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Journal of Molecular Structure 641 (2002) 119–124

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

A hydrogen-bonded dimer of a novel Co(II) complex of monoethanolamine with thiocyanate: synthesis, spectra, thermal behaviour and crystal structure

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Received 1 August 2001; revised 1 March 2002; accepted 1 March 2002

Abstract

A strongly hydrogen-bonded dimer of the Co(II) complex of monoethanolamine, $[Co(meaH)_3][Co(mea)(meaH)_2](SCN)_3$, was synthesized and characterized by single crystal X-ray diffractometry, UV–Vis and IR spectroscopy. The complex consists of $[Co(meaH)_3]^{2+}$ and $[Co(mea)(meaH)_2]^+$, and three SCN^- anions. In each cation, the Co(II) ion is coordinated by a distorted octahedral arrangement of three monoethanolamine ligands in a bidentate manner. One of the monoethanolamine ligands in the $[Co(mea)(meaH)_2]^+$ cation is in the deprotonated form by losing its hydroxyl hydrogen. The complex cation units are held together by three strong O–H…O bonds formed between three ethanolic oxygens forming a hydrogen-bonded dimer of $[Co(meaH)_3]^{2+}\cdots[Co(mea)(meaH)_2]^+$. The hydrogen bonding O···O distances are significantly short at ca. 2.41(4) Å. The SCN^- anions are involved in hydrogen bonding connecting the dimeric units to give a three dimensional infinite network. During the thermal decomposition process, the complex loses the monoethanolamine ligands in the first stage, followed by the decomposition of the SCN^- anions at higher temperatures to give metallic cobalt as the end product.

Keywords: Monoethanolamine complex; Hydrogen-bonded dimer; Crystal structure; Thermal analysis

1. Introduction

Ethanolamines are a class of alkoxides used to a large extent in sol–gel processing [1,2]. Monoethanolamine is a versatile bifunctional ligand coordinating metal ions through the amine nitrogen and ethanol oxygen atoms behaving as a bidentate ligand. Hancock [3] and Casassas et al. [4] studied the d–d spectra and stability of transition metal complexes of monoethanolamine in aqueous solution. The IR and EPR spectra of the solid metal complexes of monoethanolamine were reported by Brannon et al. [5], and Masoud et al. [6]. There are a few reports on the synthesis and structural characterization of mixed-ligand metal complexes of monoethanolamine [7–9]. These studies indicated that the monoethanolamine ligand coordinates to metal ion as a neutral ligand or ethanolaminate monoanion, which is formed by losing the ethanolic hydroxyl hydrogen. Furthermore, the X-ray structural analysis showed two monoethanolamine ligands coordinating to the Cu(II) ion mono- and bidentately [8].

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PII: S0022-2860(02)00105-9

Table 1
Crystallographic data for the Co(II) complex of monoethanolamine

Formula	$C_{15}H_{41}N_9O_6S_3Co_2$
Molecular weight	657.61
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 15.4278(9)$ Å
	$b = 8.5463(5)$ Å
	$c = 22.4539(12)$ Å
	$\alpha = 90°$
	$\beta = 109.198(1)°$
	$\gamma = 90°$
Volume	2795.9(3)Å^3
Z	4
Calculated density	1.562 Mg/m^3
μ	1.457 mm^{-1}
F(000)	1376
Crystal size	0.28 × 0.24 × 0.06 *mm*
θ range	1.41 to 26.11°
Index ranges	$-19 \leq h \leq 18$; $-7 \leq k \leq 10$; $-27 \leq l \leq 24$
Reflections collected	14,861
Independent reflections	5340 [$R_{int} = 0.0483$]
Reflections observed ($>2\sigma$)	3296
Absorption correction	Multi-scan
Max. and min. transmission	0.916 and 0.672
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5340/51/372
Goodness-of-fit on F^2	0.870
Final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0368$, $wR^2 = 0.0696$
R indices (all data)	$R^1 = 0.0751$, $wR^2 = 0.0783$
Largest diff. peak and hole	0.359 and -0.546 e Å^{-3}

As a part of our ongoing research on the synthesis and spectral, thermal and structural characterization of plain and mixed ligand complexes of monoethanolamine [10–14]; we report here the synthesis, IR spectra, thermal analysis and single crystal structure of a new monoethanolamine cobalt complex with thiocyanate, $[Co(meaH)_3][Co(mea)(meaH)_2](SCN)_3$, where meaH and mea are the neutral monoethanolamine molecule and monoethanolaminate anions, respectively.

