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研究简报

氮氧自由基配合物[Cu(NIT4Py)(IDA)]$_n$ 的合成与晶体结构

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Synthesis and Crystal Structure of a Pyridyl-Substituted Nitronyl Nitroxide Complex [Cu(NIT4Py)(IDA)]$_n$

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Abstract: A novel one-dimensional (1D) Cu(Ⅱ) nitronyl nitroxide complex bridged by iminodiacetate dianion [Cu(NIT4Py)(IDA)]$_n$, where NIT4Py=2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and IDA= iminodiacetate dianion, was synthesized and structurally characterized by X-ray diffraction. It crystallizes in monoclinic, space group $P2_1/c$ with a=0.921 09(10) nm, b=0.780 09(9) nm, c=2.486 3(3) nm, β=96.826(2)°. The Cu(Ⅱ) ion is five-coordinated with a distorted square-pyramidal geometry. Each iminodiacetate dianion bridges two Cu(Ⅱ) ions via a monodentate-tridentate mode into a 1D chain, and these 1D chains are further linked into a 2D network via hydrogen-bonding interactions. CCDC: 773132.

Key words: nitronyl nitroxide radical; iminodiacetic acid; copper(Ⅱ) complex; crystal structure

Stable organic radicals, which present high stability and good ability to chemical modifications, are widely used as ligands in the metal-radical approach to molecular magnetic materials[1-10]. However, the main drawback of nitroxide radicals has long been the poor ability of the N-O nitroxyl group to coordinate[11]. Introduction of potential donor atoms into the substituent group of the nitronyl nitroxide opens up the possibility of improving the coordination abilities and achieving compounds with a high dimensionality. Among these functionalized NITR ligands, pyridyl-substituted nitronyl nitroxides attracted considerable attention and were intensively studied[12-18].

On the other hand, appropriate bridges have always been used to design multidimensional materials in the metal-radical approach, such as dicyanide, dicyanoargentate(Ⅰ), etc. In this paper, the iminodiacetate dianion was chosen as the bridging ligand because it is a polydentate ligand having the coordination ability of both dicarboxylate and nitrogen atom, and is expected to produce new cluster topologies by virtue of its coordinative flexibility.

Taking advantage of the coordination abilities of both pyridyl-substituted nitronyl nitroxides and the

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iminodiacetate dianion, a metal-radical complex bridged by iminodiacetate dianion $[Cu(NIT4Py)(IDA)]_n$ was reported in this paper.

1 Experimental

1.1 Materials and instruments

All reagents were A.R. grade and used without further purification. The NIT4Py was prepared by the method described in the literatures[19-20]. Elemental analyses for C, H, N were carried out on a Model 1112 Flash EA elemental analyzer. The infrared spectrum was taken on a FTIR 1730 spectrometer in the 4 000~400 cm^{-1} region with KBr pellets.

1.2 Synthesis of $[Cu(NIT4Py)(IDA)]_n$

The aqueous solution of iminodiacetic acid (0.1 mmol) was dropwise added to a methanolic solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.05 mmol) and NIT4Py (0.1 mmol) with stirring. Then triethylamine was added to the solution until the pH reached 8. The mixture was stirred for 2 h and filtered. Deep blue-green single crystals suitable for X-ray structure analysis were grown at room temperature by the slow evaporation of the filtrate. Anal. Calc.(%) for $C_{16}H_{21}N_4O_6Cu$: C 44.80, H 4.93, N 13.06; found(%): C 45.47, H 5.48, N 13.47. IR spectrum: $\nu_{asym}(COO^-)$, 1 637, 1 606 cm^{-1}; $\nu_{sym}(COO^-)$, 1 403 cm^{-1}; ν(NO) of NIT4Py, 1 379 cm^{-1}.

