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Di- and triethanolamine complexes of Co(II), Ni(II), Cu(II) and Zn(II) with thiocyanate: synthesis, spectral and thermal studies. Crystal structure of dimeric Cu(II) complex with deprotonated diethanolamine, $[Cu_2(\mu\text{-dea})_2(NCS)_2]$

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Abstract

New mixed ligand Co(II), Ni(II), Cu(II) and Zn(II) complexes of di- (dea) and triethanolamine (tea) with thiocyanate were synthesized and characterized by elemental analyses, magnetic moments, UV–Vis and IR spectra. All the metal complexes of tea, and the Ni(II) and Zn(II) complexes of dea are mononuclear, while the Co(II) and Cu(II) complexes of dea are dimeric. The crystal structure of the bis(μ-diethanolaminato) bis(isothiocyanato)dicopper(II) complex were determined by single crystal X-ray diffraction. The centrosymmetric binuclear complex contains two strongly distorted square-pyramidally coordinated copper ions bound together by two alkoxo bridges. The bridging oxygen is a deprotonated oxygen of the ethanolic group of dea. The dea ligand also coordinates to the Cu(II) ions through its nitrogen, while the other ethanolic group does not involve in coordination. The thiocyanate anion coordinates to the Cu(II) ion with its nitrogen. Thermal reactivity of the complexes was studied using DTA and TG. Degradation of the amine ligands in the complexes occurs in the first stages of decomposition and the thiocyanate anions decompose at higher temperatures to give corresponding metal oxides.

Keywords: Diethanolamine; Triethanolamine; Thiocyanate; Dialkoxo-bridged binuclear Cu(II) complexes; Single crystal structures; Thermal analysis

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1. Introduction

Ethanolamines (ea's) are a class of organic molecules containing amine and alcohol groups. The amine group may be primary (monoethanolamine, mea), secondary (diethanolamine, dea) or tertiary (triethanolamine, tea) and display reactivity of the corresponding amines. Ea's are primary alcohols and, therefore, reactions are typical of primary alcohols. The bifunctional nature of ea's enables them to serve a variety of commercial applications such as corrosion inhibitors, surfactants, gas purification and herbicides [1].

Ea's are also versatile ligands that readily form coordination compounds with almost all metal ions and behave as N and O-donor ligands. Their transition metal complexes were synthesized by Sen-Dotson [2] and Brannon et al. [3]. Mea act as both an N-donor monodentate ligand and an N, O-donor bidentate ligands [4]. Dea and tea behave as bi- and tridentate ligands, respectively. In some cases, ea's lose their ethanolic hydrogen being as ethanolaminate anions, which also behave as ligands similar to ea's. Homo- and heterobimetallic ethanolaminate derivatives of a number of metals have been reported recently [5–8]. Thiocyanate complexes with the formula of $[M(NCS)_2L_4]$, where L is a monodentate N donor ligand such as pyridine, are called as Werner-type complexes which are known to act as hosts to include organic guest molecules with appropriate sizes and were used in the separation of aromatic compounds [9]. Although Ni(II) and Cu(II) thiocyanate complexes with mea appeared in the literature [10], the corresponding dea and tea complexes were not reported.

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As a part of our ongoing research on the synthesis, spectral, thermal and structural analysis of ea complexes with transition metals [11–18], we report here the synthesis, spectra and thermal reactivity of novel Co(II), Ni(II), Cu(II) and Zn(II) thiocyanate complexes with dea and tea, together with single crystal structure of the bis(μ-diethanolaminato)–bis(isothiocyanato)-dicopper(II) complex, $[Cu_2(\mu\text{-dea})_2(NCS)_2]$. Characterization of the complexes was completed with elemental analyses, magnetic susceptibility measurements, UV–Vis and FTIR spectroscopies.

2. Experimental

2.1. Materials and instrumentation

Dea, tea 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 1×10^{-3} M acetone solutions of the Co(II) and Cu(II) complexes of dea, and 1×10^{-3} M aqueous solutions of the other complexes of dea and tea in the 200–800 nm range. IR spectra were recorded on a Mattson FTIR spectrophotometer in the range 300–4000 cm^{-1} as KBr pellets. Room temperature (r.t.) 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 Analyzer. Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyzer in a dynamic nitrogen atmosphere. A sample size of 5–10 mg and heating rate of 10°C min^{-1} were used.

