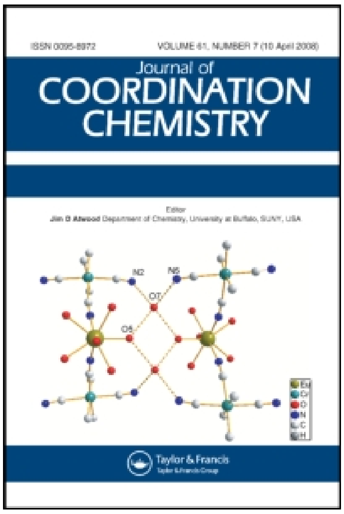

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectra, thermal analysis and crystal structure of a mononuclear oxalato-copper(II) complex with monoethanolamine, $[Cu(mea)_2(ox)]$

Veysel T. Yilmaz[a]; Evrim Senel[a]; Carsten Thöne[b]
[a] Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey [b] Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

To cite this Article Yilmaz, Veysel T. , Senel, Evrim and Thöne, Carsten(2003) 'Synthesis, spectra, thermal analysis and crystal structure of a mononuclear oxalato-copper(II) complex with monoethanolamine, $[Cu(mea)_2(ox)]$', Journal of Coordination Chemistry, 56: 16, 1417 — 1423

To link to this Article: DOI: 10.1080/00958970310001642582

URL: http://dx.doi.org/10.1080/00958970310001642582

J. Coord. Chem., Vol. 56, No. 16, 10 November 2003, pp. 1417–1423

Taylor & Francis
Taylor & Francis Group

SYNTHESIS, SPECTRA, THERMAL ANALYSIS AND CRYSTAL STRUCTURE OF A MONONUCLEAR OXALATO-COPPER(II) COMPLEX WITH MONOETHANOLAMINE, [Cu(mea)$_2$(ox)]

VEYSEL T. YILMAZ[a,*], EVRIM SENEL[a] and CARSTEN THÖNE[b]

[a]*Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey;* [b]*Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany*

(Received 29 April 2003; Revised 15 May 2003; In final form 30 October 2003)

cis-bis(Monoethanolamine)oxalatocopper(II), *cis*-[Cu(mea)$_2$(ox)], has been prepared and characterized by elemental analyses, IR, UV–Vis, thermal analysis and single crystal X-ray diffraction. The title complex crystallizes in the triclinic form with $P\bar{1}$ space group. The copper(II) ion lies on a center of symmetry and is octahedrally coordinated by two bidentate neutral mea (N,O) and one bidentate ox (O,O′) ligands. The individual molecules are held together by an extensive three-dimensional network of O–H···O, N–H···O and C–H···O type intermolecular hydrogen bonds. The IR spectrum and thermal decomposition of the title complex are described.

Keywords: Copper(II); Oxalato; Monoethanolamine; X-ray structure

INTRODUCTION

The coordination chemistry of the oxalate dianion (ox = $C_2O_4^{2-}$) has been widely studied as oxalato-containing compounds have varied structural features [1–7] and applications in biological chemistry [8], and magnetochemistry [9–12]. The ox anion acts as a mono-, bi-, tri- and tetradentate ligand [13]. Considerable attention has been devoted to the ox ligand as a building block and several mixed-ligand copper(II) complexes of ox have been reported. However, most of them have dimeric or polymeric structures due to the versality of the ox ligand to form bridged polynuclear complexes; very little has been reported to date about structures of mononuclear oxalato-copper(II) complexes [14–19].

---

*Corresponding author. Fax: +90-362-457 6081. E-mail: vtyilmaz@omu.edu.tr

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001642582

As part of our research on the preparation and characterization of mixed-ligand metal complexes with ethanolamines, we report here the synthesis, chemical characterization, spectral, thermal and structural analysis of a mononuclear mixed-ligand copper(II) complex of ox with monoethanolamine (mea), *cis*-[Cu(mea)$_2$(ox)].

