC)_2$	231 (193), 255 (352)	300 (1510)	574 (2)	5.77 (5.92)
$[Co(TEA)_2](SAC)_2$	238 (159), 256 (296)	301 (1530)	523 (39)	4.26 (3.87)
$[Ni(TEA)_2](SAC)_2$	235 (211), 253 (175)	301 (1330)	400 (16) 646 (8)	2.94 (2.83)
$[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2CH_3OH$	235 (239), 262 (1320)	295 (1940)	736 (97)	1.65 (2.83)
$[Zn(TEA)_2](SAC)_2$	238 (167), 248 (158)	289 (1260)	–	Dia.
$[Cd(TEA)_2](SAC)_2$	230 (182), 248 (232)	302 (1420)	–	Dia.
$[Hg(TEA)_2](SAC)_2$	230 (196), 251 (229)	288 (1230)	–	Dia.

[a] Spin-only values

TABLE IV IR spectral data for TEA complexes of metal saccharinates

Compounds	$v(OH)$	$v(CH)$	$v(C=O)$	$v_{asym.}(SO_2)$	$v_{sym.}(SO_2)$	$v_{sym.}(CNS)$	$v_{asym.}(CNS)$
$[Mn(TEA)_2](SAC)_2$	3478 vs, 3359 vs	2913 w	1638 vs	1292 vs	1152 vs	1354 s	959 s
$[Co(TEA)_2](SAC)_2$	3488 s, 3358 m	2949 w	1633 vs	1275 s	1150 vs	1346 s	959 m
$[Ni(TEA)_2](SAC)_2$	33414 sb	2956 w	1608 vs	1289 vs	1164 vs	1352 s	981 m
$[Cu_2(\mu\text{-}TEA)_2(SAC)_2]\cdot 2CH_3OH$	3478 vs, 3363 s	2934 w	1641 vs	1289 vs	1149 vs	1342 s	959 s
$[Zn(TEA)_2](SAC)_2$	3479 s, 3361 vs	2932 w	1636 vs	1261 vs	1148 vs	1345 s	956 s
$[Cd(TEA)_2](SAC)_2$	3470 s, 3136 sb	2913 w	1635 vs	1293 vs	1152 vs	1355 s	958 s
$[Hg(TEA)_2](SAC)_2$	3442 sb	2961 w	1630 vs	1263 vs	1160 vs	1340 s	960 s

The effective magnetic moments of the complexes at room temperature are also listed in Table III. The metal complexes exhibit a high-spin configuration. The experimental magnetic moments agree well with the octahedral geometry around the metal ions and the calculated values of the spin-only magnetic moments. The magnetic moment value of the Cu(II) complex seems to be half of its spin only value. This complex is dimeric with remarkably strong Cu–Cu bonds as will be discussed below. The Cu–Cu interaction may influence the magnetic properties by a super-exchange mechanism and similar findings were reported for dimeric Cu(II) complexes with aminoalkoxo bridges [28–30].

Selected IR data for the complexes are given in Table IV. The strong bands above 3300 cm^{-1} in the spectra of the complexes are assigned to ν(OH) absorptions of the ethanol groups of TEA. These bands appear as a doublet in the spectra of the Mn(II), Co(II), Cu(II) Zn(II) and Cd(II) complexes indicating non-equivalent coordination positions of the hydroxyl groups [2], while the Ni(II) and Hg(II) complexes give only a single and broad absorption band probably due to overlapping of the two bands. The distinct weak bands centered at *ca.* 2930 cm^{-1} can be assigned to the CH stretching of the TEA ligand. The ν(CO) vibrations of SAC appear at *ca.* 1630 cm^{-1} as very strong bands and the very strong bands at *ca.* 1280 and 1150 cm^{-1} correspond to the stretching vibrations of $\nu_{asym.}(SO_2)$ and $\nu_{sym.}(SO_2)$, respectively [11,12]. The $\nu_{sym.}$(CNS) and $\nu_{asym.}$(CNS) vibrations occur at *ca.* 1350 and 960 cm^{-1}, respectively. The weak bands in the region 400–500 cm^{-1} are due to M–N stretching vibrations [32].

Description of the Crystal Structures

[Co(TEA)$_2$](SAC)$_2$

The molecular structure and cell content of *bis*(triethanolamine-*N*,*O*,*O*′)cobalt(II) saccharinate are shown in Figs. 1 and 2, respectively. Selected bond distances and angles in the Co(II) and Cu(II) complexes are listed in Tables V and VI, respectively.

