Metal complexes with pyridone-based radicals: preparation and properties of a dinuclear paddle-wheel copper(II) complex and a mononuclear palladium(II) complex

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Abstract

We prepared and characterized dinuclear copper(II) and mononuclear palladium(II) complexes coordinated with a pyridine-based open-shell ligand, 5-(4',4',5',5'-tetramethylimidazoline-3'-oxide-1'-oxyl)-2(1*H*)-pyridone (= **HL**). In the copper(II) dinuclear complex $[\text{Cu}_2(\text{L})_4(\text{DMF})_2]$ (**1**), four deprotonated ligands are coordinated as bridging ligands to form a paddle-wheel type unit. In the palladium(II) complex *trans*- $[\text{PdCl}_2(\text{HL})_2]$ (**2**), two **HL** ligands in the neutral hydroxypyridine form are coordinated to the *trans* positions of the metal ion via the nitrogen atoms. The hydroxyl groups of the ligands are hydrogen-bonded to the chlorine atoms of neighboring molecules, thereby creating a hydrogen-bonded double-chain molecular arrangement. Magnetic susceptibilities of these complexes were measured and analyzed. The small intramolecular antiferromagnetic interaction in the latter complex may originate from superexchange through the diamagnetic metal center.

Keywords: Pyridone; Nitronyl nitroxide; Transition metal complexes; Magnetic properties; Copper; Palladium

1. Introduction

Pyridone derivatives have proven to be useful supramolecular synthons as well as highly versatile ligands for designing metal clusters [1]. The diversity of the structural chemistry of polynuclear complexes with pyridonate ligands has been investigated extensively [2]. These ligands have produced a number of interesting coordination compounds, including “platinum blues” and polynuclear clusters that behave as single molecule magnets [3–5]. Recently, nitronyl nitroxide radicals involving coordination sites have attracted considerable attention as components for metal-radical composite magnetic materials [6, 7]. However, the ligating sites that have been reported to date are limited: pyridine analogues [8], carboxylates [9], etc. Therefore, we introduced the pyridone moiety [10] as a ligating site into a stable organic radical; we prepared

5-(4',4',5',5'-tetramethylimidazoline-3'-oxide-1'-oxyl)-2(1*H*)-pyridone [11], which may be versatile for the preparation of polynuclear magnetic clusters modified by organic radicals. As the Scheme shows, the radical can assume keto-, enol-, and deprotonated forms. Herein we report the preparation, structures and magnetic properties of a dinuclear copper(II) complex and a mononuclear palladium(II) complex coordinated with this ligand. These metal species were chosen because they are known to produce dinuclear complexes when combined with pyridine type ligands [2a].

2. Experimental

2.1. General

The ligand, 5-(4',4',5',5'-tetramethylimidazoline-3'-oxide-1'-oxyl)-2(1*H*)-pyridone, was prepared from corresponding aldehyde precursors according to standard procedures [11, 12]. The UV-Vis spectra for DMF solutions were recorded on a JASCO V570 UV/VIS/NIR spectrophotometer. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer using KBr pellets in the 4000–400 cm^{-1} range. Elemental analyses were performed using a Yanagimoto MT-3 C-H-N coder. ESR spectra were measured on a JEOL JES-TE100 spectrometer (X-band microwave unit). The magnetic susceptibilities were measured with a Quantum Design MPMS-2 SQUID susceptometer in the temperature range of 2–300 K at a constant field of 1 T. Diamagnetic corrections for the samples were determined from Pascal's constants and literature values.

The X-ray data were collected using $\text{MoK}\alpha$ radiation on a CCD diffractometer (SMART APEX; Bruker Analytik, GmbH). The structures were solved by direct methods (SIR92 [13]) and refinement converged using full-matrix least squares of the CrystalStructure [14] program. All non-hydrogen atoms were refined anisotropically. Most of the hydrogen atoms were placed at ideal positions using a rigid model. The tetramethylethylene group in one of the nitronyl nitroxide moieties in **1** was disordered over two sites with occupancy of 1:1; no hydrogens were attached to these methyl carbons. The hydroxyl hydrogen in **2** was

located from the Fourier map and refined isotropically. Crystallographic data of **1** and **2** are listed in Table 1, and selected bond lengths and angles are shown in Table 2.

