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Synthesis and Crystal Structure of Tetra-[μ-O-(dimethylglyoximato-N,N′)dicopper(II) [$Cu_2(Hdmg)_4$] and dinickel(II) [$Ni_2(Hdmg)_4$]

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Two new complexes of tetra-[μ-O-(dimethylglyoximato-N,N′) dicopper(II)] and dinickel(II), $Cu_2(Hdmg)_4$ (A) and $Ni_2(Hdmg)_4$ (B), ($Hdmg^-$ = dimethylglyoxime anion) have been synthesized and their structures determined by X-ray crystallography. Both of the complexes crystallize in the monoclinic system, space group P2(1)/c, with lattice parameters a = 7.1593(1), b = 17.142(1), c = 9.809(2) Å, β = 107.00(1)°, and Z = 4 for A and a = 7.1061(1), b = 17.0437(1), c = 9.7514(2) Å, β = 108.291(1)° and Z = 4 for B. The final R = 0.0351 (0.0487) and wR = 0.0873 (0.1214) based on 1103 (2286) reflections with $I > 2\sigma(I)$ for A(B). The results indicate that copper(II) and nickel(II) atoms are connected by two μ_2-O^- bridges formed by two hydroxy oxygen atoms in the two oxime groups, respectively; each five-coordinated metal atom possesses a square pyramidal geometry.

Key Words: Copper(II) complexes, Nickel(II) complexes, Dimethylglyoxime anion, X-ray.

INTRODUCTION

Metal complexes of dimethylglyoximate ligand serve as models for vitamin B_{12}. They have been shown to exhibit some 2-dimensional metallic properties and have long been of importance in analytical chemistry. They have also played a role in molecular magnetism because of the remarkable efficiency of the oximate bridge to transmit electronic effects between the metal ions. The bis(oximato) copper(II) complexes can coordinate to another metal ion through the deprotonated oximate oxygens to give polynuclear species[1–3]. In fact, it was reported that dimethylglyoxime can coordinate to metal ions in a chelating or bis(chelating) fashion with the loss of either one or two oxime protons[4]. Further, the NO oxime group has a remarkable efficiency to mediate magnetic interactions when it acts as a bridging ligand[1, 5]. Although these features were known many years ago, the monomeric copper(II) oximato complexes were used as precursors of homo- and hetero-polynuclear species only in recent years[6–8]. Taking into account the versatility and interest of glyoximes in coordination chemistry and molecular magnetism, an investigation of their coordinating ability towards transition-metal ions both in solution and in solid state has been undertaken. In this paper, the syntheses and crystal structures of tetra-[μ-O-(dimethylglyoximato-N,N′)dicopper(II)] and tetra-[μ-O-(dimethylglyoximato-N,N′)dinickel(II) are described.

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EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. Copper(II) acrylate was prepared by mixing aqueous solutions of copper(II) sulfate and acrylic acid according to the literature method[9]. To a warm solution of dimethylglyoxime (1.16 g, 10 mmol) in H_2O (50 mL), 1.03 g of $Cu(CH_2{=}CHCOO)_2$ (5 mmol) was added with stirring and the mixture was refluxed for 30 min. The brown solution was filtered and the filtrate was kept aside undisturbed. Upon slow evaporation at room temperature, a brown crystalline solid which appeared several weeks later was separated by filtration. The red crystalline solid of nickel(II) complex was obtained similarly.

The C, H and N analysis were obtained using a Carlo-Erba 1106 elemental analyzer and the results are shown in Table-1. The IR spectrum was recorded on a Nicolet 510P FTIR spectrometer using KBr pellets.

TABLE-1
ELEMENTAL ANALYSIS DATA FOR A AND B

Complexes	Analysis: Found (Calcd.) %		
	C	H	N
A	32.80 (32.71)	4.90 (4.80)	19.02 (19.08)
B	33.34 (33.25)	5.01 (4.88)	19.35 (19.40)

A summary of the key crystallographic information is given in Table-2. The selected crystal of metal complex was mounted on a Nonius CAD4 diffractometer. Reflection data and reflections for the unit cell determination were measured at 293 K using MoK_α radiation (λ = 0.071073 nm) with a graphite monochromator.

