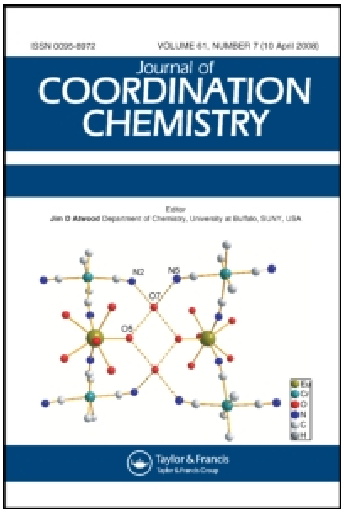

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Mixed-Ligand Metal Succinate Complexes with 1,10-Phenanthroline and Ethylenediamine: Synthesis, Characterization, Spectroscopic and Thermal Studies. Crystal Structure of Succinatocobalt(II) Complex with Phenanthroline

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MIXED-LIGAND METAL SUCCINATE COMPLEXES WITH 1,10-PHENANTHROLINE AND ETHYLENEDIAMINE: SYNTHESIS, CHARACTERIZATION, SPECTROSCOPIC AND THERMAL STUDIES. CRYSTAL STRUCTURE OF SUCCINATOCOBALT(II) COMPLEX WITH PHENANTHROLINE

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The novel mixed-ligand metal succinate (suc) complexes with 1,10-phenanthroline (phen) and ethylenediamine (en) have been synthesized and characterized by elemental analyses, magnetic moments, UV–VIS and IR spectra. Thermal reactivity of the complexes was studied in air using DTA and TG, and decomposition of the complexes resulted in the formation of corresponding metal oxides. The crystal structure of the $[Co(suc)(H_2O)(phen)_2]\cdot 1.5H_2O\cdot C_4H_{10}O$ complex was determined by x-ray diffraction. The Co(II) complex crystallizes as a monobutanol solvate. In the complex, the cobalt ion lies on an inversion center and displays a distorted octahedral coordination with one aqua, one suc and two phen ligands. The suc ligand acts as a monodentate ligand through one of the negatively charged O atoms, while phen behaves as N-donor bidentate ligand. The crystal also contains disordered lattice water molecules and the structure is stabilized by extensive hydrogen bonding to form a three-dimensional infinite network.

Keywords: Succinate complexes; 1,10-phenanthroline complexes; Ethylenediamine complexes; Crystal structure; Thermal analysis

INTRODUCTION

The succinate anion [suc, $(C_4H_4O_4)^{2-}$] is a versatile ligand and offers the possibility of different modes of coordination towards transition metal ions. It can behave as a monodentate, bidentate, multidentate or bridging ligand. The bidentate chelating

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and bridging modes of suc are most common and have been demonsrated crystallographically [1–6], while the monodentate structure is very rare; recently a study reporting the succinate dianion coordinating to the Mn(II) atom as a monodentate ligand has appeared in the literature [7].

Spectral and thermal properties of divalent transition metal complexes of suc were studied by a number of researchers [8–11]. It was shown that suc formed stable compounds with Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), whereas anionic complexes of Cu(II) such as $K_2[Cu(C_4H_4O_4)_2]$ and $K_4[Cu(C_4H_4O_4)_3]\cdot 2H_2O$ were found to be very unstable. Mixed-ligand metal complexes of suc with hydrazine [12], bipyridine [13] diethylenetriamine [14] and phenanthroline [7,15] were reported. Although plain divalent transition metal complexes of suc were prepared and well-characterized, mixed-ligand complexes of suc with transition metal ions are still rare. In this paper, we report preparation, spectral characterization and thermal decomposition of novel mixed-phenanthroline (phen) and mixed-ethylenediamine (en) complexes of some divalent transition metal succinates, together with the single crystal x-ray structure of aquabis(1,10-phenanthroline)succinatocobalt(II) one and half hydrate *n*-butanol solvate.

