Available online at www.sciencedirect.com
ScienceDirect
Inorganica Chimica Acta 360 (2007) 3777–3784
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis, characterization, and magnetic properties of new homotrinuclear bis(oxamato) copper(II) complexes with an asymmetric central *N*,*N*′-bridge

Tobias Rüffer [a,*], Björn Bräuer [a], François Eya'ane Meva [a], Bernhard Walfort [a], Georgeta Salvan [b], Annie K. Powell [c], Ian J. Hewitt [c], Lorenzo Sorace [d], Andrea Caneschi [d]

[a] *Chemnitz University of Technology, Institute of Chemistry, Strasse der Nationen 62, D-09107 Chemnitz, Germany*
[b] *Chemnitz University of Technology, Institute of Physics, Reichenhainer Strasse 70, D-09107 Chemnitz, Germany*
[c] *University Karlsruhe, Institute of Inorganic Chemistry, Engesserstrasse 15, D-76131 Karlsruhe, Germany*
[d] *University of Florence, Department of Chemistry, Via della Lastruccia 3, 50019 Florence, Italy*

Received 3 May 2007; accepted 15 May 2007
Available online 2 June 2007

Abstract

The new mononuclear bis(oxamato) complex [*n*-Bu_4N]$_2$[Cu(obbo)] (**1**) (obbo=*o*-benzyl-bis(oxamato)) has been synthesized as a precursor for trinuclear oxamato-bridged transition metal complexes. Starting from **1** the homotrinuclear complexes [Cu_3(obbo)(pmdta)$_2$(NO_3)][NO_3]·CH_2Cl_2·H_2O (**2**) and [Cu_3(obbo)(tmeda)$_2$(NO_3)$_2$(dmf)] (**3**) have been prepared, where pmdta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and dmf = dimethylformamide. The crystal structures of **1**–**3** were solved. The magnetic properties of **2** and **3** were studied by susceptibility measurements versus temperature. For the intramolecular *J* parameter values of -111 cm^{-1} (**2**) and -363 cm^{-1} (**3**) were obtained.

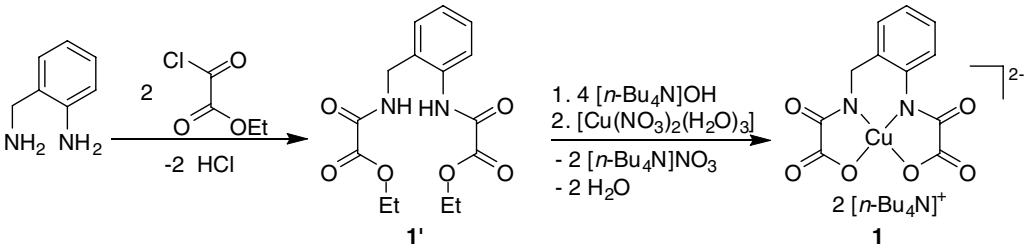
Keywords: Flexidentate ligands; Oxamato ligands; Magnetochemistry; Copper; X-ray diffraction

1. Introduction

The tuning of molecular magnetic properties by introducing modifications in the molecular structure has been successfully put into practice since several decades [1]. In the case of discrete homotrinuclear copper(II) bis(oxamato) type transition metal complexes. Magneto-structural correlations have shown that it is possible to markedly change the magnitude of magnetic interactions by changing only tridentate amines as terminal blocking ligands [2–7]. All previously investigated bis(oxamato) type complexes contain a symmetric bridge based on *N*,*N*′-1,3-propylene [2–6] or *N*,*N*′-*o*-phenylene units [6,7]. The presence of an asymmetric N_{aryl}, N'_{alkyl} bridge in homotrinuclear copper(II) bis(oxamato) complexes is expected to break the molecular symmetry and thereby result in different mediations of the magnetic super exchange coupling between the central copper(II) ion and each of the two terminal copper(II) ions. In order to check this, two trinuclear complexes, i.e. [Cu_3(obbo)(pmdta)$_2$(NO_3)][NO_3]$\cdot$ $CH_2Cl_2\cdot H_2O$ (**2**) and [Cu_3(obbo)(tmeda)$_2$(NO_3)$_2$(dmf)] (**3**) (pmdta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and dmf = dimethylformamide), were synthesised from the building block [*n*-Bu_4N]$_2$[Cu(obbo)] (**1**) (obbo = *o*-benzyl-bis(oxamato)). Compounds **2** and **3** are the first discrete homotrinuclear copper(II) bis(oxamato) type transition metal complexes having an asymmetric N_{aryl}, N'_{alkyl} bridge prepared to date. Herein, we report their synthesis, structure and magnetic properties.

* Corresponding author.
E-mail address: tobias.rueffer@chemie.tu-chemnitz.de (T. Rüffer).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.05.043



Scheme 1. Synthesis of **1′** and **1**.

2. Results and discussion

The copper(II) bis(oxamato) complex **1** and its precursor **1′** having an asymmetrical *N*,*N′*-bridge were prepared in analogy to the literature [8,19], cf. Scheme 1. Complex **1** was characterized by X-ray crystallography studies.