The structure of Co(II) complex consists of a $[Co(TEA)_2]^{2+}$ cation and two SAC anions. In the cation, the Co(II) ions sits on an inversion center and exhibits a distorted octahedral coordination with two TEA ligands. Each TEA ligand acts as a tridentate donor (*N*,*O*,*O*′) through its nitrogen (N1) and two hydroxyl oxygens (O1 and O2), and the third hydroxyl group (O3) remains uncomplexed. The ethanol groups of TEA are disordered over two positions with approximately equal occupancy. The M–N bond lengths are 2.149(2) Å and M–O bond lengths are in the range 2.072(3)–2.093(3) Å. The *trans* angles are 180°, while the *cis* angles are in the range 79.30(13)–100.73(13)°. Therefore, the coordination geometry around the Co(II) ion is best described as a distorted octahedron.

Both SAC ions are essentially planar with an r.m.s deviation of 0.023 Å. The bond distances and angles within the SAC ions are virtually identical to those found in free SAC [33] and other amine complexes with SAC as the counter-ion [34,35]. The SAC ions adopt a parallel alignment. The phenyl rings approximately superimpose on each other and are connected by weak π–π interactions [4.1084(2) Å] (see Fig. 2). The hydrogen atoms of the free and coordinated hydroxyl groups are involved in intermolecular hydrogen bonding with the SAC ions. The coordinated hydroxyl hydrogens (O1–H1 and O2–H2) from hydrogen bonds with the nitrogen (N2#1)

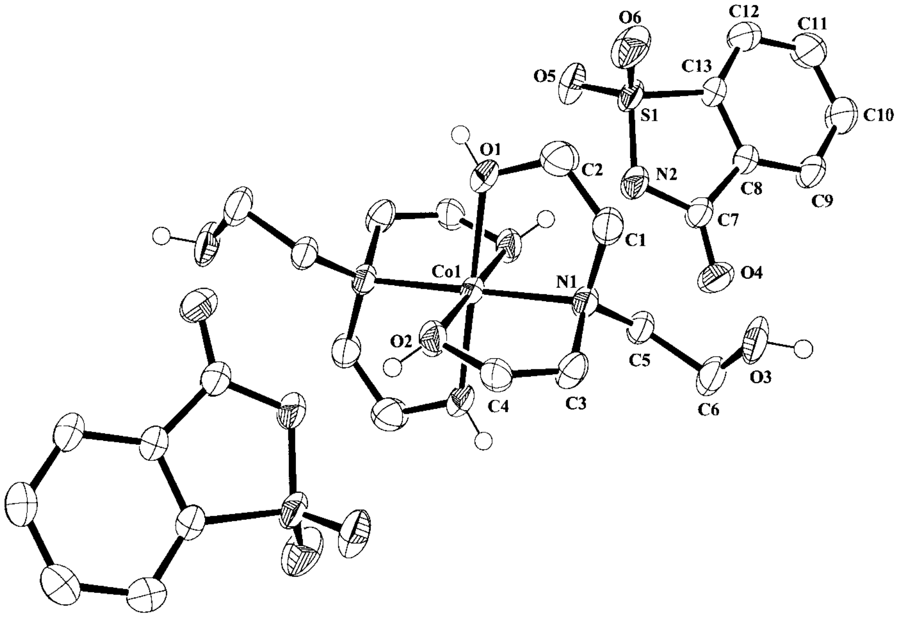

FIGURE 1 A view of $[Co(TEA)_2](SAC)_2$ showing the atomic numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms and ethylene and phenyl hydrogens of the TEA ligand have been omitted for clarity.