2.2. Synthesis of metal complexes

Solid KSCN (1.94 g, 20 mmol) was added slowly with continuous stirring to the solutions of the metal sulphates ($CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$, 20 mmol) in 20 cm^3 of distilled water. Dea (2.10 g, 20 mmol) and tea (2.98 g, 20 mmol) were dissolved in 30 cm^3 of distilled water and mixed with the previously prepared KSCN–metal sulphate solutions. The final solutions were stirred for 2 h at r.t. Polycrystalline precipitates were filtered off and the resulting solutions were left to stand at r.t. 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 ethanol, and dried in air. Table 1 lists analytical data together with the melting or decomposition points and colors of the complexes.

2.3. X-ray structure determination

A blue single crystal of $[Cu_2(\mu\text{-dea})_2(NCS)_2]$ with dimensions $0.15 \times 0.10 \times 0.07$ mm^3 was mounted on a glass fibre and determination of the unit cell parameters and collection of reflections were performed on a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å) in the 2θ range of 2.13–28.28° at 143(2) K.

The crystal is monoclinic, space group $P2_1/c$ with $a = 10.3108(8)$, $b = 17.1229(14)$, $c = 10.4990(8)$ Å, $\beta =$

Table 1
Analytical data for the metal complexes

Complexes	Color	Melting point	Molecular weight	*Anal.* found (calc.) (%)				Yield (%)
				C	H	N	S	
$[Co_2(dea)_2(NCS)_2]$	dark blue	226	442.26	26.95	4.41	12.37	14.60	65
$C_{10}H_{20}N_4O_4S_2Co_2$				(27.16)	(4.55)	(12.67)	(14.50)	
$[Ni(dea)_2(NCS)_2]$	blue	204	385.12	31.08	5.65	14.56	16.36	70
$C_{10}H_{22}N_4O_4S_2Ni$				(31.18)	(5.75)	(14.55)	(16.65)	
$[Cu_2(dea)_2(NCS)_2]$	dark green	137	451.48	26.52	4.37	12.36	14.44	74
$C_{10}H_{20}N_4O_4S_2Cu_2$				(26.60)	(4.46)	(12.41)	(14.20)	
$[Zn(dea)_2(NCS)_2]$	white	122 [a]	391.78	30.42	5.56	14.23	16.18	68
$C_{10}H_{22}N_4O_4S_2Zn$				(30.66)	(5.65)	(14.30)	(16.37)	
$[Co(tea)(NCS)]$	violet	232 [a]	265.18	31.55	5.25	10.53	12.31	81
$C_7H_{14}N_2O_3SCo$				(31.70)	(5.32)	(10.56)	(12.09)	
$[Ni(tea)(NCS)_2]$	blue	248	324.05	29.69	4.66	12.58	19.49	79
$C_8H_{15}N_3O_3S_2Ni$				(29.65)	(4.66)	(12.96)	(19.78)	
$[Cu(tea)(NCS)]$	green	160	269.79	31.20	5.29	10.37	11.36	85
$C_7H_{14}N_2O_3SCu$				(31.16)	(5.22)	(10.38)	(11.88)	
$[Zn(tea)(NCS)]$	white	220	271.62	30.99	5.14	10.19	11.85	62
$C_7H_{14}N_2O_3SZn$				(30.95)	(5.19)	(10.31)	(11.80)	

[a] Decomposition point.

Table 2
Electronic spectra and magnetic moments of the metal complexes

Complexes	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Found (calc.) μ_{eff}
$[Co_2(dea)_2(NCS)_2]$	536, 575, 624	239, 230, 252	4.23 (3.87)
$[Ni(dea)_2(NCS)_2]$	374, 626, 752	95, 63, 64	2.93 (2.83)
$[Cu_2(dea)_2(NCS)_2]$	667	272	2.11 (1.73)
[Co(tea)(NCS)]	545, 635, 752	105, 75, 65	3.81 (3.87)
$[Ni(tea)(NCS)_2]$	377, 647, 752	83, 57, 60	2.71 (2.83)
[Cu(tea)(NCS)]	743	121	1.87 (1.73)

111.842(3)°, $V = 1720.5(2)$ Å^3, $M = 451.50$, $Z = 4$, $D_x = 1.743$ g cm^{-3} and $\mu = 2.734$ mm^{-1}.