2. Experimental

2.1. Materials and instrumentation

Monoethanolamine ($NH_2CH_2CH_2OH$), $CoCl_2{\cdot}6H_2O$ and KSCN were purchased from Merck and used without further purification.

The electronic spectrum was measured on a Unicam UV2 spectrophotometer in a 1×10^{-3} M aqueous solution of the monoethanolamine complex in the 200–900 nm range. The IR spectrum was recorded on a Mattson FTIR spectrophotometer in the range 300–4000 cm^{-1} as KBr pellets. The elemental analyses (C, H and N contents) were performed at TUBITAK Marmara Research Center (Gebze). Thermal analysis curves (TG, DTA and DTG) were obtained using a Rigaku TG8110 thermal analyser in a dynamic nitrogen atmosphere with a flow rate of 80 cm^3 min^{-1}. A sample size of 5–10 mg and a heating rate of 10 °C min^{-1} were used.

2.2. Synthesis

A quantity of 20 mmol (1.94 g) solid KSCN were dissolved in a 20 cm^3 aqueous solution of $CoCl_2{\cdot}6H_2O$ (10 mmol, 2.38 g), and 20 mmol (1.22 g) monoethanolamine were added to this solution slowly with stirring. The resulting solution was stirred for one hour at room temperature. The polycrystalline precipitate formed was removed by suction filtration and the dark violet solution was left at room temperature until evaporation resulted in the formation of violet crystals suitable for X-ray diffraction analysis. The crystals were filtered off, washed with ethanol and dried in air. Yield, ca. 87%. Anal. Found: C, 26.31; H, 6.01; N, 18.23%; $C_{15}H_{41}N_9O_6S_3Co_2$ Calcd: C, 26.40; H, 6.28; N, 18.57%.

2.3. Crystal structure analysis

A suitable single crystal was mounted on a glass fibre with cyanoacrylate glue and data collection was performed on a BRUKER SMART 1000 CCD area detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were collected in the θ range 1.41–26.11° at 298(2)K. Crystal data and details of data collection and refinement are given in Table 1, while fractional atomic coordinates with isotropic displacement parameters are listed in Table 2. An absorption correction was made using the program SADABS [15]. The structure was solved by direct-methods using SHELXS-97 [16] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for the Co(II) complex of monoethanolamine