2.2. Preparation of $[\text{Cu}_2(\text{L})_4(\text{DMF})_2]$ (**1**)

Sodium methoxide (30 mg, 0.55 mmol) was added to a methanol solution (5 ml) of **HL** (136 mg, 0.54 mmol) cooled in an ice bath. After stirring for 1 h, copper(II) nitrate trihydrate (65 mg, 0.27 mmol) dissolved in methanol (5 ml) was added dropwise. The reaction mixture was stirred overnight at room temperature to obtain light blue powders. The precipitate was dissolved in DMF, and slow evaporation of the solution afforded dark blue plate crystals of $[\text{Cu}_2(\text{L})_4(\text{DMF})_2]$ over several weeks, yield 52 mg (30.4%). ESR in DMF solution: $a_N = 0.77$ mT (2 N) at $g = 2.007$; IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1659s, 1611s, 1559m, 1507m, 1394m, 1368m, 1336m, 1133m, 871w, 830, 474w, 437w; $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) (DMF) 286 (36000), 362 (19500), 615 (3300); Anal. Calcd. for $\text{C}_{54}\text{H}_{74}\text{N}_{14}\text{O}_{14}\text{Cu}_2$: C, 50.69; H, 5.78; N, 15.35. Found: C, 51.06; H, 5.87; N, 15.44%.

2.3. Preparation of *trans*- $[\text{PdCl}_2(\text{HL})_2]$ (**2**)

To a solution of 18-crown-6 ether (84.7 mg, 0.32 mmol) in 2 ml of dichloromethane:methanol (1:1 v/v) solution was added potassium tetrachloropalladate(II) (26.1 mg, 0.080 mmol). After stirring for 10 min, a methanol solution (2 ml) of **HL** (40.1 mg, 0.16 mmol) was added dropwise. Slow evaporation of the solution afforded deep blue needle crystals of *trans*- $[\text{PdCl}_2(\text{HL})_2]$ in a week, yield 41.7 mg (77%). ESR in DMF solution: $a_N = 0.78$ mT (2 N) at $g = 2.008$; IR (KBr): $\nu_{\text{max}}/\text{cm}^{-1}$ 1655s, 1613s, 1425m, 1386m, 1371s, 1307m, 1216m, 1134s, 834m, and 543m; $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) (DMF) 289 (35000), 312sh (21500), 365 (10400), 620 (1460), 672 (1200); Anal. Calcd. for $\text{C}_{24}\text{H}_{32}\text{Cl}_2\text{N}_2\text{O}_6\text{Pd}$: C, 42.52; H, 4.76; N, 12.40. Found: C, 41.76; H, 4.89; N, 11.63%.

3. Results and discussion

3.1. Preparation and Crystal Structures

Complexes **1** and **2** were prepared by reactions of deprotonated **L**[−] with copper(II) nitrate and **HL** with potassium tetrachloropalladate(II), respectively. Complex **1** was found to be a dinuclear paddle-wheel copper complex with deprotonated pyridonate ligands, while **2** was a mononuclear palladium complex with neutral ligands. We also attempted preparation of dinuclear palladium(II) complexes with **L**[−], but crystalline materials were unobtainable for the reaction.

The structure of **1** in the crystal is shown in Fig. 1. The copper atoms are penta-coordinated to form a square-pyramidal coordination geometry. Four pyridonate ligands are coordinated to the copper atoms as bridging ligands in the equatorial planes and two DMF molecules are ligated at axial positions. This complex has a crystallographic inversion center, and orientation of the four pyridonate ligands confers approximate C_{2h} symmetry upon the complex. The Cu–Cu distance of 2.602(1) Å is slightly longer than those for typical dinuclear copper(II) complexes [2b]. Within the ligands, the pyridonate plane and the nitronyl nitroxide plane are twisted by 20.3° and 37.0° for the two crystallographically independent ligands. The radical moieties are intermolecularly well-separated from each other: the shortest intermolecular distance between the neighboring nitronyl nitroxide groups is 4.29 Å.

Figure 2(a) shows the molecular structure of **2** in the crystal. The complex has a centrosymmetric structure; the palladium ion is located on the inversion center and coordinated with two **HL** ligands and two chlorine atoms in *trans* positions, exhibiting a square planar coordination geometry. Interestingly, the ligand is in a 2-hydroxypyridine form, in which the nitrogen atoms are coordinated to the metal ion and the phenolic group is hydrogen-bonded to the chlorine atom of the adjacent unit. The hydroxypyridine ring of the ligand is almost perpendicular to the coordination plane of the palladium ion, with the dihedral angle of 91.1(2)°. The dihedral angle between the nitronyl nitroxide plane and the hydroxypyridine ring is 20.7(5)°. Figure 2(b) shows the

packing diagram of the complex. One chlorine atom [Cl(1)] of the complex is hydrogen-bonded by the phenolic groups of two neighboring molecules ($-\text{O}-\text{H}\cdots\text{Cl}\cdots\text{H}-\text{O}-$) to form a double-chain hydrogen-bonded network along the *c*-axis, whereas the other chlorine atom Cl(2) is free. The hydrogen-bond distance ($\text{O}-\text{H}\cdots\text{Cl}$: 3.11 Å) is comparable to those observed in $\text{NH}\cdots\text{Cl}$ type hydrogen bonds (3.10–3.15 Å) [15]. Several short intermolecular distances exist between the neighboring NO-groups, which are ca 3.9–4.0 Å.