A total of 22864 reflections were collected between 2.13 and 28.28° θ angles within the index ranges $-13 \leq h \leq 13$, $-22 \leq k \leq 22$, $-13 \leq l \leq 13$. A total of 4264 intensity data were found to be independent ($R_{int} = 0.0440$). An absorption correction was made using the multiscan method (program SADABS). The maximum and minimum transmissions were 0.962 and 0.868, respectively. The structures were solved by direct methods [19] and refined by a full-matrix least-squares procedure on F^2 [20]. The refinement with 4264/215 data parameter ratio resulted in R values ($I > 2\sigma(I)$) of $R_{obs} = 0.0252$, $R_w = 0.0556$ and $R_{wtot} = 0.0590$. The goodness-of-fit was 0.972. The largest diffraction peak and hole in the final difference map were 0.508 and -0.367 e Å^{-3}, respectively. Neutral atomic scattering factors were taken from the International Tables for X-ray Crystallography, vol. C [21].

3. Results and discussion

3.1. General properties

The mixed ligand metal complexes were prepared by the reaction of dea or tea with the respective metal sulphates and KSCN. The complexes were obtained in good yields and the elemental analyses conformed to their proposed formula (Table 1). The results clearly indicate that the Co(II) and Cu(II) complexes of dea are dimeric while all the other complexes of dea and tea are mononuclear. Dimeric compositions are achieved by alkoxo-bridges, and require deprotonation of one of the ethanolic groups of the dea ligand in order to compensate for the positive charges of metal ions. Dimeric structures of these complexes were also evidenced from thermal analysis and single crystal X-ray analysis as will be discussed later in this paper. In the mononuclear complexes, dea acts as a bidentate ligand through its nitrogen, and oxygen of the ethanolic group, whereas tea behaves as a tripodal and tridentate N, O, O′ donor ligand. Deprotonation of tea occurs in the Co(II), Cu(II) and Zn(II), and results in a composition of [M(tea)(NCS)]. The structure of the Ni(II) complex with tea differs from the other tea complexes. The Ni(II) complex contains one neutral tea molecule and two NCS ligands. Evidence for the deprotonation of tea also came from single crystal X-ray analysis of these complexes. However, the structural data were not good enough, due to the severe disorder occurred in the crystals. Microanalyses conformed the 2:2:2 metal:dea:NCS stoichiometry for the dimeric complexes, the 1:2:2 metal:dea:NCS stoichiometry for the monomeric complexes, the 1:1:2 metal:tea:NCS stoichiometry for the Ni(II) complex, and the 1:1:1 metal:tea:NCS stoichiometry for the complexes containing the deprotonated tea.

All the metal complexes complexes are non-hygroscopic, stable in air, and do not contain any coordinate or lattice water. They are very soluble in water, acetone and ethanol. All the metal complexes except for the Zn(II) complex of dea and the Co(II) complex of tea exhibit sharp melting points as determined by DTA, but the Zn(II) complex of dea and the Co(II) complex of tea decompose at 122 and 232°C, respectively.

The metal complexes of dea and tea with NCS may be considered as analogues of Werner-type clathrates containing bi- and tridentate amines and their inclusion ability towards to small organic molecules is under investigation.

3.2. Spectral and magnetic characteristics

The λ_{max} values of the d–d transitions displayed by the complexes are given in Table 2, together with the ε_{max} values. The Co(II) and Ni(II) complexes show mainly three maxima as expected for coordinated metal ions with d^7 and d^8 configuration. The Cu(II) complexes exhibit single absorption peak centered at 667 and 743 nm for the dea and tea complexes, respectively. The Zn(II) complexes did not display any peak in the visible region that indicates the absence of charge transfer transitions.

The most important IR absorption bands of the metal complexes are summarized in Table 3. The dea ligand shows infrared absorptions [2–4] (in cm^{-1}) at: 3475 (br) νOH, 3250 (br) νNH, 2949 (w) νC–H, 1469 (s) $\delta(CH_2)$, 1067 (vs) νC–O. The metal complexes of dea exhibit broad bands in the range 3320–3487 cm^{-1}, due to hydrogen bonded OH stretching vibrations of dea. The broad peaks at around 3150 cm^{-1} correspond to the νNH stretching vibrations of dea. A comparison of the νNH data for the metal complexes with that of the free dea ligand shows lowering of 60–90 cm^{-1}, indicating the possible coordination of dea through its nitrogen to the metal. The splitting of the CH stretching absorption bands occurs in the 2868–2976 cm^{-1} range as medium bands. The $\delta(CH_2)$ bands appear as relatively strong bands in the 1440–1465 cm^{-1} region. The weak bands in the region 400–550 cm^{-1} are due to M–N and M–O stretching vibrations [22].