TABLE-2
SUMMARY OF CRYSTALLOGRAPHIC RESULTS FOR A AND B

Formula	$C_8H_{14}N_4O_4Cu$	$C_8H_{14}N_4O_4Ni$
Formula weight	293.77	288.94
Colour	Brown	Red
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	7.159 (1)	7.1061
b (Å)	17.142 (2)	17.0437
c (Å)	9.809 (2)	9.7514
β (°)	107.00 (3)	108.29(3)
V (Å^3)	1151.2 (4)	1121.4
Z	4	4
$D_{(calcd.)}$ (Mg m^{-3})	1.695	1.711
μ (cm^{-1})	19.07	17.40
F (000)	604	600
Crystal size (mm)	0.24 × 0.20 × 0.20	0.32 × 0.18 × 0.20

TABLE-2 (*Contd.*)

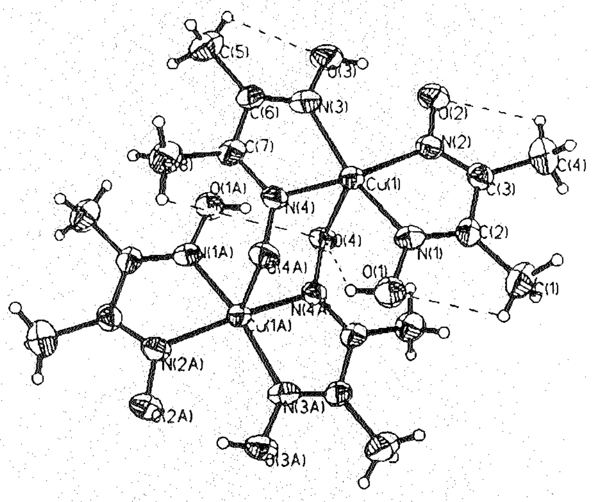
Radiation	MoK_α (λ = 0.071073 nm)	MoK_α (λ = 0.071073 nm)
Temp. (K)	293	293
θ ranges (°)	2.38–20.21	2.39–29.41
H/k/l	–6.6/–16.0/–9.0	–9.9/–23.16/–12.13
Reflections collected	1103	2826
Independent reflections	906	2286
Absorption correction	Empirical	Empirical
No. restraints	0	0
No. parameters	154	155
GOF	1.131	0.977
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0351$, $wR_2 = 0.0873$	$R_1 = 0.0487$, $wR_2 = 0.1214$
R indices (all data)	$R_1 = 0.0508$, $wR_2 = 0.1006$	$R_1 = 0.0682$, $wR_2 = 0.1284$
Largest peak and hole (e $Å^{-3}$)	0.304 and –0.627	0.870 and –1.582

The technique used was ω-scan with θ limits 2.38–20.21° for **A** and 2.39–29.41° for **B**. Absorption correction was made with psi-scans. The structure was solved by direct method and refined by full-matrix least-squares method on F^2 by using the SHELXTL[10] software package. All non-H atoms were anisotropically refined. The hydrogen atoms were geometrically fixed and allowed to ride on the parent atoms to which they are attached. The final convention for **A** was R = 0.0351 and wR = 0.0873 for 1103 reflections with $I > 2\sigma(I)$; $\omega = 1/[\sigma^2(F_0^2) + (0.0481P)^2 + 1.3527P]$ where $P = (F_0^2 + 2(F_c^2))/3$ and **B** was R = 0.0487 and wR = 0.1214 for 2826 reflections with $I > 2\sigma(I)$; $\omega = 1/[\sigma^2(F_0^2) + (0.0661P)^2 + 0.0000P]$ where $P = (F_0^2 + 2(F_c^2))/3$. The molecular graphics were created by using SHELXTL. Atomic scattering factors and anomalous dispersion correction were taken from International Table for X-Ray Crystallography[11].

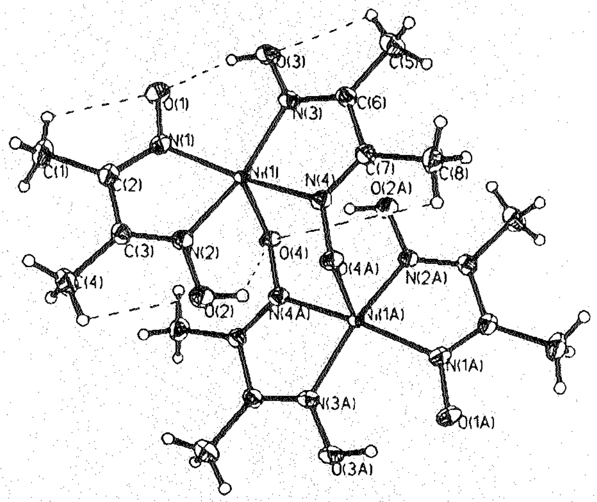
RESULTS AND DISCUSSION

The X-ray structures[12] of the complexes **A** and **B** are built up of discrete dimeric molecules. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme and Fig. 2 a perspective view of the crystal packing in the unit cell. Table-3 contains atomic positions and equivalent temperature factors for non-hydrogen atoms. Selected bond lengths and angles and hydrogen bonds are present.