It has been reported that mononuclear palladium(II) or platinum(II) complexes with pyridone analogues or nucleobases ligands bind metal ions upon deprotonation, producing dinuclear and polynuclear metal complexes [16]. We found that the addition of barium hydroxide to **2** in water engender a slight broadening of the ESR spectra, without decomposition, possibly indicating the barium ion binding. Such a radical complex as **2**, bearing additional coordination sites, will be potentially useful for chemical sensing purposes, and useful as a building block for polynuclear metal complexes with radical ligands.

3.2. Magnetic properties

Magnetic susceptibility data for **1** and **2** are shown in Fig. 3 in the form of a χT vs. T plot. The room temperature value of χT for **1**, 1.88 emu K mol⁻¹, is markedly smaller than the expected value for an uncorrelated six $S = 1/2$ spin system (2.25 emu K mol⁻¹). The lower value of χT results from the cancellation of the moderately strong antiferromagnetic interaction between the dimeric copper atoms. The χT values decrease steadily with decreasing temperature, then drop rapidly below 10 K. The magnetic susceptibility data were analyzed on the basis of a model consisting of the singlet-triplet term ($\mathbf{H} = -2J_{\text{ST}}\mathbf{S}_a\cdot\mathbf{S}_b$) for the dinuclear copper unit and the Curie-Weiss term for the radical spins (eq. 1). In that equation, J_{ST} is the exchange coupling of the intramolecular Cu–Cu interaction, n ($= 4$) is the number of organic radicals per dimer, and θ is the intermolecular interaction [16]. The best result was obtained with the parameters $g_{\text{Cu}} = 2.2$, $g_{\text{rad}} = 2.0$ (fixed), $J_{\text{ST}}/k_{\text{B}} = -235$ K, and $\theta = -2.2$ K.

$$\chi = \frac{2Ng_{Cu}^2\mu_B^2}{k_B T [3 + \exp(-2J_{ST}/k_B T)]} + n \left[\frac{2Ng_{rad}^2\mu_B^2 S(S+1)}{3k_B (T - \theta)} \right] \quad (1)$$

Density functional theory (DFT) calculations of the optimized, i.e. planar, geometry of **L** reveal a small spin density delocalized on the phenolic oxygen, which may engender a metal-radical exchange interaction. However, the magnetic behavior of **1** was analyzed without assuming any such magnetic interactions between the ligands and the metal ions; the interactions are too small to be determined precisely, if at all. This situation is similar to those found in dinuclear copper(II) acetates involving nitroxide pendants [17].

On the other hand, the χT value for **2** at room temperature, $0.74 \text{ emu K mol}^{-1}$, is close to the theoretical one calculated for two $S = 1/2$ non-interacting spins. The χT value showed a rapid decrease below ca. 20 K, suggesting the presence of a marked antiferromagnetic interaction. The magnetic susceptibility was analyzed on the basis of a singlet-triplet model. The parameters of best fit were $g = 1.99$, $J/k_B = -2.78 \text{ K}$, and $\theta = -2.79 \text{ K}$. Antiferromagnetic intramolecular interaction may be explained by superexchange through the metal ion. As demonstrated crystallographically, the coordination plane around the metal ion and the hydroxypyridine moiety of the ligand are almost perpendicular to each other, thereby causing the overlap of the $2p\pi$ orbital of the nitrogen atom of the ligand and the d_{xy} orbital of the metal ion [18]. This can be an antiferromagnetic interaction pathway, but the interaction magnitude may be small because of the small spin density on the nitrogen.

Previously, we reported the preparation and magnetic properties of a mononuclear platinum(II) complex with pyridyl nitronyl nitroxide radicals, *trans*-[Pt(NH₃)₂(NITpPy)₂](NO₃)₂ [19]. This complex, which is structurally relevant to **2**, exhibits a Curie-Weiss-like magnetic behavior with only a small antiferromagnetic interaction ($\theta = -1.4 \text{ K}$). However, **2** exhibited a larger antiferromagnetic interaction that is considered to be intramolecular, as shown above, despite the identical configuration of metal-radical interactions. This is ascribable to the larger spin density on the nitrogen atom of **HL** than that of NITpPy as well as the difference of

metal species.