Atom	*x*	*y*	*z*	*U*(eq.)[a]
Co(1)	2782(1)	6393(1)	1135(1)	35(1)
Co(2)	2406(1)	7560(1)	−914(1)	32(1)
O(1)	1674(1)	6162(2)	444(1)	38(1)
O(2)	3479(1)	5460(3)	669(1)	41(1)
O(3)	2972(1)	8441(3)	839(1)	41(1)
O(4)	1539(1)	6343(2)	−657(1)	36(1)
O(5)	3388(1)	6386(2)	−361(1)	34(1)
O(6)	2478(1)	9088(2)	−277(1)	37(1)
N(1)	2017(2)	7292(3)	1580(1)	46(1)
N(2)	2645(2)	4275(3)	1396(1)	44(1)
N(3)	3921(2)	6771(3)	1822(1)	51(1)
N(4)	2274(2)	5984(3)	−1554(1)	43(1)
N(5)	3345(2)	8666(3)	−1141(1)	42(1)
N(6)	1414(2)	8831(3)	−1447(1)	44(1)
C(1A)	1135(4)	7777(9)	1081(3)	53(2)
C(2A)	862(4)	6524(10)	581(4)	47(2)
C(1B)	1025(4)	6895(16)	1239(5)	53(2)
C(2B)	996(8)	7109(15)	566(6)	47(2)
C(3)	2734(3)	3225(4)	899(2)	53(1)
C(4)	3528(2)	3802(4)	714(2)	51(1)
C(5)	4162(3)	8447(5)	1824(2)	60(1)
C(6)	3897(2)	8945(4)	1151(2)	51(1)
C(7)	1468(2)	4996(4)	−1594(2)	50(1)
C(8)	1440(2)	4823(4)	−936(2)	46(1)
C(9)	4225(2)	8432(4)	−623(2)	50(1)
C(10)	4257(2)	6757(4)	−426(2)	42(1)
C(11)	1422(2)	10357(4)	−1139(2)	52(1)
C(12)	1674(2)	10045(4)	−447(2)	51(1)
S(1)	685(1)	2335(2)	1367(1)	102(1)
C(13)	1530(3)	1288(5)	1811(2)	61(1)
N(7)	2152(3)	566(4)	2150(2)	72(1)
S(2)	1336(1)	7615(1)	−3970(1)	61(1)
C(14)	1450(3)	7718(5)	−3233(2)	64(1)
N(8A)	1540(9)	7782(17)	−2697(5)	129(3)
N(8B)	1260(70)	8400(120)	−2870(40)	129(4)
S(3A)	4501	2609	2353	78(1)
C(15A)	5455	2746	2220	60(2)
N(9A)	6257	3063	2315	115(4)
S(3B)	4576	2923	2534	78(1)
C(15B)	5388	2953	2245	59(2)
N(9B)	5981	2704	2018	116(4)
S(3C)	5782	3623	2198	91(2)
C(15C)	4921	2832	2314	60(2)
N(9C)	4249	2607	2462	119(7)

[a] *U*(eq.) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

refinement based on F^2 using SHELXL-97 [17]. All the non-H atoms were refined anisotropically. The coordinates of S3A, S3B, S3C, C15A, C15B, C15C, N9A, N9B and N9C were fixed and approximate occupation factors were entered. The H atoms attached to O1, O2 and O6 were located from difference map and the other OH hydrogen atoms were placed in calculated positions. All the hydrogen were refined with a riding model with U_{iso} 1.2 times that of their attached atoms. Molecular drawings were obtained using ORTEPIII [18].

3. Results and discussion

3.1. Spectral properties

The electronic spectrum exhibits intraligand transitions with high intensity in the 200–300 nm range, while the absorption bands occurred at 541, 737 and 851 nm with the ε values of 566, 86 and 84 M^{-1} cm^{-1}, respectively are attributed to the d–d transitions, which are consistent with the octahedral geometry around the Co(II) ion [18].

The FTIR spectrum of the Co(II) complex of monoethanolamine shows a broad and weak absorption band centred at 3460 cm^{-1} for the OH stretching vibration, due to the strong hydrogen bonding [5]. The very sharp bands at 3245 and 3110 cm^{-1} correspond to the ν(NH) stretching vibration. This band shifts by ca. 80 cm^{-1} to the low frequency region and splits into two bands compared to the free monoethanolamine. These observations clearly indicate coordination of the amine group of monoethanolamine to the Co(II) ion. Splitting of the CH stretching absorption band observed in the 2800–3000 cm^{-1} region is attributed to the presence of the ethanolate functional group, which may be due to a partially deprotonated monoethanolamine ligand. The spectrum of the complex presents a strong absorption bands at 2075 cm^{-1} for the ν(CN) vibration and a medium band at 900 cm^{-1} for the ν(CS) vibration of the SCN anion [19]. The strong and medium band observed in the 1000–1200 cm^{-1} range are assigned to the ν(CN), ν(CC) and ν(CO) stretching vibrations of monoethanolamine [5]. The weak bands in the 300–600 cm^{-1} region are due to the ν(MN) and ν(MO) vibrations [20].