The tea ligand shows infrared absorptions [2,3] (in cm^{-1}) at: 3434 (br,s) νOH, 2949 (m) νC–H, 1467 (s) $\delta(CH_2)$, 1089 (vs) νC–O. A broad and strong absorption around 3450 cm^{-1} in all the metal complexes of tea is assigned to the stretching of the OH group. The other part of the spectra of the tea–metal complexes is similar to that of the dea–metal complexes.

The infrared spectra of the complexes present strong absorption bands at around 2100cm^{-1} for the νCN vibration and medium bands in the range 790–905 cm^{-1} for the νCS vibration. The stretching vibrations of the CN and CS groups shift significantly to higher frequencies in the complexes as indicated by $\Delta\nu$ in Table 3, compared to free SCN group ($\nu CN = 2045$ cm^{-1} and $\nu CS = 751$ cm^{-1}). These findings indicate the coordination of the SCN group through the nitrogen resulting in the formation of isothiocyanate complexes [22], as supported by single crystal X-ray studies reported elsewhere [18] and also in this paper.

The effective magnetic moments of the complexes of both dea and tea measured at room temperature are listed in Table 2. The metal complexes show high-spin configuration. The magnetic moments agree well with the coordination geometry around the metal ions and the calculated values of the spin-only magnetic moments. The Cu(II) complex of dea exhibits significantly high magnetic moment which may be a result of its doubly oxygen-bridged dimeric structure. It is reported that oxygen-bridged Cu(II) complexes are known to show subnormal magnetic moments due to super-exchange interaction [23–25]. The EPR spectra of a single crystal of the dimeric Cu(II) complex exhibits only a narrow line, and therefore shows an envelope of four hyperfine structure lines of copper, due to an exchange interaction among copper atoms.

3.3. Thermal analysis

The Co(II) complex of dea is thermally stable up to about 225°C. It melts at 226°C and then degradation of the dea moiety in the complex takes place in two exothermic stages between 229 and 307°C. The mass loss and IR analysis indicate that the solid intermediate formed at 315°C consists mainly of $Co(SCN)_2$ containing some oxygen left from the dea ligand. The solid residue decomposes in the temperature range 307–782°C to give cobalt oxide as the final decomposition product, which indicates the oxidative nature of the decomposition reaction. The Ni(II) complex of dea begins to decompose after melting at 204°C. Decomposition of the dea ligand occurs in two consecutive stages at 209 and 280°C. The total mass loss calculation for these stages (calc. 50.45%) agrees well with the experimental value of 50.04%. The third stage between 280 and 811°C corresponds to decomposition of the SCN residue. The end product was found to be NiO. The dimeric Cu(II) complex of dea is stable up to 135°C and decomposes in three stages. Degradation of dea is observed in three stages at 174 and 230°C. The last stage between 270 and 750°C is due to decomposition of the SCN anion to form CuO. Decomposition of the Zn(II) complex begins at 122°C and continue in three stages. This complex follows a decomposition mode similar to those of other dea complexes giving a solid decomposition product of ZnO_2 at 600°C.

Decomposition of the Co(II) complex of the tea ligand begins at 232°C and proceeds in five stages. The degradation of tea ends at 464°C. The subsequent steps correspond to decomposition of the thiocyanate anion. The final solid product was found to be cobalt oxide. The Ni(II) complex melts at 248°C and then begins to decompose in two distinct stages. In the first stage between 250 and 271°C, the tea ligand exothermically degradates and the second stage is related to decomposition of the two thiocyanate ions in the temperature range 271–780°C. The experimental mass loss data are consistent with the calculated values. The end product was found to be NiO. The Cu(II) complex of tea decomposes at three stages as deducted from the DTG curves, since the decomposition of the complex is very complicated including non-distinguishable steps. Mass loss calculations (found 48.79%, calc. 48.99%) indicate that degradation of tea takes place in the temperature

Table 3
IR spectral data for the metal complexes

Complexes	ν(OH)	ν(NH)	ν(C–H)	ν(C–N)	$\Delta\nu$(C–N)	ν(C–O)	ν(C–S)	δ(NCS)	ν(MN)
$[Co_2(dea)_2(NCS)_2]$	3487br,s	3191w	2950w, 2895w	2120vs	68	1048vs	795w	542w	483w
$[Ni(dea)_2(NCS)_2]$	3354s	3164m	2976m, 2895m	2113vs	68	1038vs	790m	543w	476w
$[Cu_2(dea)_2(NCS)_2]$	3326s	3164m	2949m, 2868m	2140vs	95	1051vs	822m	601w	470w
$[Zn(dea)_2(NCS)_2]$	3515s	3407s	2975sh, 2895sh	2105s	60	1078sh	840m	512w	453w
[Co(tea)(NCS)]	3434s		2976w, 2922w	2086vs	41	1067s	904m	552w	430m
$[Ni(tea)(NCS)_2]$	3461s		2976m, 2922m	2120vs	75	1063s	899m	542w	483w
[Cu(tea)(NCS)]	3488s		2949w, 2868w	2105vs	60	1063s	870w	557m	438m
[Zn(tea)(NCS)]	3488s		2921w, 2895w	2090vs	45	1063s	900m	557w	453m