EXPERIMENTAL

Materials and Instrumentation

All metal salts, phen monohydrate and en were purchased from Merck, while succinic acid 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 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 and N contents) were performed at the TUBITAK Marmara Research Centre. Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyser in a static air atmosphere. A sample size of 5–10 mg and heating rate of $10°\mathrm{C\,min^{-1}}$ were used.

Preparation of Metal Complexes

The suc's of Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) were prepared by dissolving freshly prepared metal carbonates in 0.2 M solution of succinic acid at *ca.* 40°C. Excess metal carbonates were removed by filtration, then the resulting solutions were left at room temperature until evaporation resulted in the formation of the crystals of the corresponding metal succinates. The Cu(II)–suc compound was prepared by addition of 0.2 M solution of Na–suc (pH 5.0) to a hot 0.2 M solution of Cu(II) nitrate. All metal succinates were dried at room temperature to a constant mass.

The suc's of Cu(II), Zn(II), Cd(II) and Hg(II) (0.1 mmol) were dissolved in H_2O (20 mL) with stirring at a water bath of 70°C and then, phen (0.2 mmol) dissolved in

TABLE I Analytical data for metal succinate complexes with the phen and en ligands

Complexes	*Color*	*D.p. (°C)*[a]	*Fw*	*Anal. (Calcd. and Found) (%)*			*Yield (%)*	*μ_{eff} (BM)*
				C	*H*	*N*		
$[Co(suc)(H_2O)(phen)_2]\cdot 1.5H_2O\cdot C_4H_{10}O$	Orange	280	654.57	58.7	5.4	8.6	40	4.23
$C_{32}H_{35}N_4O_{7.5}Co$				58.0	5.2	8.6		
$[Ni(suc)(H_2O)(phen)_2]\cdot 2H_2O\cdot C_4H_{10}O$	Blue	317	663.35	57.9	5.8	8.5	64	2.75
$C_{32}H_{36}N_4O_8Ni$				58.0	5.6	8.9		
$[Cu(suc)(phen)]$	Pale-Blue	251	359.83	53.4	3.3	7.8	66	1.64
$C_{16}H_{12}N_2O_4Cu$				53.1	3.1	7.7		
$[Zn(suc)(phen)]$	White	300	361.67	53.1	3.3	7.7	63	Dia.
$C_{16}H_{12}N_2O_4Zn$				52.6	3.3	7.3		
$[Cd(suc)(phen)]\cdot H_2O$	White	350	426.71	45.0	3.3	6.6	84	Dia.
$C_{16}H_{14}N_2O_5Cd$				45.3	3.2	6.4		
$[Hg(suc)(phen)]\cdot 2H_2O$	White	185	532.90	36.1	3.0	5.3	62	Dia.
$C_{16}H_{16}N_2O_6Hg$				35.7	2.9	5.2		
$[Ni(suc)(en)]\cdot 2H_2O$	Blue	160	270.89	26.6	6.0	10.3	58	2.80
$C_6H_{16}N_2O_6Ni$				26.4	6.4	10.5		
$[Cu(suc)(en)_2]\cdot 2.5H_2O$	Deep-blue	147	335.85	27.9	7.3	16.3	36	1.54
$C_8H_{24}N_4O_6Cu$				28.4	7.2	16.5		
$[Zn(suc)(en)_2]\cdot 3H_2O$	White	120	355.67	27.0	7.4	15.8	58	Dia
$C_8H_{26}N_4O_7Zn$				27.4	7.5	16.3		
$[Cd(suc)(en)]\cdot H_2O$	White	162	306.57	23.5	4.6	9.1	69	Dia
$C_6H_{14}N_2O_5Cd$				23.9	5.0	9.3		

[a] Decomposition point.

ethanol (10 mL) was added to the solution of the metal–suc with continuous stirring for *ca.* 60 min at room temperature. The phen complexes of Co(II) and Ni(II) and all the en complexes of metal–suc's, were prepared in *n*-butanol using the same procedure. The phen complexes with Cu(II), Zn(II), Cd(II) and Hg(II), and the en complexes with Zn(II) and Cd(II) immediately precipitated as polycrystalline solids after addition of the amine ligands. The resulting solutions of the other complexes 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