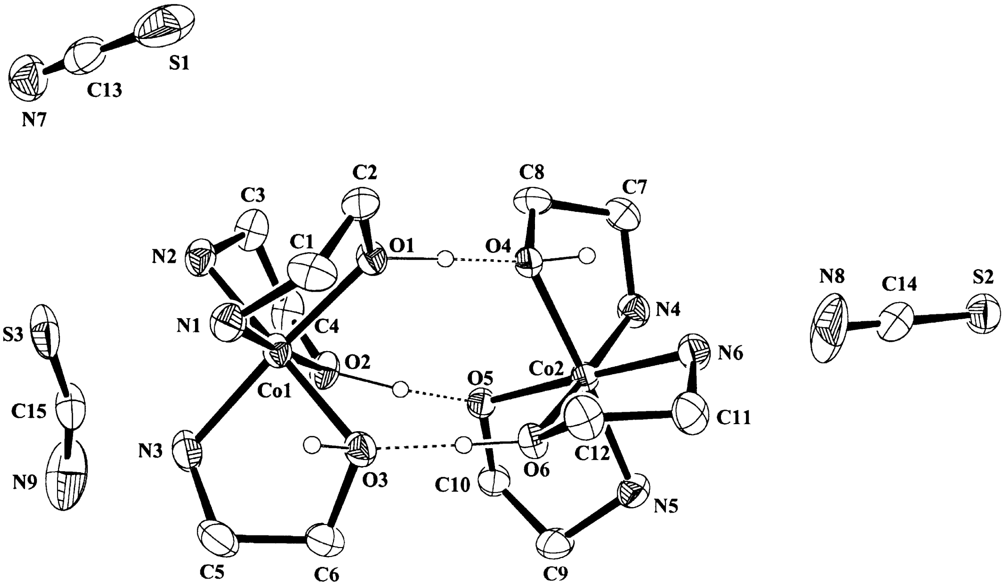

Fig. 1. A labelled drawing of the asymmetric unit of the Co(II) complex of monoethanolamine. Displacement ellipsoids are plotted at the 30% probability level. The ethylene and amine hydrogen atoms have been omitted for clarity.

Table 3
Selected bond distances and hydrogen bonding geometry for the Co(II) complex of monoethanolamine

Bond lengths			
Co1–O1	1.904(2)	Co2–O4	1.925(2)
Co1–O2	1.904(2)	Co2–O5	1.900(2)
Co1–O3	1.929(2)	Co2–O6	1.912(2)
Co1–N1	1.939(3)	Co2–N4	1.930(3)
Co1–N2	1.936(3)	Co2–N5	1.934(3)
Co1–N3	1.948(3)	Co2–N6	1.936(2)
Bond angles			
O1–Co1–O2	91.57(9)	O4–Co2–O5	90.14(8)
O1–Co1–O3	90.63(9)	O4–Co2–O6	91.20(9)
O1–Co1–N1	85.70(10)	O4–Co2–N4	86.12(10)
O1–Co1–N2	89.54(10)	O4–Co2–N6	90.17(10)
O1–Co1–N3	176.17(11)	O4–Co2–N5	175.69(10)
O2–Co1–O3	90.79(9)	O5–Co2–O6	91.95(8)
O2–Co1–N1	177.09(10)	O5–Co2–N6	177.30(10)
O2–Co1–N2	85.01(10)	O5–Co2–N4	89.06(10)
O2–Co1–N3	88.82(11)	O5–Co2–N5	85.66(10)
O3–Co1–N1	90.27(11)	O6–Co2–N5	89.91(10)
O3–Co1–N2	175.80(11)	O6–Co2–N4	177.15(11)
O3–Co1–N3	85.56(10)	O6–Co2–N6	85.36(10)
N1–Co1–N3	93.97(12)	N4–Co2–N5	92.83(11)
N2–Co1–N1	93.93(12)	N4–Co2–N6	93.63(11)
N2–Co1–N3	94.29(12)	N5–Co2–N6	94.07(11)

3.2. Thermal analysis

The complex does not have a melting point and begins to decompose at 120 °C. The decomposition stages between 90 and 388 °C correspond to elimination of the monoethanolamine ligands appeared as four endotherms at 142, 200, 242 and 265 °C in the DTA curve. The calculated weight loss for the removal of the monoethanolamine ligands is 55.2% and is in good agreement with the experimental value of 55.6%. The solid intermediate formed after the removal of the monoethanolamine ligands is $Co(SCN)_2$, which decomposes in the temperature range 390–960 °C with a mass loss of 26.4% (calculated 26.5%) to give metallic cobalt as the final decomposition product under nitrogen atmosphere.