EXPERIMENTAL

Materials

All reagents were purchased from commercial sources and used as supplied. The starting compound $Cu(ox)_2 \cdot 0.5H_2O$ was prepared by reacting basic copper carbonate $[CuCO_3 \cdot Cu(OH)_2]$ with a stoichiometric amount of oxalic acid in water.

Preparation of [Cu(mea)$_2$(ox)]

The ligand mea (0.12 cm^3, 2 mmol) was added drop-wise to a suspension of $Cu(ox)_2 \cdot 0.5\,H_2O$ (0.16 g, 1.0 mmol) in water (30 cm^3) at 50°C. The resulting solution was stirred for 30 min at 50°C and then filtered. The resultant filtrate was mixed with methanol (30 cm^3) and left at room temperature. Dark blue crystals suitable for X-ray diffraction analysis were obtained after a few days. [Cu(mea)$_2$(ox)]: Yield *ca.* 40.0%; dp 140°C. Anal. Calcd. (%): C, 26.3; H, 5.2; N, 10.2. Found: C, 26.2; H, 5.0; N, 10.3; $C_6H_{14}N_2O_6Cu$].

Physical Measurements

IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range 4000–300 cm^{-1}. Electronic spectra were measured on a Unicam UV2 in the 200–900 nm range. Elemental analyses (C, H and N) were performed on a Vario EL Elemental Analyser. Room-temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Evans magnetic balance. Thermal analysis curves (TG, DTA and DTG) were obtained with a Rigaku TG8110 thermal analyzer in a flowing nitrogen atmosphere, using *ca.* 10 mg samples.

X-ray Structure Determination

Intensity data for the copper(II) complex were collected using a Bruker SMART 1000 CCD area detector diffractometer (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$ Å) at 133 K. The structure was solved by direct methods using SHELXS-97 [20] and refined by a full-matrix least-squares procedure (SHELXL-97) [21]. All non-hydrogen atoms were refined with anisotropic parameters. Ethylenic hydrogen atoms were included using a riding model, while the hydrogens of the amine and hydroxyl groups were refined freely. Details of data collection, refinement and crystallographic data are summarized in Table I. The remaining electron density of 1.69 Å seems to be significantly high and is attributed to unidentified twinning and/or disorder phenomena.

TABLE I Crystallographic data for [Cu(mea)$_2$(ox)]

Compounds	*[Cu(mea)$_2$(ox)]*
Empirical formula	$C_6H_{14}N_2O_6Cu$
M_r	273.73
T (K)	133(2)
Radiation, λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.7491(8)
b (Å)	8.1690(8)
c (Å)	8.6073(10)
α (°)	107.922(3)
β (°)	94.725(3)
γ (°)	101.058(3)
V (Å^3)	748.89(6)
Z	2
D_c (g cm^{-3})	502.93(9)
μ (mm^{-1})	0.928
F(000)	282
Crystal size (mm^3)	$0.20 \times 0.12 \times 0.10$
θ range (°)	2.52–30.03
Index range (h, k, l)	$-10/10$, $-11/11$, $-12/12$
Reflections collected	10254
Independent reflections (R_{int})	2892 (0.0274)
Completeness to $\theta = 30.00°$	98.4%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8112 and 0.6692
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2892/0/160
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	0.0372
R indices (all data)	0.1096
Largest diff. peak and hole (e Å^{-3})	1.690 and -0.477

RESULTS AND DISCUSSION

Synthesis

An oxalato-copper(II) complex of mea prepared under similar experimental conditions to this paper was reported to have a dimeric composition $Cu_2(ox)_2 \cdot 5\,$mea [22], without performing a single-crystal X-ray structural analysis. The title complex *cis*-[Cu(mea)$_2$(ox)] was synthesized by reacting mea with $Cu(ox)_2 \cdot 0.5\,H_2O$ in solution. A color change from pale blue to dark blue occurred during complexation. Crystallization of the complex results in the formation of deep blue crystals. The elemental analyses are consistent with the formula of the complex, which was also shown by single crystal X-ray diffraction analysis. The solid complex is non-hygroscopic and stable and retains structural integrity indefinitely at ambient temperatures. The complex is soluble in water at room temperature and does not dissolve in methanol, ethanol or diethyl ether.