A summary of crystal data, intensity collection and structure refinement is given in Table II. The intensities were collected at 293 ± 2 K on a Bruker SMART 1000 CCD area detector using Mo-K_α radiation ($\lambda = 0.71069$) to a maximum 2θ value of 27.055°. The structures were solved by direct methods [16] and refined by a full-matrix least-squares procedure [17] on F^2. All non-hydrogen atoms were refined anisotropically. The water and the hydroxyl group hydrogens were located from a difference map and refined by riding. The other hydrogens were geometrically positioned and refined by riding. Molecular drawings were obtained using ORTEPIII [18].

TABLE II Crystallographic data for $[Co(suc)(H_2O)(phen)_2] \cdot 1.5H_2O \cdot C_4H_{10}O$

Empirical formula	$C_{32}H_{35}N_4O_{7.5}Co$
F_w	654.57
Temperature (K)	293(2)
Radiation	Mo K_α, 0.71069 Å
Crystal system	Triclinic
Space group	P-1
Cell dimensions	
a (Å)	10.2329(5)
b (Å)	11.5435(5)
c (Å)	12.9602(6)
α (°)	94.1020(10)
β (°)	100.3680(10)
γ (°)	94.4190(10)
V (Å^3)	1495.73(12)
Z	2
D_{calcd} (Mg m^{-3})	1.453
μ (mm^{-1})	0.631
$F(000)$	684
θ range (°)	2.03 to 27.55
Index ranges	$-13 \leq h \leq 13;\ -15 \leq k \leq 12;\ -16 \leq l \leq 14$
Reflections collected	11322
Independent reflections	6827 [R(int) = 0.0244]
Reflections observed (> 2σ)	4878
Absorption correction	Semi-empirical from equivalents
Goodness-of-fit	0.955
Final R indices [$I > 2_{\sigma(I)}$]	$R1 = 0.0482$, $wR2 = 0.1199$
R indices (all data)	$R1 = 0.0708$, $wR2 = 0.1319$
Largest diff. Peak and hole (e Å^3)	0.507 and −0.380

RESULTS AND DISCUSSION

General Properties

The composition of the complexes was determined by elemental analyses, FT-IR and DTA-TG analysis. The molar ratio of M : suc in all the complexes is 1 : 1, while one or two molecules of the phen and en ligands are attached to the M(II) ion. The complexes were obtained in good yields and the elemental analyses conformed to their proposed formula (see Table I). All the complexes, except the Cu(II) and Zn(II) complexes with the phen ligand contain lattice water molecules as determined by IR, DTA and TG. In addition, the Co(II) and Ni(II) complexes of phen also include one H_2O ligand and one *n*-butanol molecule.

All the metal complexes except the Zn(II) complex of en are non-hygroscopic and stable in air, but the Zn(II) complex is somewhat hygroscopic. The Co(II) complex with en prepared in this work was found to be highly hygroscopic and therefore, its characterization and properties were not studied. The highly hygroscopic behavior of the Co(II) complex with en may be attributed to the fact that Co(II) octahedral complexes are usually labile. Attempts to prepare the Hg(II) complex of en also failed due to the insolubility of the Hg(II) succinate in *n*-butanol. Furthermore, the synthesis of the Hg(II) complex with en in water gave a gelatinous product. The Zn(II) and Hg(II) complexes with phen are insoluble in water, while the Cu(II)–phen and Cd(II)–en complexes are slightly soluble in hot water. All the other complexes are very soluble in water. The Co(II) and Ni(II) complexes of both phen and en are somewhat soluble in DMF and DMSO, whereas the other complexes are not soluble in these solvents. The metal complexes do not exhibit melting points, but decompose at the temperatures given in Table I.

Spectroscopic and Magnetic Characteristics

The effective magnetic moments of the complexes at room temperature are listed in Table I. The metal complexes show a high-spin configuration. The magnetic moments agree well with the high-spin octahedral or tetrahedral nature of the complexes and also the calculated values of the spin-only magnetic moments. However, the corresponding Zn(II), Cd(II) and Hg(II) complexes are diamagnetic as expected.