3.3. Description of the crystal structure

The molecular structure of the complex is shown in Fig. 1, while Table 3 lists the selected bond lengths and angles.

The structure of the complex consists of two complex cations, $[Co(meaH)_3]^{2+}$ and $[Co(mea)(meaH)_2]^+$, and three SCN^- anions. Two cations are very similar and exhibit the same structural features.

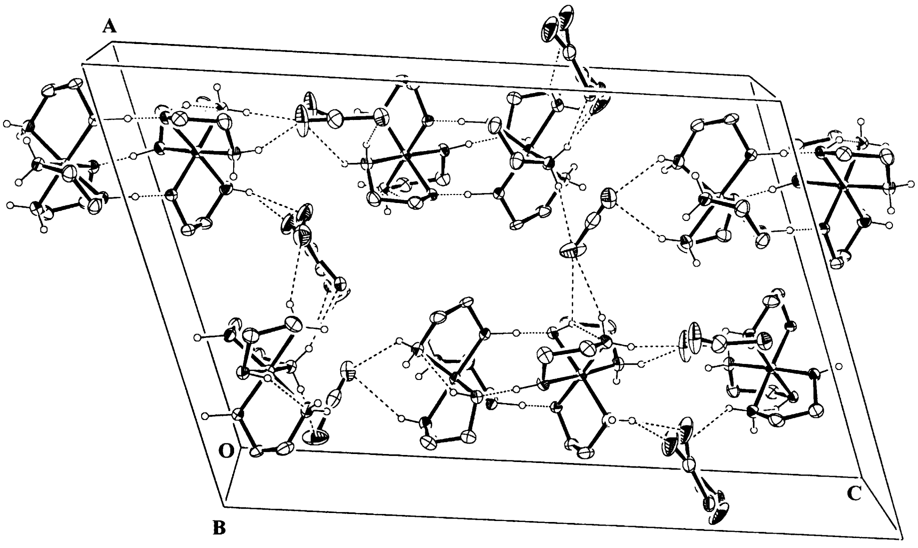

Fig. 2. A packing diagram of the unit cell of the Co(II) complex of monoethanolamine showing hydrogen bonding scheme.

In each cation, the Co(II) ion lies on the centre of symmetry and are octahedrally coordinated by three monoethanolamine moieties. The $[Co(mea)(meaH)_2]^+$ cation contains two neutral and one deprotonated monoethanolamine ligands, while all the monoethanolamine ligands are the neutral molecules in the $[Co(meaH)_3]^{2+}$ cation. Both the monoethanolamine molecule and monoethanolaminate anion act as bidentate ligands through the amine nitrogen and ethanol oxygen atoms and form five-membered chelate rings. The ethylene carbon atoms (C1–C2) of one of the monoethanolamine ligands are noticeably disordered over two positions with the occupancies of 41 and 59%, while all the atoms of the thiocyanate anion S3–C15–N9 and the N8 atom of the thiocyanate anion (S2–C14–N8) are extensively disordered. Both the $Co(meaH)_3]^{2+}$ and $[Co(mea)(meaH)_2]^+$ cations show the same coordination and bond geometry. The Co–N and Co–O bond distances are in the range 1.928(3)–1.949(3) and 1.899(3)–1.915(3) Å, respectively. The *cis* angles of the coordination octahedron range from 85.01(10) and 94.29(12)°, while the *trans* angles are in the range 175.80(10)–177.30(10)°. Therefore, the coordination geometry around the Co(II) ion is best described as a distorted octahedron. Bond distances and angles within the monoethanolamine molecules and the thiocyanate anions have expected values.