Spectral and Magnetic Properties

Selected IR bands of the complex are listed in Table II. The band at 3331 cm^{-1} may be assigned to the hydroxyl group of the mea ligand, while the NH_2 group absorption

TABLE II Selected IR spectral data[a] for [Cu(mea)$_2$(ox)]

Assignment	*Frequencies* (cm^{-1})
νOH)	3311 m
ν(NH)	3279 w, 3225 m
ν(CH)	2939 w, 2897 vw, 2855 vw
ν_{asym}(COO)	1711 s, 1690 vs, 1655 vs
ν_{sym}(COO)	1396 s, 1254 s
δ(OCO)	791 m
ν(MN)	642 w
ν(MO)	525 w

[a] w = weak; vw = very weak; vs = very strong; s = strong; m = medium.

appears as two split bands at 3279 and 3225 cm^{-1}. The relatively weak absorption bands in the range 2939–2855 cm^{-1} are due to ν(CH) vibrations. The presence of the ox ligand is clearly observed as very strong bands in the spectrum of the title compound: the ν_{asym}(COO) (1711, 1690 and 1655 cm^{-1}), ν_{sym}(COO) (1396 and 1254 cm^{-1}) and δ(OCO) (791 cm^{-1}) bands are characteristic of the bidentate coordination mode of ox with $C_{2\upsilon}$ symmetry [23]. The ν(MO) and ν(MN) vibrations are observed at 525 and 642 cm^{-1}, respectively, as weak bands.

The electronic spectrum of the title compound in water exhibits a distinct absorption band at 665 nm ($\varepsilon = 46\,M^{-1}cm^{-1}$) due to a d–d transition. Although crystallographic analysis of the bond lengths around the copper(II) ion indicates a Jahn–Teller effect, it was not observed in the electronic spectra as a separate absorption band. The absorption bands below 300 nm are due to intraligand transitions.

Thermal Analysis

The thermal behaviour of [Cu(mea)$_2$(ox)] was followed up to 600°C in a flowing atmosphere of nitrogen. The complex is stable up to 140°C but begins to decompose at higher temperatures. The DTA and TG curves indicate that the complex shows a three-step decomposition process with small temperature intervals, as observed for Cu$_2$(ox)$_2$ · 5 mea [22]. The mass losses of 12.1% and 32.4% in the range 140–180°C and 182–238°C, respectively, are attributed to the endothermic evolution of 0.5 (calcd. 11.2%) and 1.5 moles (calcd. 33.5%) of mea. A similar decomposition behavior has been reported for [Cu(mea)$_2$(sac)$_2$], where sac is the saccharinate anion [24]. The decomposition of the ox ligand takes place in the range 245–560°C to give the black end product CuO. The total mass loss of 71.5% agrees well with the calculated mass loss of 70.9%.

Crystal Structure of [Cu(mea)$_2$(ox)]

The molecular structure of [Cu(mea)$_2$(ox)] with atom labelling (Fig. 1) and selected bond lengths and angles together with the hydrogen bonding geometry (Table III) are given here. The title complex crystallizes in the triclinic form with $P\bar{1}$ space group. The structure consists of individual molecules of [Cu(mea)$_2$(ox)], in which the copper(II) ion sits on a center of symmetry and coordinates two mea and one ox ligands, forming an octahedral CuN$_2$O$_4$ chromophore. Each mea ligand acts as a bidentate donor through the amine N and hydroxyl O atoms, creating a five-membered chelate ring, while ox behaves as a O,O′ donor bidentate ligand. All the ligands occupy *cis* positions.