The electronic spectra of the water-soluble complexes show a band at *ca.* 350 nm to attributed absorption of the suc ligand and the band below 300 nm is due to the $\Pi \rightarrow \Pi^*$ transitions of the amine ligands. The broad bands in the region 500–700 nm are assigned to *d–d* transitions.

Selected IR data for the complexes are summarized in Table III. A strong and broad band at *ca.* 3300–3400 cm^{-1} in the spectra of the hydrated complexes is assigned to ν(OH) absorption of the water molecules. The distinct medium bands in the range 3220–3365 cm^{-1} can be referred to the NH vibration of the en ligand. The phen complexes exhibit two partially resolved bands in the 1510–1585 cm^{-1} region, attributable to $\nu_{as}(COO^-)$ and a single band at *ca.* 1420 cm^{-1} for $\nu_s(COO^-)$ [19]. The en complexes show only a single intense band at *ca.* 1560 and 1405 cm^{-1} for $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$. These two bands for the suc ligand indicate a difference in the strength of binding of the carboxylate group with the M(II) ions. The $\Delta\nu$ ($\nu_{as} - \nu_s$) values can be used to determine the mode of coordination. The $\Delta\nu$ value for Na–suc was calculated as 108 cm^{-1}. The $\Delta\nu$ values of the Co(II) and Ni(II) complexes are similar to that of Na–suc, suggesting that the suc ligand coordinates to the M(II) ion monodentately, whereas bidentate chelation of the suc ligand results in higher $\Delta\nu$ values [19] as given in Table III. Furthermore, the $\nu_{as}(COO^-)$ bands shift to a higher wave number, also suggesting the formation of a chelate [19]. The two weak bands in the region 400–600 cm^{-1} are due to both M–N and M–O stretching vibrations, respectively. Although the M–N and M–O stretching vibrations seem to be rather high compared

TABLE III IR spectral data for metal succinate complexes with the phen and en ligands

Complexes	*ν(OH)*	*ν(NH)*	*$\nu_{asym}(COO^-)$*	*$\nu_{sym}(COO^-)$*	$\Delta\nu^a$	*ν(MN)*	*ν(MO)*
$[Co(suc)(H_2O)(phen)_2] \cdot 1.5H_2O \cdot C_4H_{10}O$	3381sb	–	1554vs, 1520s	1428vs	109	590w	421w
$[Ni(suc)(H_2O)(phen)_2] \cdot 2H_2O \cdot C_4H_{10}O$	3390sb	–	1553s, 1522vs	1432vs	106	579w	427w
[Cu(suc)(phen)]	–	–	1581vs, 1520s,	1399vs	152	526w	433w
[Zn(suc)(phen)]	–	–	1585vs, 1567vs	1427vs	149	581w	428w
$[Cd(suc)(phen)] \cdot H_2O$	3407bs	–	1570vs, 1518s	1422vs	122	579w	420w
$[Hg(suc)(phen)] \cdot 2H_2O$	3400bs	–	1564vs, 1516s	1416vs	124	537w	421w
$[Ni(suc)(en)] \cdot 2H_2O$	3365bs	3310m, 3168 m	1556vs	1399vs	157	502w	419w
$[Cu(suc)(en)_2] \cdot 2.5H_2O$	3370bs	3315m, 3224 m	1580vs	1405s	175	530w	489w
$[Zn(suc)(en)_2] \cdot 3H_2O$	3337bs	3294m, 3250 m	1566vs	1407s	159	552w	420w
$[Cd(suc)(en)] \cdot H_2O$	3320bs	3279m, 3243 m	1560vs	1416vs	144	509w	452w

[a] The average values for the split bands of the $\nu_{asym}(COO^-)$ vibrations were used in the calculation of the $\Delta\nu$ values for the phen complexes

to most metal complexes of phen and en reviewed by Nakamoto [19], similar vibration frequencies were reported for the metal complexes with dicarboxylates [20,21].