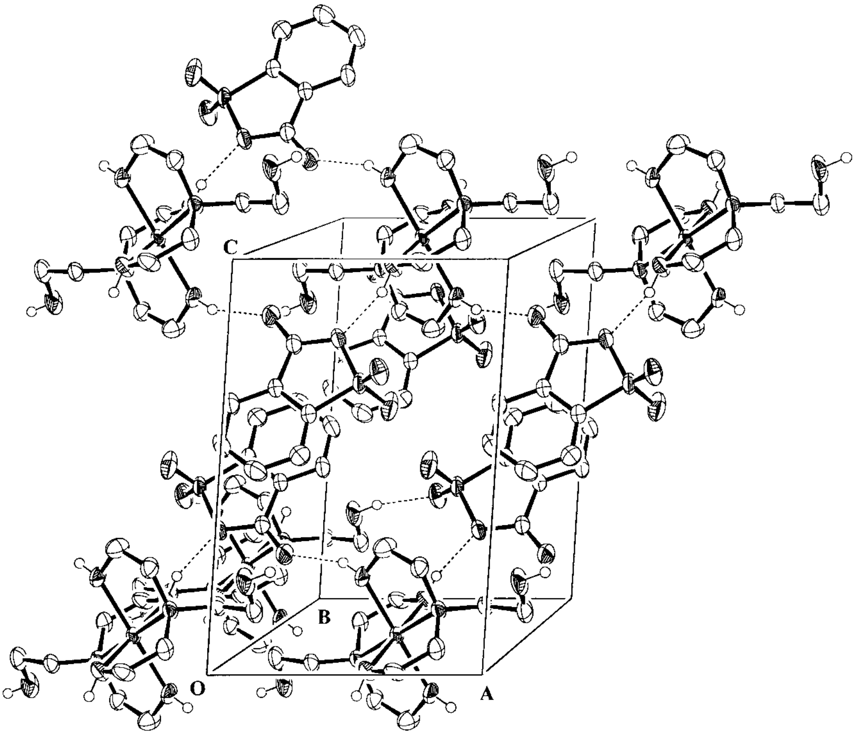

FIGURE 2 A packing diagram of $[Co(TEA)_2](SAC)_2$ showing hydrogen bonding scheme.

TABLE V Selected bond distances(Å) and angles(°) for $[Co(TEA)_2](SAC)_2$[a]

Bond distances				
Co1–N1	2.149(2)	N2–C7	1.352(2)	
Co1–O1	2.093(3)	C7–O4	1.228(2)	
Co1–O2	2.072(3)	C7–C8	1.496(2)	
N1–C1	1.468(3)	C8–C9	1.376(2)	
C1–C2	1.499(8)	C9–C10	1.384(3)	
C2–O1	1.413(6)	C10–C11	1.376(3)	
N1–C3	1.520(3)	C11–C12	1.386(3)	
C3–C4	1.472(9)	C12–C13	1.373(3)	
C4–O2	1.414(5)	C13–C8	1.380(2)	
N1–C5	1.480(3)	C13–S1	1.754(2)	
C5–C6	1.505(5)	S1–O5	1.442(2)	
C6–O3	1.401(6)	S1–O6	1.429(2)	
Bond angles				
N1–Co1–N#1	180.0(7)	O1–Co1–O2	92.2(3)	
O1–Co1–O1#1	180.0(7)	O1–Co1–O2#1	87.8(3)	
O2–Co1–O2#1	180.0(7)	O1–Co1–N1#1	100.73(13)	
N1–Co1–O1	79.30(13)	O2–Co1–N1	81.69(15)	
N1–Co1–O1#1	100.73(13)	O2–Co1–N1#1	98.31(15)	
Hydrogen–bonding				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O1–H1···O4#2	0.82	1.84	2.641(2)	165.4
O2–H2···N2#1	0.82	1.93	2.749(2)	174.7
O3–H3···O5#3	0.82	2.03	2.821(2)	162.1

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

TABLE VI Selected bond lengths (Å) and angles(°) for $[Cu_2(\mu\text{–}TEA)_2(SAC)_2] \cdot 2CH_3OH$[a]

Bond distances				
Cu1–N1	2.069(2)	N2–C7	1.360(3)	
Cu1–N1	2.047(2)	C7–O4	1.232(3)	
Cu1–O1	2.302(2)	C7–C8	1.490(3)	
Cu1–O2	1.936(2)	C8–C9	1.392(3)	
Cu1–O2#1	1.930(2)	C9–C10	1.379(4)	
Cu1–Cu1#1	2.971(6)	C10–C11	1.381(4)	
N1–C1	1.497(3)	C11–C12	1.390(4)	
C1–C2	1.519(4)	C12–C13	1.381(4)	
C2–O1	1.417(3)	C13–C8	1.383(3)	
N1–C3	1.491(3)	C13–S1	1.763(2)	
C3–C4	1.529(4)	S1–N2	1.663(2)	
C4–O2	1.393(3)	S1–O5	1.438(2)	
N1–C5	1.484(3)	S1–O6	1.433(2)	
C5–C6	1.512(4)			
C6–O3	1.418(4)			
Bond angles				
N1–Cu1–N2	99.43(8)	N2–Cu1–O2	175.39(8)	
N1–Cu1–O1	78.69(8)	N2–Cu1–O2#1	96.27(8)	
N1–Cu1–O2	84.19(8)	O1–Cu1–O2	95.22(8)	
N1–Cu1–O2#1	159.30(9)	O1–Cu1–O2#1	115.32(8)	
N2–Cu1–O1	88.32(8)	O2–Cu1–O2#1	79.56(8)	
Hydrogen–bonding				
D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O1–H1···O7	0.82	1.89	2.697(3)	169.2
O3–H3···O4	0.82	1.81	2.626(3)	179.7
O7–H7···O3#1	0.82	1.90	2.720(3)	176.3
C–12–H12···O5#2	0.93	2.38	3.293(3)	165.8