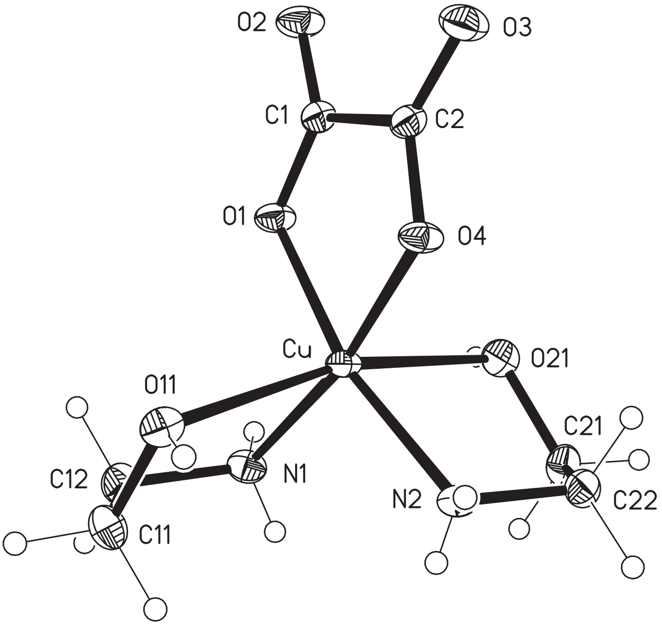

FIGURE 1 Molecular structure of [Cu(mea)$_2$(ox)] with the atom labelling scheme and 50% thermal ellipsoids.

TABLE III Selected bond lengths and hydrogen bonding geometry for [Cu(mea)$_2$(ox)]^{a}

Bond lengths (Å) *and angles* (°)				
Cu–N(1)	2.023(2)	O(4)–Cu–O(1)	82.46(8)	
Cu–N(2)	2.008(2)	O(4)–Cu–N(2)	89.81(9)	
Cu–O(1)	1.982(2)	O(1)–Cu–O(21)	90.30(8)	
Cu–O(4)	1.970(2)	N(2)–Cu–O(21)	79.42(9)	
Cu–O(11)	2.433(2)	O(1)–Cu–N(1)	91.24(10)	
Cu–O(21)	2.412(2)	N(2)–Cu–N(1)	97.73(11)	
		O(4)–Cu–O(21)	95.56(8)	
		N(1)–Cu–O(21)	91.76(9)	
		O(4)–Cu–O(11)	95.59(8)	
		O(1)–Cu–O(11)	99.53(8)	
		N(2)–Cu–O(11)	92.19(9)	
		N(1)–Cu–O(11)	78.17(9)	
		O(21)–Cu–O(11)	166.00(7)	
		O(1)–Cu–N(2)	166.50(9)	
		O(4)–Cu–N(1)	170.34(9)	
Hydrogen bonds				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	< (DHA)
O(11)–H(11)···O(4)$^{(i)}$	0.71(5)	1.99(5)	2.680(3)	164(5)
O(21)–H(21)···O(1)$^{(iv)}$	0.71(6)	2.02(6)	2.727(3)	172(6)
N(2)–H(2B)···O(4)$^{(i)}$	0.88(5)	2.50(5)	3.202(3)	138(4)
N(1)–H(1B)···O(2)$^{(ii)}$	0.81(5)	2.26(5)	3.034(3)	158(4)
N(2)–H(2A)···O(2)$^{(ii)}$	0.73(5)	2.27(5)	2.985(3)	166(5)
N(2)–H(2A)···O(3)$^{(ii)}$	0.73(5)	2.53(5)	2.993(3)	123(5)
C(22)–H(22A)···O(3)$^{(ii)}$	0.99	2.67	3.289(4)	121
C(11)–H(11A)···O(1)$^{(iii)}$	0.99	2.64	3.526(4)	149
C(12)–H(12B)···O(11)$^{(iii)}$	0.99	2.58	3.543(4)	165

^{a}Symmetry operations: $^{(i)}-x, -y, -z$; $^{(ii)}1+x, y, z$; $^{(iii)}-x, 1-y, -z$; $^{(iv)}-x, 1-y, 1-z$.