Thermal Decomposition Behavior

The thermal behavior of the complexes in air has been studied by DTA and TG. The thermoanalytical data together with temperature ranges and solid decomposition products are given in Table IV.

The Co(II) and Ni(II) complexes containing the phen ligand show the same type of decomposition behavior; losing the lattice water and butanol molecules below about 150°C in the first stage of decomposition. The second stage corresponds to the exothermic elimination of one phen molecule and the other phen molecule and the suc anion decomposes exothermically in the last stage to form the corresponding metal oxides. Similar modes of decomposition were observed for the anhydrous Cu(II) and Zn(II) complexes with phen. The removal of the phen molecule occurs in the first stage to form the respective metal–suc intermediates, and the decomposition of the suc ligand

TABLE IV Thermoanalytical data for the decomposition of metal succinate complexes with the phen and en ligands in air

Complexes	*Stage*	*Temperature range* (°C)	DTG_{max} (°C)[a]	*Mass loss (%)*		*Solid decomp. product*	*Color*
				Found	*Calcd.*		
$[Co(suc)(H_2O)(phen)_2]\cdot 1.5H_2O\cdot C_4H_{10}O$	1	35–120	57(+), 93(+)	17.7	18.2	$[Co(suc)(phen)_2]$	
	2	280–332	322(−)	26.9	27.5	[Co(suc)(phen)]	
	3	332–400	350(−)	41.6	42.0	Co_2O_3	Black
$[Ni(suc)(H_2O)(phen)_2]\cdot 2H_2O\cdot C_4H_{10}O$	1	37–150	79(+), 111(+)	18.9	19.3	$[Ni(suc)(phen)_2]$	
	2	317–396	345(−)	26.6	27.1	[Ni(suc)(phen)]	
	3	396–450	431(−)	42.5	42.2	NiO	Green
[Cu(suc)(phen)]	1	251–394	281(−), 381(−)	50.0	50.0	[Cu(suc)]	
	2	394–450	423(−)	28.0	27.8	CuO	Black
[Zn(suc)(phen)]	1	300–411	408(−)	50.8	49.8	[Zn(suc)]	
	2	411–536	454(−)	28.0	27.8	ZnO	White
$[Cd(suc)(phen)]\cdot H_2O$	1	35–135	72(+)	4.2	4.2	[Cd(suc)(phen)]	
	2	350–520	411(−), 448(−)	66.6	65.7	CdO	White
$[Hg(suc)(phen)]\cdot 2H_2O$	1	30–163	40(+), 58(+)	6.4	6.8	[Hg(suc)(phen)]	–
	2	185–229	199(+)	33.6	33.8	[Hg(suc)]	
	3	232–550	420(+)	–	–	–	
$[Ni(suc)(en)]\cdot 2H_2O$	1	89–159	148(+)	13.4	13.3	[Ni(suc)(en)]	
	2	159–351	323(−)	21.8	22.2	[Ni(suc)]	Black–green
	3	351–470	410(−)	36.1	36.9	NiO	
$[Cu(suc)(en)_2]\cdot 2.5H_2O$	1	40–125	63(+), 114(+)	13.0	13.1	$[Cu(suc)(en)_2]$	
	2	147–287	186(−), 225(−)	34.9	34.8	[Cu(suc)]	
	3	287–433	417(−)	28.7	29.0	CuO	Black
$[Zn(suc)(en)_2]\cdot 3H_2O$	1	38–98	82(+),	9.6	10.1	$[Zn(suc)(en)_2].H_2O$	
	2	98–145	114(+), 124(+)	21.3	21.9	[Zn(suc)(en)]	
	3	155–304	184(+), 234(+), 263(+)	17.6	16.9	[Zn(suc)]	
	4	320–528	362(−), 474(−)	28.2	28.1	ZnO	White
$[Cd(suc)(en)]\cdot H_2O$	1	98–162	136(+)	5.9	5.9	[Cd(suc)(en)]	
	2	162–323	219(−), 262(−)	20.4	19.6	[Cd(suc)]	
	3	323–500	428(−), 446(−)	31.2	32.6	CdO	White