The crystal structures of **A** and **B** have the same space group P2(1)/c and the same crystal system (monoclinic). Copper(II) and nickel(II) atoms are connected by two μ_2-O^- bridges formed by two hydroxy oxygen atoms in the two oxime groups. The geometry around metal ion (both copper(II) and nickel(II)) is best described as distorted square-pyramidal. Four oxime nitrogen atoms build the bottom planes and the fifth coordination position of the square pyramid around the copper (or nickel) is occupied by weakly-bonded oximate oxygen of another dimethylglyoxime anion [2.299 Å for Cu(1)-O(4) and 2.284 Å for Ni(1)-O(4), respectively]. In the equational plane, the four equal bonds to Cu(1) lie in the range of 1.95-1.98 Å and is compatible with those of the in-plane Cu-N (oxime) distance[4]. The four donor atoms around each copper(II) (or nickel(II)) are nearly coplanar.



A. Tetra-[μ-O-(dimethylglyoximato-N,N')dicopper(II)]

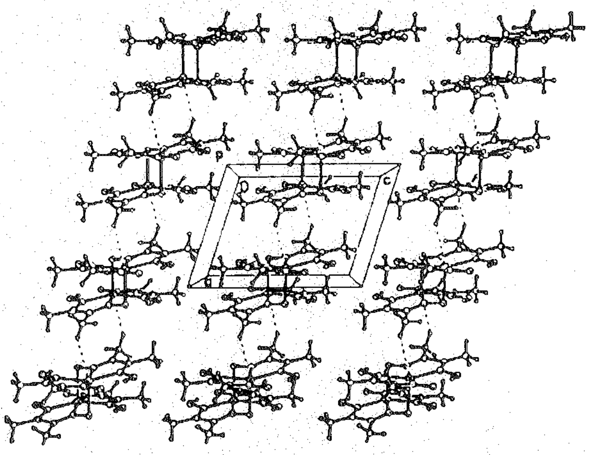


B. Tetra-[μ-O-(dimethylglyoximato-N,N')dinickel(II)]

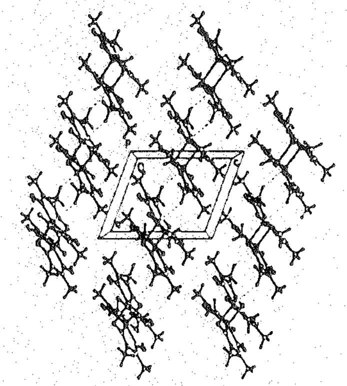
Fig. 1. Molecular structures for title compounds with the atomic numbering scheme. Atoms are represented as thermal ellipsoids at 50% level.

The central six-membered Cu(1)-O(4)-N(4A)-Cu(1A)-O(4A)-N(4) ring in the complex exhibits a chair conformation and the two molecules of $Cu(HL)_2$ are linked by this central six-membered ring. The $Hdmg^-$ ligands coordinate to the copper(II) (or nickel(II)) ions in a chelating fashion through the oxime nitrogen atoms, each five-membered ring being nearly coplanar. The nitrogen-oxygen bonds lie in the range 1.34–1.40 Å.

Charge-balance considerations indicate that four of the eight protons from the four dimethylglyoxime ligands have been lost in forming the complex. The O(2), O(2A), O(4) and O(4A) oxime protons are lost, and four mono-deprotonated $Hdmg^-$ groups are bound to two copper(II)/nickel(II). In the solid state for the copper(II) complex, five intramolecular hydrogen bonds (Fig. 1A and Table-5) are found, while six intramolecular hydrogen bonds (Fig. 1B and Table-5) exist in the nickel(II) complex. In both compleesx A and B the packing is linked by C—H····O intermolecular interactions into infinite chains along the a-axis (Fig. 2).