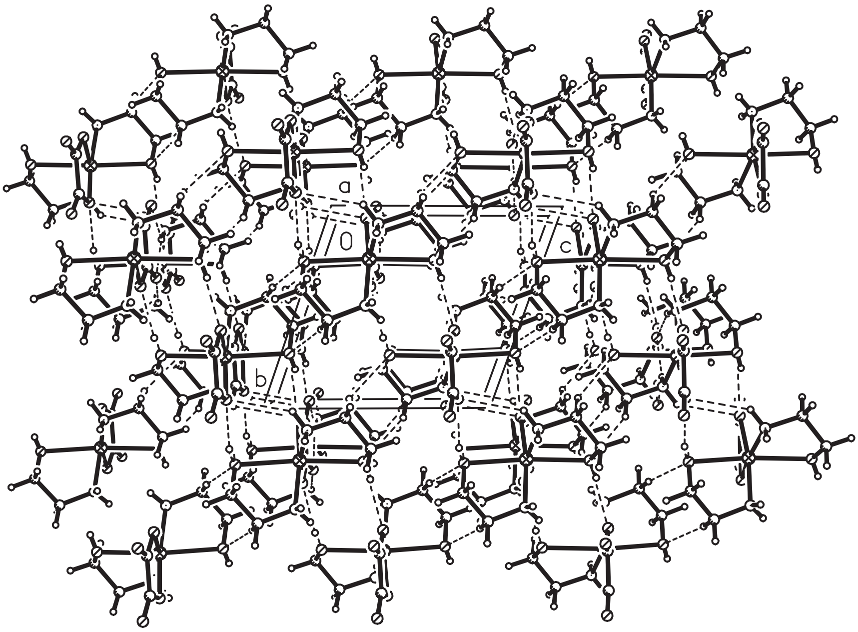

FIGURE 2 Packing diagram of $[Cu(mea)_2(ox)]$.

The average $Cu–O_{ox}$ bond distance of 1.976(6) Å in the copper(II) complex is comparable with those reported for $[Cu(ox)(C_4H_{12}N_2O)(H_2O)] \cdot 2H_2O$ [16] and is slightly longer than those found in $[Cu(ox)_2(Hhyd)_2)]$ H_2O [17] and $[K_2Cu(ox)_2 \cdot 4H_2O]$ [18], but somewhat shorter than that in $[Cu(ox)(phen)_2)] \cdot 5H_2O$ [19]. The average Cu–N and $Cu–O_{mea}$ bond distances of 2.015(7) and 2.422(10) Å, respectively, are typical for reported mixed-ligand copper(II) complexes [25–27].

The $Cu–O_{ox}$ and Cu–N bond lengths are similar, but significantly longer than the $Cu–O_{mea}$ bonds, resulting in an elongated distorted octahedral geometry along the $Cu–O_{mea}$ bonds as a consequence of the Jahn–Teller effect. Thus, the N and O_{ox} atoms form the equatorial plane of the coordination octahedron, while the hydroxyl O atoms occupy the axial positions. This significant distortion is also evident from the angles in the coordination polyhedron (Table III).

Torsion angles clearly indicate that the ox ligand is essentially planar [O(1)–C(1)–C(2)–O(3) = 178.0(3)° and O(2)–C(1)–C(2)–O(4) = 179.7(3)°]. The coordinated C–O bonds are much longer than those observed for the uncoordinated bonds, as expected. The C–C bond length [1.560(4) Å] is indicative of a single bond and is in accord with the previously reported values [16,17].

Figure 2 shows the crystal packing of the compound. The neutral molecules stack to form parallel chains held together by an extensive three-dimensional network of O–H···O, N–H···O and C–H···O type intermolecular hydrogen bonds.