[a] (+), Endothermic; (−), exothermic.

occurs in the next step. The final decomposition products are CuO and ZnO. The Cd(II) complex is dehydrated at 72°C and the anhydrous complex exhibits a high thermal stability up to about 350°C at which it begins to decompose. For the Cd(II) complex with phen, the exothermic decomposition processes of the phen and suc ligand occur simultaneously and therefore it was impossible to distinguish the overlapped stages. However, the end product was found to be CdO. The Hg(II) complex of phen undergoes endothermic dehydration in the temperature range of 30–165°C. The liberation of the phen ligand takes place endothermically at 199°C, while the suc ligand decomposes at 255°C. The intermediate formed at *ca.* 300°C sublimes at higher temperatures without leaving any residue.

The dehydration of the Ni(II) complex with en occurs at 148°C. The anhydrous complex decomposes in two stages between 160 and 470°C. The decompositions of the en and suc ligands are observed at 323°C and 410°C, respectively, and result in the formation of NiO. In the case of the Cu(II) complex, the endothermic dehydration takes place as the first stage of decomposition in the temperature range 40–125°C with two DTA endotherms. The peaks at 63°C and 114°C correspond to the loss of 0.5 mol and two moles of water, respectively. The exothermic elimination of the two en molecules occurs in the temperature range 147–287°C with two distinct peaks at 186 and 225°C and results in the formation of the Cu–suc intermediate. The suc ligand decomposes at 417°C to give CuO as the end product. The partial dehyration of the Zn(II) complex of en occurs at 82°C and the rest of the water is lost together with one molecule of en in the range 98 and 145°C. The other en molecule and suc anion decompose at higher temperatures to form ZnO at *ca.* 530°C. The Cd(II) complex of en exhibits an initial endothermic decomposition due to loss of a water molecule at 136°C. In the second step, the en molecule is lost endothermically in the range 162–323°C to give Cd–suc as intermediate. In the final stage, the suc as an intermediate of cadmium decomposes endothermically at about 440°C to form CdO.

The actual weight losses reported in the Table IV for the decomposition processes of the metal complexes are favorably compared with the calculated values. The thermal decomposition behavior of the complexes may be summarized as follows. The succinato complexes containing the phen and en ligands lose their lattice and/or ligand water molecules in the first stage of decomposition. The elimination of amine ligands takes place in the second stage and usually results in the formation of the corresponding M(II)–suc intermediates which decompose in the last stage of decomposition to give the respective metal oxides. It was reported that thermal decomposition of the transition metal–suc's gave the corresponding metal oxides as the final decomposition products [9,11]. If the initial decomposition temperatures are taken as a measure of thermal stability, the phen complexes exhibit much higher thermal stability than the corresponding en complexes. This difference may be due to the difference in strengths of coordination of phen and en to the M(II) ions.

Description of the Crystal Structure

Selected bond distances and angles in aquabis(1,10-phenanthroline)succinatocobalt(II) one a half hydrate *n*-buthanol solvate are listed in Table V. The molecular structure of the complex is shown in Fig. 1.

The title molecule contains one *n*-butanol solvate and lattice water molecules and a metal complex moiety [Co(suc)(H_2O)(phen)$_2$]. However, one of the lattice water,

TABLE V Selected bond distances (Å) and angles (°) for $[Co(suc)(H_2O)(phen)_2] \cdot 1.5H_2O \cdot C_4H_{10}O^a$