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

and carbonyl oxygen (O4#2) of the adjacent SAC ions, while the free hydroxyl hydrogen (O3–H3) participates in hydrogen bonding with sulfonyl oxygen (O5#3) of the neighboring SAC ion. An extensive network of hydrogen bonds and other molecular interactions maintains the crystal structure by forming a three-dimensional infinite lattice.

$[Cu_2(\mu\text{-}TEA)_2(SAC)_2] \cdot 2CH_3OH$

The molecular structure of the doubly alkoxo-bridged dimeric Cu(II) complex, *bis*(μ-triethanolaminato-*N*,*O*,*O′*)bis(saccharinato-*N*)dicopper(II) dimethanol, is shown in Fig. 3. Selected bond distances and angles are listed in Table VI.

The structure consists of a dimeric complex and two methanol solvate molecules. In the complex, the TEA ligand is in the deprotonated form by losing one of the ethanolic hydrogens and acts as a tridentate donor through its nitrogen (N1), ethanolic oxygen (O1) and deprotonated oxygen (O2), while the other ethanolic group (O3) is not involved in coordination. Each Cu(II) ion is coordinated by two oxygen atoms and one N atom from the deprotonated TEA ligand, and by one N atom of the SAC ligand. In the complex, the hydroxyl group, the deprotonated oxygen atom and the nitrogen atom of the TEA ligand form a five-membered chelate ring the with the Cu(II) ion (N1–C1–C2–O1–Cu1, and N1–C3–C4–O2–Cu1). The Cu(II) ions are bridged by two bifurcated coordination bonds of two triethanolaminate oxygen atoms (O2 and O2#1, symmetry code: #1 $-x+1, -y+1, -z+1$). The

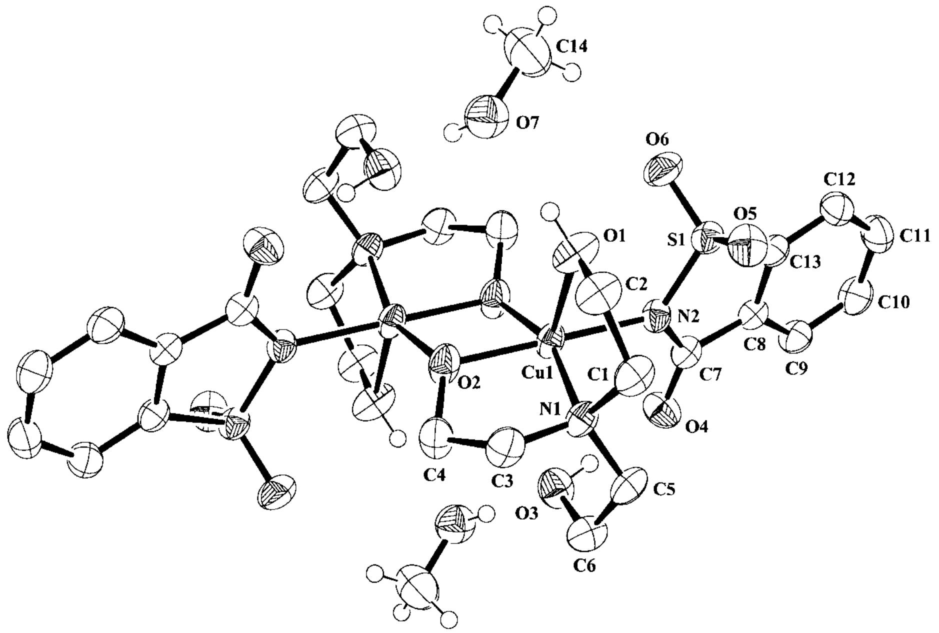

FIGURE 3 A view of $[Cu_2(\mu\text{-TEA})_2(SAC)_2]\cdot 2CH_3OH$ showing the atomic numbering scheme. Atomic displacement ellipsoids are drawn at the 50% probability level for non-hydrogen atoms and ethylene and phenyl hydrogens of the TEA ligand have been omitted for clarity.