Table 4
Thermoanalytical data for the metal complexes

Complex	Stage	Temperature range (°C)	DTG_{max} (°C) [a]	Mass loss (%)		Total mass loss (%)		Solid decomposition product	Color
				Found	Calc.	Found	Calc.		
$[Co_2(dea)_2(NCS)_2]$	1	229–271	250(−)	25.53					
	2	271–307	297(+)	10.71	36.69				
	3	307–782	520(+)	26.28	26.31	62.52	63.00	Co_2O_3	black
$[Ni(dea)_2(NCS)_2]$	1	209–246	236(+)	31.18					
	2	246–280	256(+)	18.86	50.45				
	3	280–811	596(+)	30.83	30.21	80.83	80.66	NiO	green–black
$[Cu_2(dea)_2(NCS)_2]$	1	140–196	174(−)	17.15					
	2	196–270	230(+)	21.99	39.04				
	3	270–750	353(+)	25.97	25.73	65.40	64.77	2CuO	black
$[Zn(dea)_2(NCS)_2]$	1	122–220	152(+)	19.28					
	2	230–352	322(+)	26.03	45.51				
	3	352–600	380(−)	29.44	29.70	74.75	75.21	ZnO_2	yellow
[Co(tea)(NCS)]	1	232–285	262(−)	28.00					
	2	285–464	350(+)	21.14	49.85				
	3	464–580	478(+)	12.03					
	4	580–794	741(−)	8.25					
	5	794–920	903(+)	1.25	21.90	70.67	71.75	CoO	gray–black
$[Ni(tea)(NCS)_2]$	1	250–271	256(−)	41.39	41.10				
	2	271–780	614(+)	36.12	35.91	77.51	77.01	NiO	green–black
[Cu(tea)(NCS)]	1	163–233	214(−)	26.35					
	2	233–305	256(+)	22.44	48.99				
	3	305–804	318(+)	21.56	21.53	70.35	70.52	CuO	black
[Zn(tea)(NCS)]	1	225–256	230(−)	14.60					
	2	256–410	342(+)	28.32	42.77				
	3	500–787	544(−)	21.18	21.38	64.10	64.15	ZnO_2	yellow

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

range 163–305°C. The last step is due to the decomposition of the thiocyanate anion to form CuO. Thermal decomposition of the Zn(II) complex of tea begins at 225°C after its melting at 220°C and proceeds in three stages. The first and second stages correspond to degradation of the tea ligand. A solid intermediate containing the SCN and O groups is stable between 400 and 500°C and finally decomposes to give zinc peroxide at 544°C.

The following general explanation of the thermal decompositions of the complexes can be given. Although the dea and tea ligands are degraded and evolved thermally, their degradation is not complete under nitrogen and results in the formation of a solid intermediate consisting of the metal, thiocyanate anion and some oxygen from the amines. Because of the complexity of the thermal decomposition process, it was impossible to identify the intermediates, although in some cases IR spectroscopy was used. However, mass loss calculations clearly support these explanations. Thermoanalytical data given in Table 4 show that the tea complexes exhibit higher thermal stability than those corresponding dea complexes, as the initial decomposition temperatures are taken as a measure of thermal stability. This may be explained by the bond strength between the metal and the ligand, since the tea ligand acts as a tridentate ligand and form much stable complexes.