Bond distances			
Col–N1	2.133(2)	C7–C11	1.399(3)
Co1–N2	2.151(2)	C7–C8	1.400(4)
Co1–N3	2.154(2)	C8–C9	1.360(4)
Co1–N4	2.153(2)	C9–C10	1.397(4)
Col–O1	2.101(5)	C10–N2	1.334(3)
Col–O1W	2.089(2)	C11–N2	1.359(3)
N1–C1	1.334(3)	C12–N1	1.351(3)
C1–C2	1.396(4)	C11–C12	1.440(3)
C2–C3	1.357(5)	C25–O1	1.259(6)
C3–C4	1.407(4)	C25–O2	1.252(6)
C4–C12	1.404(3)	C25–C26	1.524(5)
C4–C5	1.421(4)	C26–C27	1.497(5)
C5–C6	1.338(4)	C28–O3	1.242(6)
C6–C7	1.443(4)	C28–O4	1.263(7)
Bond angles			
N1–Co1–N2	77.60(7)	N2–Co1–N3	92.16(8)
N1–Co1–O1	92.60(3)	N2–Co1–N4	98.85(7)
N1–Co1–O1W	97.29(7)	N2–Co1–O1W	84.88(7)
N1–Co1–N3	94.87(9)	O1–Co1–O1W	89.24(18)
N1–Co1–N4	170.98(8)	N2–Co1–O1	167.8(3)
N3–Co1–O1W	166.56(8)		

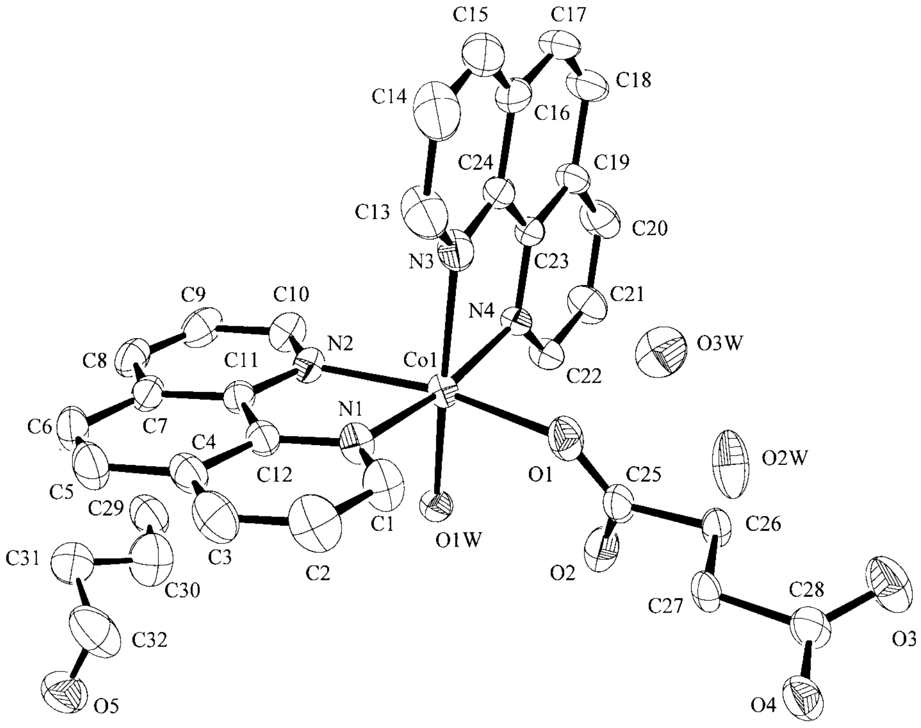

FIGURE 1 A view of $[Co(suc)(H_2O)(phen)_2] \cdot 1.5H_2O \cdot C_4H_{10}O$ showing the atomic numbering scheme. Atomic displacement ellipsoids are drawn at the 30% probability level and the hydrogen atoms have been omitted for clarity.

the phen and the butanol molecules are somewhat disordered. Because of a continuous positional disorder, *n*-butanol was placed on an approximate position in the unit cell. In the complex, the Co(II) species occupies an inversion center and is octahedrally coordinated to one suc ion, one water and two phen molecules. Although bidentate coordination of the suc ligand is a basic feature of dicarboxylates, in this complex, the suc ion behaves as a monodentate ligand, while the other carboxylate end remains uncomplexed (Fig. 1). A similar mode of coordination of suc in $[Mn(suc)(H_2O)_3(phen)] \cdot 2H_2O$ was structurally reported by Liu [7], whereas the suc ligand behaves as a bidentate bridging ligand in the succinato complex, $[Cu(suc)(H_2O)(phen)]_2 \cdot (H_2suc)$, containing phen and succinic acid [15].