A packing diagram with hydrogen bonding scheme is shown in Fig. 2. The structure exhibits extensive intra- and intermolecular hydrogen bonds as listed in Table 4. The two complex cation units form a hydrogen-bonded dimer of $Co(meaH)_3]^{2+}\cdots[Co(mea)(meaH)_2]^+$ and are held together by three strong O–H···O bonds formed between three ethanolic oxygens of each complex cation. The hydrogen bonding O···O distances are significantly short at ca. 2.41(2) Å. This type of strong hydrogen bonds (2.42 Å) was reported for 1,4,7-tris(hydroxyethyl)-1,4,7-triazacyclononane containing ethanol groups with ionisable hydrogens similar to mea [21]. The N and S atoms of the thiocyanate anions are involved in weaker hydrogen bonding with the H atoms of the amine group of the monoethanolamine ligands. The dimeric units are connected to each other by the hydrogen bonds through the SCN^- anions to form a three dimensional infinite network.

4. Supplementary data

Crystallographic data (atomic coordinates, atomic displacement parameters and bond geometries) for the structure reported in the paper has been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary material with a deposition number

Table 4
Hydrogen bonding for the Co(II) complex of monoethanolaminea (Symmetry transformations used to generate equivalent atoms: [#1] $-x, -y+1, -z$; [#2] $-x+1/2, y+1/2, -z+1/2$; [#3] $x, y+1, z$; [#4] $-x+1/2, y-1/2, -z-1/2$; [#5] $-x+1, -y+1, -z$; [#6] $-x+1/2, y+1/2, -z-1/2$; [#7] $x-1/2, -y+3/2, z-1/2$; [#8] $-x, -y+1, -z$)

D–H···A	d(D–H)	d(H···A)	d(D···A)	< (DHA)
O1–H1···O4	1.12	1.30	2.417(3)	178.2
O2–H2···O5	1.16	1.25	2.404(3)	173.2
O3–H3···N1	0.84	2.11	2.741(4)	131.3
O4–H4···N6	0.85	2.10	2.734(3)	131.5
O4–H4···S1 [#1]	0.85	2.92	3.463	123.8
O6–H6···O3	0.98	1.45	2.432(3)	178.5
N1–H1A···N7 [#2]	0.90	2.42	3.091(4)	132.0
N1–H1B···N7 [#3]	0.90	2.26	3.056(4)	147.5
N2–H2A···S3A	0.90	2.48	3.285(3)	148.6
N2–H2A···S3B	0.90	2.57	3.425(3)	158.4
N2–H2A···N9C	0.90	2.32	3.160(3)	155.7
N2–H2B···S1	0.90	2.63	3.431(3)	148.9
N3–H3A···N7 [#2]	0.90	2.60	3.413(5)	151.3
N3–H3B···S3C	0.90	3.01	3.820(3)	151.3
N4–H4A···N8A	0.90	2.04	2.886(16)	155.7
N4–H4A···N8B	0.90	2.71	3.53(11)	150.6
N4–H4B···S2 [#4]	0.90	2.74	3.551(3)	150.1
N5–H5A···N9A [#5]	0.90	2.37	3.252(3)	167.4
N5–H5A···N9B [#5]	0.90	1.93	2.771(3)	153.8
N5–H5A···S3C [#5]	0.90	2.84	3.657(3)	152.0
N5–H5B···S2 [#6]	0.90	2.59	3.408(3)	151.8
N6–H6A···N8A	0.90	2.23	3.014(7)	145.0
N6–H6A···N8B	0.90	2.31	3.15(7)	155.0
N6–H6A···S3C [#7]	0.90	2.94	3.605(3)	131.8
N6–H6NB···S1 [#8]	0.90	2.59	3.449(3)	159.3

CCDC 167247. Copies of the data can be obtained, free of charge, on an application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

VTY, OA and AK wish to thank Ondokuz Mayis University for financial support given to the project.

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