Acknowledgment

This work was supported financially by Ondokuz Mayıs University.

Supplementary Material

Crystallographic data for the structure reported here have been deposited at the CCDC as supplementary data, CCDC No. 208949. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

References

[1] R. Vicente, A. Escuer, J. Ferretjans, H. Stoeckli-Evans, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* 167 (1997).

[2] S.G. Carling, C. Mathoniere, P. Day, K.M. Abdul-Malik, S.J. Coles and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1839 (1996).

[3] S. Decurtins, H.W. Schmalle, R. Pellaux, P. Schneuwly and A. Hauser, *Inorg. Chem.* **35**, 1451 (1996).

[4] X. Sun, M. Miao, P. Cheng, D. Liao, Z. Jiang and G. Wang, *Polyhedron* **15**, 2927 (1996).

[5] R. Vicente, A. Escuer, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* 1835 (1996).

[6] J. Suarez-Varela, J.M. Dominguez-Vera, E. Colacio, J.C. Avila-Roson, M.A. Hidalgo and D. Martin-Ramos, *J. Chem. Soc., Dalton Trans.* 2143 (1995).

[7] G. De Munno, M. Julve, F. Nicolo, F. Lloret, J. Faus, R. Ruiz and E. Sinn, *Angew. Chem. Int. Ed. Engl.* **32**, 613 (1993).

[8] M.J. Cleare, *Coord. Chem. Rev.* **12**, 349 (1974).

[9] J. Larionova, B. Mombelli, J. Sanchiz and O. Khan, *Inorg. Chem.* **37**, 679 (1998).

[10] S. Decurtins, H.W. Schmalle, R. Pellauz, R. Huber, P. Fischer and B. Ouladdiaf, *Adv. Mater.* **8**, 647 (1996).

[11] O. Khan, *Molecular Magnetism.* (VCH, New York, 1993).

[12] O. Khan, *Angew. Chem. Int. Ed. Engl.* **24**, 834 (1985).

[13] C. Oldham, Carboxylates, squarates and related species. In: G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry* (Pergamon Press, New York, 1987), Vol. 2, pp. 435–459.

[14] T. Weichert and J. Lohn, *Z. Kristallogr.* **139**, 223 (1974).

[15] A. Michalowicz, J.J. Girerd and J. Goulon, *Inorg. Chem.* **18**, 3004 (1979).

[16] A. Pajunen and M. Nasakkala, *Acta Crystallogr., Sect. B* **36**, 1650 (1980).

[17] D. Gajapathy, S. Govindarajan, K.C. Patil and H. Manohar, *Polyhedron* **2**, 865 (1983).

[18] J. Fan, W.Y. Sun, T.A. Okamura, K.B. Yu and N. Ueyama, *Inorg. Chim. Acta* **319**, 240 (2001).

[19] O. Castillo, A. Luque and P. Roman, *J. Mol. Struct.* **570**, 181 (2001).

[20] G.M. Sheldrick, *Acta Crystallogr., Sect. A* **46**, 467 (1990).

[21] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures (University of Göttingen, Germany, 1997).

[22] V. Jordanovska and R. Trojko, *J. Thermal Anal.* **44**, 1333 (1995).

[23] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York, 1997), 5th Edn., Part B, pp. 74–77.

[24] V.T. Yilmaz, Y. Topcu, F. Yilmaz and C. Thoene, *Polyhedron* **20**, 3209 (2001).

[25] M.B. Hursthouse, K.J. Izod, M.A. Mazid and P. Thornton, *Polyhedron* **9**, 231 (1990).

[26] P. Bombicz, E. Madarasz, E. Forizs and I. Foch, *Polyhedron* **16**, 3607 (1997).

[27] V.T. Yilmaz, O. Andac, Y. Topcu and W.T.A. Harrison, *Acta Crystallogr., Sect. C* **57**, 271 (2001).