1.3 X-ray crystallography and structure determination

A deep blue-green crystal of the title complex with approximate dimensions of 0.12 mm×0.08 mm×0.06 mm were put on a Bruker SMART APEX Ⅱ CCD area detector, equipped with a graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). Data were collected at room temperature by φ-ω scan mode. The structure was solved with direct methods using SHELXS-97 program[21]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full matrix least-squares refinement on F^2 was carried out using SHELXL-97[22]. Reliability factors were defined as $R_1=\sum(||F_o|-|F_c||)/\sum|F_o|$, and the function minimized was $wR_2=(\sum w(|F_o|^2-|F_c|^2)^2/\sum w|F_o|^2)^{1/2}$, where in the least squares calculation the unit weight was used. All nonhydrogen atoms were refined anisotropically. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

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Table 1 Crystal data and structure refinement for the $[Cu(NIT4Py)(IDA)]_n$

Formula	$C_{16}H_{21}CuN_4O_6$	F(000)	888
Formula weight	428.91	θ rang for data collection / (°)	1.65 to 25.05
Temperature / K	273(2)	Limiting indices	$-10 \leqslant h \leqslant 10$, $-5 \leqslant k \leqslant 9$, $-26 \leqslant l \leqslant 29$
Wavelength / nm	0.071 073	Reflections collected / unique (R_{int})	8 764 / 3 136 (0.024 8)
Crystal system	Monoclinic	Observed reflections ($I>2\sigma(I)$)	2 882
Space group	$P2_1/c$	Refinement method	Full-matrix least-squares techniques on F^2
a / nm	0.921 09(10)	Data / restraints / parameters	3 136 / 0 / 244
b / nm	0.780 09(9)	Goodness-of-fit on F^2	1.082
c / nm	2.486 3(3)	Final R indices ($I>2\sigma(I)$)	R_1=0.030 7, wR_2=0.081 3
β / (°)	96.826(2)	R indices (all data)	R_1=0.033 8, wR_2=0.083 1
Volume / nm^3	1.773 8(3)	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	673 and −436
Z	4	Weighing scheme ($P=(F_o^2+2F_c^2)/3$))	$w=1/[\sigma^2(F_o^2)+(0.042\,7P)^2+1.370\,4P]$
Calculated density / ($Mg \cdot m^{-3}$)	1.602	$(\Delta/\sigma)_{max}$	0.001
Absorption coefficient / mm^{-1}	1.274		

Table 2 Selected bond lengths (nm) and bond angles (°)

Cu(1)-O(3)	0.195 46(16)	Cu(1)-O(5)	0.195 89(16)	Cu(1)-N(3)	0.198 14(19)
Cu(1)-N(4)	0.196 09(19)	Cu(1)-O(4)A	0.231 21(18)	O(1)-N(1)	0.127 3(3)
O(2)-N(2)	0.126 9(3)	O(3)-C(13)	0.126 9(3)	O(4)-C(13)	0.123 4(3)

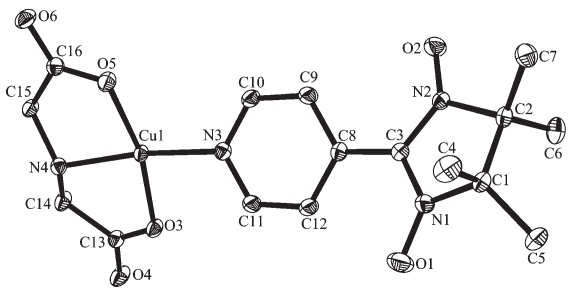
Continued Table 2

O(3)-Cu(1)-N(4)	83.84(7)	O(3)-Cu(1)-O(5)	166.38(7)	N(4)-Cu(1)-O(5)	83.87(7)
O(3)-Cu(1)-N(3)	94.23(7)	N(4)-Cu(1)-N(3)	168.86(8)	O(5)-Cu(1)-N(3)	96.56(7)
O(3)-Cu(1)-O(4)A	96.07(7)	N(4)-Cu(1)-O(4)A	92.29(8)	O(5)-Cu(1)-O(4)A	90.26(7)
N(3)-Cu(1)-O(4)A	99.84(8)				

Symmetry transformations used to generate equivalent atoms: A: $-x$, $y-1/2$, $-z+1/2$.