A. Tetra-[μ-O-(dimethylglyoximato-N,N′)dicopper(II)]



B. Tetra-[μ-O-(dimethylglyoximato-N,N′)dinickel(II)

Fig. 2. A view of the crystal packing for the title compounds

TABLE-3
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR A AND B

	X	y	z	U_{eq}		X	y	z	U_{eq}
Cu(1)	0.13254	0.90608	0.97216	0.0329	N(1)	0.6227	0.0955	0.9678	0.0138
N(1)	0.1653	0.8868	1.1758	0.0340	N(1)	0.6075	0.2098	0.9636	0.0208
N(2)	0.1266	0.7824	0.9736	0.0378	N(2)	0.6588	0.1158	1.1737	0.0188
N(3)	0.2081	0.9167	0.7970	0.0413	N(3)	0.6918	0.0848	0.7897	0.0217
N(4)	0.2077	1.0160	0.9870	0.0313	N(4)	0.7093	–0.0138	0.9878	0.0180
O(1)	0.1742	0.9455	1.2760	0.0443	O(1)	0.5988	0.2514	0.8456	0.0278
O(2)	0.1252	0.7498	0.8590	0.0493	O(2)	0.6756	0.0586	1.2775	0.0241
O(3)	0.1925	0.8574	0.7003	0.0530	O(3)	0.6670	0.1431	0.6896	0.0299
O(4)	–0.1935	0.9381	0.9043	0.0360	O(4)	0.2968	0.0594	0.9001	0.0201
C(1)	0.1435	0.7905	1.3556	0.0528	C(1)	0.6284	0.3307	1.1056	0.0333
C(2)	0.1524	0.8155	1.2124	0.0331	C(2)	0.6218	0.2436	1.0866	0.0212

TABLE-4
SELECTED BOND DISTANCES (Å) AND BOND ANGLES(°) OF A AND B

Cu(1)-N(2)	1.949(1)	Ni(1)-N(2)	1.973(3)
Cu(1)-N(4)	1.953(1)	Ni(1)-N(4)	1.953(4)
Cu(1)-N(3)	1.955(3)	Ni(1)-N(3)	1.956(3)
Cu(1)-N(1)	1.970(3)	Ni(1)-N(1)	1.951(3)
Cu(1)-O(4)	2.299(3)	Ni(1)-O(4)	2.284(4)
N(2)-Cu(1)-N(4)	165.92(14)	N(2)-Ni(1)-N(4)	165.58(9)
N(2)-Cu(1)-N(3)	96.4(2)	N(2)-Ni(1)-N(3)	95.87(9)
N(4)-Cu(1)-N(3)	80.5(2)	N(4)-Ni(1)-N(3)	80.78(9)
N(2)-Cu(1)-N(1)	79.7(2)	N(2)-Ni(1)-N(1)	80.50(9)
N(4)-Cu(1)-N(1)	97.9(2)	N(4)-Ni(1)-N(1)	97.47(9)
N(3)-Cu(1)-N(1)	157.7(2)	N(3)-Ni(1)-N(1)	158.60(11)
N(2)-Cu(1)-O(4)	102.61(12)	N(2)-Ni(1)-O(4)	102.64(8)
N(4)-Cu(1)-O(4)	91.46(10)	N(4)-Ni(1)-O(4)	91.78(8)
N(3)-Cu(1)-O(4)	103.99(14)	N(3)-Ni(1)-O(4)	103.43(9)
N(1)-Cu(1)-O(4)	98.23(13)	N(1)-Ni(1)-O(4)	97.94(8)

TABLE-5
HYDROGEN BOND DISTANCES (Å) OF A AND B

	D	H	A	D—H	H·····A	D·····A	D—H·····A
A	O(1)	H(1A)	O(4)	0.82	1.92	2.90	158
	C(1)	H(1B)	O(1)	0.96	2.36	2.80	106
	C(4)	H(4A)	O(2)	0.96	2.39	2.81	105
	C(5)	H(5A)	O(3)	0.96	2.40	2.82	105
	C(8)	H(8A)	O(4)	0.96	2.41	2.83	106
	C(8)	H(8C)	$O(2)^{i}$	0.96	2.59	3.25	127
B	O(2)	H(2A)	O(4)	0.82	1.92	2.70	157
	O(3)	H(3A)	O(1)	0.82	1.74	2.53	160
	C(1)	H(1A)	O(1)	0.96	2.40	2.82	106
	C(4)	H(4A)	O(2)	0.96	2.39	2.81	106
	C(5)	H(5A)	O(3)	0.96	2.41	2.82	105
	C(8)	H(8A)	O(4)	0.96	2.42	2.84	105
	C(8)	H(8B)	$O(1)^{ii}$	0.96	2.56	3.21	125

Symmetry code: (i): 1 – x, 1/(2 + y), –1/(2 – z); (ii): –x, –1/(2 + y), –1/(2 – z).

The IR spectrum showed the characteristic bands of the complexes **A** and **B**. The most important absorptions in the spectrum are the vibrations of —C=N which appears at 1540cm^{-1} and the vibration of —N—O which appears at 1215 cm^{-1}. The very strong absorption band in the region of acrylate antisymmetric carboxyl vibration which appears at 1586 cm^{-1} are the symmetric carboxyl stretching frequency occurring at 1371 cm^{-1} were disappeared.

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12. CCDC (212014 for **A** and 212015 for **B**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (44)(1223)336033; e-mail: deposit@ccdc.cam.ac.uk).

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