3.4. Crystal structure

The molecular structure of the doubly oxygen-bridged dimeric Cu(II) complex of dea, bis(μ-diethanolaminato)bis(isothiocyanato)dicopper(II), is shown in

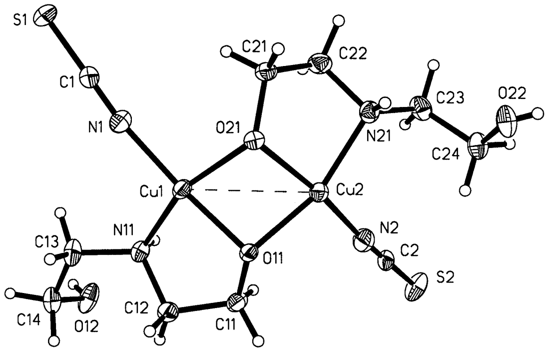

Fig. 1. Molecular structure of $[Cu_2(\mu\text{-}dea)_2(NCS)_2]$ with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

Table 5
Selected bond lengths (Å) and bond angles (°) for $[Cu_2(\mu\text{-}dea)_2(NCS)_2]$ [a]

Bond lengths			
Cu1–N1	1.9262(17)	N1–C1	1.160(3)
Cu1–O11	1.9330(13)	C1–S1	1.638(2)
Cu1–O21	1.9923(13)	N11–C12	1.478(3)
Cu1–N11	2.0386(17)	C12–C11	1.501(3)
Cu2–N2	1.9286(17)	C11–O11	1.422(2)
Cu2–O21	1.9617(13)	N11–C13	1.474(2)
Cu2–O11	1.9404(13)	C13–C14	1.516(3)
Cu2–N21	1.9991(17)	C14–O12	1.413(2)
Cu1–Cu2	2.8648(4)		
N21–H1···O11 # 1	2.913(2)	N11–H2···S1 # 3	3.4605(18)
O12–H3···S2 # 2	3.1685(18)	O22–H4···O12 # 4	2.807(2)
Bond angles			
N1–Cu1–O11	178.85(6)	O11–Cu1–O21	77.52(5)
O11–Cu1–N11	84.41(6)	Cu1–O21–Cu2	92.86(6)
N1–Cu1–O21	98.43(7)	Cu1–O11–Cu2	95.39(6)
N1–Cu1–N11	99.39(5)		

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

Fig. 1. Selected bond distances and angles are listed in Table 5.

The complex is binuclear and each copper ion is four-coordinated. The copper ions have two diethanolaminate oxygen bridges. The –Cu–O–Cu–O– bridging group is planar. The bridging oxygen atoms and copper atoms form a centrosymmetric Cu_2O_2 core and an inversion center is located between the two copper ions.

In the complex, the dea ligand is in the deprotanated form by loosing one of the ethanolic H and act as a bidentate donor through its N and deprotonated O. The other ethanolic group does not involve in coordination. Two N atoms, one from the thiocyanate anion and the other from the diethanolaminate ion, and two O atoms of the diethanolaminate ions form a strongly distorted square-planar coordination geometry around the copper ions with the bond angles in the range 77.52(5)–98.43(7). The Cu1–Cu2 distances of 2.8648(4) Å agrees well with the distances found in other dimeric alkoxo-bridged Cu(II) complexes [10,26]. The Cu–O bridging bond lengths, Cu1–O11 1.9330(3), Cu1–O21 1.9923(13), are within the range of corresponding values observed in related Cu(II) complexes [10,26]. The bridging angles Cu1–O21–Cu2 and O11–Cu2–O21 are 92.86(6) and 78.08(5)°, respectively. There are reports in the literature that the Cu–O–Cu bridging angle influences the magnetic properties of the complexes and results in subnormal magnetic moments [23–25].

The NCS ligand is almost linear (N1–C1–S1 179.6(2). The $Cu-N_{amine}$ bonds (Cu1–N11 2.0386(17) and Cu2–N21 1.9991(17)) are noticeably longer than the $Cu-N_{NCS}$ bonds (Cu1–N1 1.9262(17) and Cu2–N2 1.9286(17)). The same observations were observed in the analogues dea Ni(II) [18] and the mea Cu(II) complexes [10].

The NH and free OH groups are involved in intermolecular hydrogen bonding. The H atoms of the NH of one diethanolaminate in the complex participate in hydrogen bonding with the alkoxo O (N21–H1...$O1^{i}$ 2.913(2) Å), while the H atoms of the NH of the other diethanolaminate form relatively weak hydrogen bonds with the S atoms of the thiocyanate anion of the adjacent molecules (N11–H2···$S1^{iii}$ 3.4605(18) Å). The H atoms of the uncoordinated OH groups form hydrogen bonds with the OH and SCN groups neighboring molecules (O12–H3···$S2^{ii}$ 3.1685(18) Å and O12–H4···$O22^{iiii}$ 2.807(2) Å). Thus individual dimeric molecules are linked by hydrogen bonds forming a three-dimensional infinite network. Similar hydrogen bonding was reported for the other ea complexes [12,13,15,18].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 149631. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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