–Cu–O–Cu–O– bridging group is planar. The bridging oxygen atoms and Cu(II) atoms form a centrosymmetric Cu_2O_2 core and an inversion center is located between the two Cu(II) ions. Each Cu(II) ion displays a distorted square-pyramidal coordination, in which the N1, O2, O2#1 and N2 atoms form a distorted square plane and the O1 atom occupies the apical site.

The distortion of the metal coordination sphere from square-planar geometry is revealed in large deviations from ideal values. The *cis* angles are in the range 78.69(8)–99.43(8)°, while the *trans* angles N1–Cu1–O2#1, and N2–Cu1–O2 are 159.30(8) and 175.39(8)°, respectively. The Cu–O–Cu bridging angles range from 79.56(8) to 100.44(8)°. The Cu–Cu distance of 2.9707(6) Å agrees well with distances found in other dimeric alkoxo-bridged Cu(II) complexes [28–30]. The average Cu–O bridging bond length is 1.933(2) Å, significantly shorter than the other Cu–O bond [2.302(2) Å]. Both Cu–O bond distances are comparable with the corresponding values observed in related Cu(II) complexes [28–30]. The Cu–N_{TEA} and Cu–N_{SAC} bond distances are 2.069 and 2.047 Å, respectively. Additionally, the O atoms of the free ethanolic groups of the deprotonated TEA ligands form very weak interactions [2.827(2) Å] with the Cu(II) atoms and the coordination geometry may also be considered as a distorted octahedron when the interaction is taken into account.

A packing diagram of the title complex is shown in Fig. 4. The methanol molecules are involved in intermolecular hydrogen bonding with the free (O3#1) and coordinated (O1) ethanolic groups of the triethanolaminate ion. The hydrogen of the free ethanolic group (O3–H3) forms an intramolecular hydrogen bond with the carbonyl oxygen (O4) of the SAC ligand. In addition, the phenyl hydrogen (C12–H12) of the SAC ligand

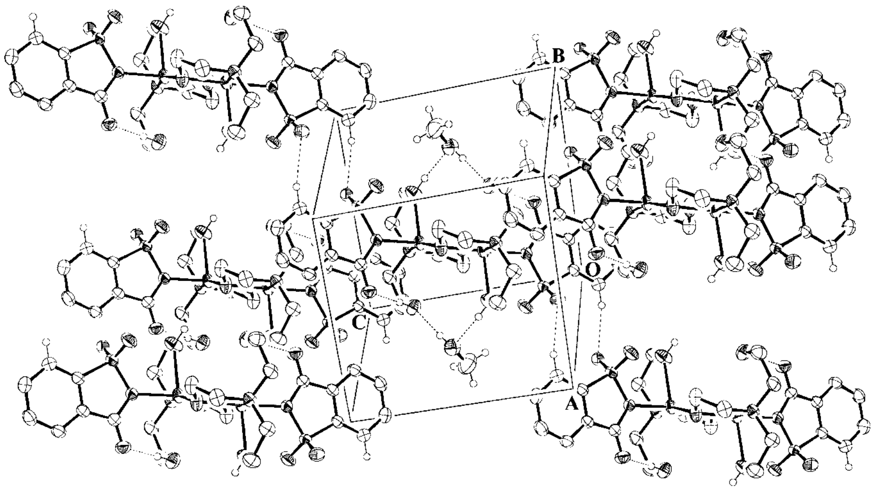

FIGURE 4 A packing diagram of $[Cu_2(\mu\text{-TEA})_2(SAC)_2]\cdot 2CH_3OH$ showing hydrogen bonding scheme.

participates in relatively weak hydrogen bonding with the sulfonyl oxygens (O5#2) of adjacent molecules. Thus, individual dimeric molecules are linked by hydrogen bonds forming 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 157859 for the cobalt complex and CCDC 158960 for the dimeric copper complex. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