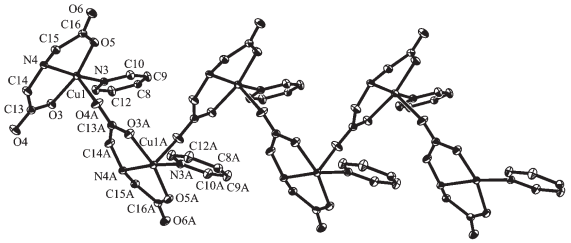
2 Results and discussion

The ORTEP drawing of the asymmetric unit [Cu(NIT4Py)(IDA)] is shown in Fig.1. The title complex consists of infinite 1D zigzag neutral chains (Fig.2), in which [Cu(NIT4Py)] moieties are connected by iminodiacetate dianion in monodentate-tridentate mode. The Cu(Ⅱ) ion is five-coordinated with a distorted square-pyramidal geometry. One NIT4Py radical ligand coordinates to the Cu(Ⅱ) ion through the nitrogen atom of its pyridyl ring and occupies one basal position of the Cu(Ⅱ) ion. Each iminodiacetate dianion coordinates to the Cu(Ⅱ) ion as a tridentate chelating ligand and occupies the other three basal positions. The bond lengths of Cu(1)-N(4) and Cu(1)-N(3) are 0.196 09(19) and 0.198 14(19) nm, respectively. The bond lengths of Cu(1)-O(3) and Cu(1)-O(5) are 0.195 46(16) and 0.195 89(16) nm. The apical position is occupied by the carboxylate oxygen atom from another IDA dianion, and the bond length of Cu(1)-O(4A) is 0.231 21(18) nm, which is longer than the Cu-O bond lengths in the basal plane. The bond angles around Cu(Ⅱ) ion are slightly distorted from ideal values (83.84(7)°~99.84(8)°). The dihedral angle between the pyridyl ring and the nitronyl nitroxide group O(1)N(1)-C(3)-N(2)O(2) is 22.4°. The shortest interchain distance between N-O groups of NIT4Py is 0.461 9 nm. The intra- and interchain Cu-Cu distances are 0.587 0 and 0.696 3 nm, respectively.



Hydrogen atoms were omitted for clarity

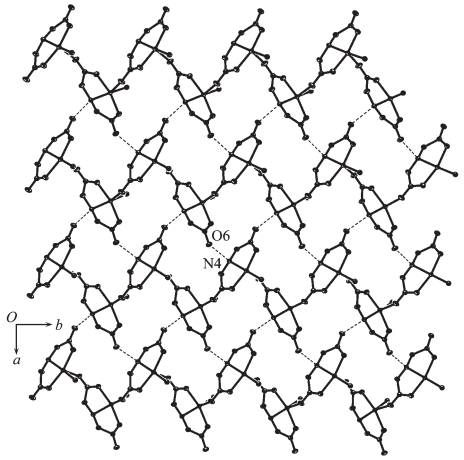
Fig.1 ORTEP drawing of the asymmetric unit [Cu(NIT4Py)(IDA)] with 30% thermal ellipsoids level



A: $-x$, $y-1/2$, $-z+1/2$, NIT4Py groups were omitted except pyridyl ring for clarity

Fig.2 1D zigzag chain structure of complex [Cu(NIT4Py)(IDA)]$_n$

A sketch of the intermolecular hydrogen bonds in the title complex is shown in Fig.3. The interchain hydrogen bonds exist between the nitrogen atom of iminodiacetate and the uncoordinated carboxyl oxygen atom of another iminodiacetate (N4⋯O6 ($-x+1$, $y+1/2$, $-z+1/2$)=0.283 4 nm). Finally, a 2D network along the ab plane is formed by the 1D zigzag chains through hydrogen bonds, and the radicals reside outside the 2D network along the c axis. The structural characteristics are similar to the related complexes [Cu(NIT3Py)(IDA)]$_n$ and [Cu(IM4Py)(IDA)]$_n$[23].



NIT4Py groups were omitted except pyridyl-N for clarity

Fig.3 View of 2D layer structure along ab plane for [Cu(NIT4Py)(IDA)]$_n$

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