2.1. Solid state structure of $[n\text{-}Bu_4N]_2[Cu(obbo)]$ (1)

Compound **1** crystallizes in the monoclinic space group C2/c. The crystal structure of **1** consists of discrete $[Cu(obbo)]^{2-}$ anions and $[n\text{-}Bu_4N]^+$ cations, without any unusual short intermolecular interactions. Along a crystallographically imposed C_2 symmetry, which intersects Cu1, two identical molecules of $[Cu(obbo)]^{2-}$ anions (**1a** and **1b**, cf. Fig. 1) are statistically disordered. Perspective views of **1a** and **1b**, showing the atomic labelling, are given in Fig. 1, selected bond lengths and angles are listed in Table 1. Crystallographic data of **1** are summarized in Table 3.

The two statistically disordered $[Cu(obbo)]^{2-}$ anions, **1a** and **1b**, exhibit analogous bond lengths and angles and therefore only the structure of **1a** will be further discussed. The copper(II) ion is coordinated by two deprotonated amido nitrogens and two carboxylate oxygens, respectively, resulting in a $\eta^4(\kappa^2N{:}\kappa^2O)$ distorted square-planar coordination of the $[obbo]^{4-}$ ligands. This coordination type is usually observed for related complexes of bis(oxamato) ligands, although exceptions have been observed [9,10]. The Cu1 ion deviates by 0.030 Å from the calculated mean plane of the atoms N3A, N2, O4A and O1. Due to

Table 1
Selected bond lengths (Å) and angles (°) for **1a**[a]

Bond lengths[b]		*Bond angles*[b]	
Cu1–N3A	1.889(19)	N3A–Cu1–O1	170.5(6)
Cu1–N2	1.921(19)	N2–Cu1–O4A	166.4(6)
Cu1–O4A	1.983(16)	N3A–Cu1–O4A	84.3(6)
Cu1–O1	1.869(17)	N3A–Cu1–N2	95.2(3)
C25A–C26A	1.562(13)	N2–Cu1–O1	87.1(6)
C18–C17	1.566(13)	O1–Cu1–O4A	95.6(2)
N3A–C26A	1.328(11)	Cu1–N3A–C26A	116.0(10)
O4A–C25A	1.297(11)	Cu1–O4A–C25A	113.0(9)
C25A–O5A	1.205(11)	Cu1–N2–C18	112.5(10)
N3A–C19A	1.38(2)	Cu1–O1–C17	113.3(10)
N2–C18	1.323(11)		
C18–O3	1.276(16)		
O1–C17	1.300(11)		
C17–O2	1.212(11)		
N2–C27	1.461(19)		

[a] Data for **1b** are analogous to **1a** with respect to the statistical disorder and crystallographical symmetry.

[b] Symmetry transformation used to generate equivalent atoms: (A) $-x$, y, $-z+3/2$.

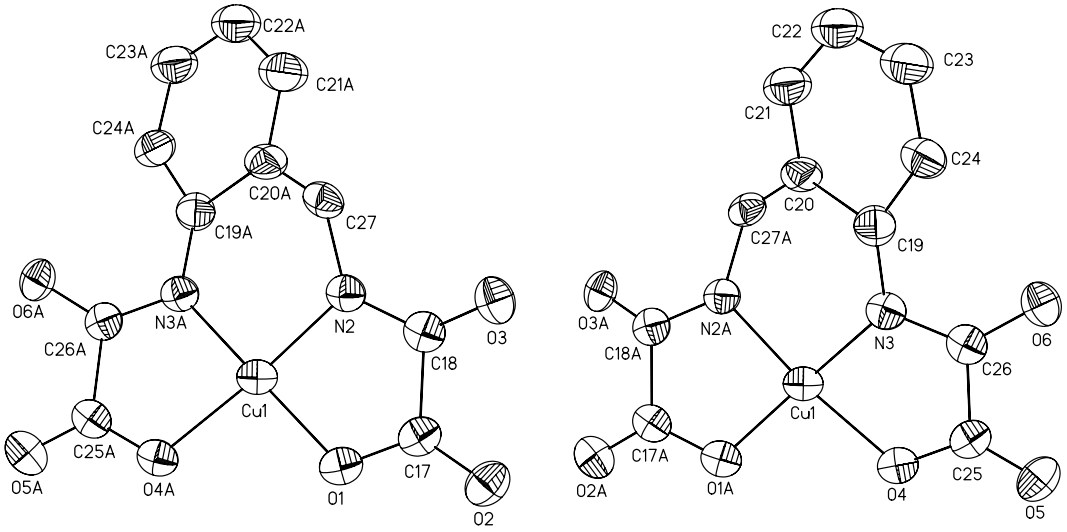


Fig. 1. ORTEP-plots (25% probability level) of the two statistically disordered molecules of **1** (Left: **1a**. Right: **1b**). The $[n\text{-}Bu_4N]^+$ cations and the hydrogen atoms have been omitted for clarity. Label 'A' refers to symmetry generated atoms of the respective disordered molecule.