References

[1] B. Sen and R.L. Dotson (1970). *J. Inorg. Nucl. Chem.*, **32**, 2707.
[2] D.G. Brannon, R.H. Morrison, J.L. Hall, G.L. Humphrey and D.N. Zimmerman (1971). *J. Inorg. Nucl. Chem.*, **33**, 981.
[3] N.S. Poonia, N. Chhabra, W.S. Sheldrick, G. Hundal, S. Orbai and M.S. Hundal (1999). *Acta Cryst.*, **C55**, 24.
[4] D.C. Bradley, R.C. Mehrotra and D.P. Gaur (1978). *Metal Alkoxides*. Academic Press, London.
[5] V.G. Kessler, L.G. Hubert-Pfalzgraf, S. Halut and J.C. Daran (1994). *J. Chem. Soc. Chem. Commun.*, **70**.
[6] R.C. Mehrotra and A. Singh (1997). *Prog. Inorg. Chem.*, **46**, 239.
[7] M. Sharma, A. Singh and R.C. Mehrotra (2000). *Polyhedron*, **19**, 77.

[8] L.O. Nabors and C.G. Robert (1991). *Alternative Sweeteners*, 2nd Edn. Marcel Dekker, New York.
[9] B. Kamenar and G. Jovanovski (1982). *Cryst. Struct. Commun.*, **11**, 257.
[10] Z. Haider, K.M.A. Malik, K.J. Ahmed, H. Hess, H. Riffel and M.B. Hursthouse (1983). *Inorg. Chim. Acta*, **72**, 21.
[11] Z. Haider, K.M.A. Malik and K.J. Ahmed (1985). *Inorg. Synth.*, **23**, 47.
[12] F.A. Cotton, G.E. Lewis, C.A. Murillo, W. Schwotzer and G. Valle (1984). *Inorg. Chem.*, **23**, 4038.
[13] F.A. Cotton, G.E. Lewis, C.A. Murillo and G. Valle (1990). *Inorg. Synth.*, **27**, 306.
[14] Y. Zhang (1998). *Spect. Lett.*, **31**, 1609.
[15] H. Icbudak and V.T. Yilmaz (1997). *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 1571.
[16] V.T. Yilmaz, Y. Topcu and F. Yilmaz (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 409.
[17] V.T. Yilmaz (1999). *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 621.
[18] H. Icbudak, T.K. Yazicilar and V.T. Yilmaz (1999). *Thermochim. Acta*, **335**, 93.
[19] V.T. Yilmaz, A. Karadag and C. Thoene (2000). *J. Coord. Chem.*, **55**, 609.
[20] H. Icbudak, V.T. Yilmaz and H. Olmez (1995). *J. Thermal Anal.*, **44**, 605.
[21] H. Icbudak, V.T. Yilmaz, O. Andac, R.A. Howie and H. Olmez (1995). *Acta Cryst.*, **C51**, 1759.
[22] V.T. Yilmaz, H. Icbudak, H. Olmez and R.A. Howie (1996). *Turk. J. Cem.*, **20**, 69.
[23] H. Icbudak, V.T. Yilmaz and H. Olmez (1996). *Thermochim. Acta*, **289**, 23.
[24] V.T. Yilmaz, H. Icbudak and R.A. Howie (1997). *Acta Cryst.*, **C53**, 294.
[25] G.M. Sheldrick (1990). *Acta Cryst.*, **A46**, 467.
[26] G.M. Sheldrick (1997). *SHELXL-97. Program for Refinement of Crystal Structures*. University of Göttingen, Germany.
[27] L.J. Farrugia (1997). *J. App. Cryst.*, **30**, 565.
[28] M.B. Hursthouse, K.J. Izod, M.A. Mazid and P. Thornton (1990). *Polyhedron*, **9**, 530.
[29] J. Madarasz, P. Bombicz, M. Czugler and G. Pokol (2000). *Polyhedron*, **19**, 457.
[30] A. Karadag, V.T. Yilmaz and C. Thoene (2001). *Polyhedron*, **20**, 635.
[31] A.B.P. Lever (1984). *Inorganic Electronic Spectrosocopy*. Elsevier, Amsterdam.
[32] K. Nakamoto (1978). *Infrared and Raman spectra of Inorganic and Coordination Compounds*. Wiley, New York.
[33] Y. Okaya (1969). *Acta Cryst.*, **B25**, 2257.
[34] V.T. Yilmaz, F. Yilmaz, Y. Topcu, Ö. Andac and K. Guven (2001). *J. Mol. Struct.*, **560**, 9.
[35] R.M.K Deng, C. Bilton, K.B. Dillon and J.A.K. Howard (2000). *Acta Cryst.*, **C56**, 142.