The phen molecules coordinate to the Co(II) ion through both N atoms in the usual bidentate manner and occupy the *cis* positions of the octahedron. Both phen ligands are essentially planar with an r.m.s. deviation of 0.021 Å. The phen chelate-ring planes are nearly perpendicular to each other and the dihedral angle between the corresponding phen planes is 86.94(05)°. The Co–N_{phen} bond distances range from 2.133(2) to 2.154(2) Å, while the bond lengths of Co–O_{suc} and Co–O_{water} are 2.101(5) Å and 2.089(2) Å, respectively. The Co–O_{suc} bond distances are comparable to that of the bidentate succinato Co(II) complex [22]. The interaxial angles around the Co(II) ion are in the range 77.60(7)–98.85(7)°. Large deviations of bond angle from 90° of the idealized octahedral geometry clearly indicate that the coordination geometry around the Co(II) ion is best described as a distorted octahedron. The unit cell contains two molecules of the solvate butanol, which are connected by hydrogen bonds to form an infinite chain arrangement. The presence of the *n*–butanol molecules indicates that the structure of the title compound has solvent-accessible voids. The total volume of the voids in the unit cell is 309 $Å^3$ as calculated by PLATON [23].

The structure presents extensive hydrogen bonding and the details for the hydrogen bonding geometry are given Table VI. The coordinated water molecule (O1W) forms intra- and intermolecular hydrogen bonds with the O atoms of the suc ligands. The complex moieties are linked by the hydrogen bond between the coordinated water molecule (O1W–H2) and the O atom (O4) of the uncoordinated end of the suc ligand of the neighboring complex. The lattice water molecules (O2W and O3W) also hydrogen bond with the suc ligand, the coordinated water and *n*-butanol molecules. The hydrogens of the phen ligands appear to be participating in weak intermolecular hydrogen bonds

TABLE VI Hydrogen bonding for $[Co(suc)(H_2O)(phen)_2] \cdot 1.5H_2O \cdot C_4H_{10}O$[a]

	D–H	*H···A*	*D···A*	*<(DHA)*
O1W–H1···O2	0.81	1.80	2.592(6)	165.5
O1W–H2···O4#1	0.80	1.68	2.473(9)	175.9
O2W–H1···O2#2	0.85	1.91	2.75(3)	169.8
O2W–H2···O1W	0.88	2.10	2.97(3)	174.1
O3W–H1···O5#3	0.82	2.31	3.020(15)	145.2
O3W–H2···O1#4	0.82	2.54	3.353(12)	173.8
O5–H5···O3#2	0.83	1.61	2.42(3)	169.7
C5–H5···O3#5	0.93	2.40	3.22(3)	146.8
C6–H6···O2W#6	0.93	2.37	3.279(17)	166.8
C18–H18···O3W#7	0.93	2.47	3.345(9)	156.5

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, -z+1$; #2 $-x, -y+1, -z+1$; #3 $x, y-1, z$; #4 $x-1, y, z$; #5 $x, y, z-1$; #6 $-x, -y+1, -z$; #7 $-x, -y, -z+1$

with the oxygens of the lattice water molecules and the suc ligand of the adjacent molecules. The structure is stabilized by the intensive hydrogen bonds in the solid-state to form a three-dimensional infinite network.

The crystal structure of the Ni(II) complex with phen has also been studied. The results showed that it consists of a complex moiety [Ni(suc)(H_2O)(phen)$_2$] and severely disordered water and butanol molecules. The disorder did not permit refinement.

Supplementary Material

Crystallographic data (atomic coordinates, atomic displacement parameters and bond geometries) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material with a deposition number CCDC 156876. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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