4. Concluding remarks

This study demonstrated that the pyridone-based radical **HL** is useful as a ligand for metal complexes carrying radical moieties. In particular, the dinuclear complex **1** represents a fundamental polynuclear complex with the open-shell pyridonate ligand. Furthermore, a mononuclear complex like **2** is potentially useful for stepwise construction of polynuclear complexes. Application of the pyridone chemistry to molecular magnetism may allow access to multifunctional compounds of further interest. In addition, construction of complexes involving larger numbers of metals with open-shell pyridone ligands is progressing in our laboratory.

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Figure Captions

Fig. 1. ORTEP [20] drawing of the molecular structure of **1** showing 50% probability ellipsoids. One of the dimethylethylene groups of the nitronyl nitroxide is disordered over two sites. For clarity, only one moiety is shown.

Fig. 2. (a) ORTEP drawing of the molecular structure of **2**, showing 50% probability ellipsoids. (b) Packing diagram of **2**. Hydrogen atoms are omitted for clarity. The dashed lines represents the hydrogen bond along the *c*-axis (O–H...Cl: 3.11Å).

Fig. 3. Plots of χT vs. T for crystalline samples of **1** and **2**. The solid curve corresponds to the data that were fit using the parameters given in the text.

Scheme

Fig. 1

Fig. 2

Fig. 3

Table 1

Crystallographic data for **1** and **2**

	1	2
Formula	C ₅₄ H ₇₄ N ₁₄ O ₁₄ Cu ₂	C ₂₄ H ₃₂ Cl ₂ N ₆ O ₆ Pd
Formula weight	1270.74	677.86
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>a</i> [Å]	10.988(2)	21.809(2)
<i>b</i> [Å]	27.235(3)	10.9736(9)
<i>c</i> [Å]	10.6839(13)	12.0466(10)
β [°]	109.596(6)	101.233(1)
<i>V</i> [Å ³]	3012.0(6)	2827.8(4)
<i>Z</i>	1	4
<i>d</i> _{calcd.} [g cm ⁻³]	1.267	1.592
<i>T</i> [K]	90	153
μ , cm ⁻¹	4.33	8.95
Final <i>R</i> ^a	0.080	0.038
Final <i>R</i> _w ^b	0.210	0.105
Goodness of fit	1.01	1.00

^a $R = \sum ||Fo| - |Fc|| / \sum |Fo|$.^b $R_w = [\sum w (Fo^2 - Fc^2)^2 / \sum w (Fo^2)^2]^{1/2}$.

Table 2

Selected bond lengths (Å), bond angles (°), and torsion angles (°) for **1** and **2**

1			
Cu–Cu*	2.602(1)	Cu–N(1)	2.022(5)
Cu–N(4)	2.006(6)	Cu–O(1)*	1.969(5)
Cu–O(4)*	1.968(5)	Cu–O(7)	2.187(4)
C1–O(1)	1.270(6)	C(13)–O(4)	1.297(6)
N(1)–Cu–N(4)	86.8(2)	N(1)–Cu–O(1)*	170.2(2)
N(1)–Cu–O(4)*	92.8(2)	O(1)*–Cu–N(4)	89.0(2)
O(1)*–Cu–O(4)*	90.1(2)	N(4)–Cu–O(4)*	171.4(2)
Cu*–O(1)–C(1)	127.3(4)	Cu*–O(4)–C(13)	127.4(4)
N(2)–C(6)–C(4)–C(3)	20.3(14)	N(6)–C(18)–C(16)–C(17)	37.2(14)
2			
Pd–Cl(1)	2.324(1)	Pd–Cl(2)	2.276(1)
Pd–N(1)	2.019(3)	O(3)–C(4)	1.332(4)
N(1)–C(4)	1.349(4)	N(1)–C(5)	1.341(4)
Cl(1)–Pd–Cl(2)	180	Cl(1)–Pd–N(1)	90
Pd–N(1)–C(4)	121.4(2)	C(4)–N(1)–C(5)	119.8(3)
Cl(1)–Pd–N(1)–C(4)	91.0(8)	O(2)–N(3)–C(6)–C(1)	1.9(5)

* Symmetry operators: $-x+1/2, y+1/2, -z+1/2$

Graphical abstract

By reaction of a pyridine-based open-shell ligand (**HL**) involving a nitronyl nitroxide moiety with copper(II) and palladium(II) ions, a dinuclear paddle-wheel type complex $[\text{Cu}_2(\text{L})_4(\text{DMF})_2]$ (**1**, Figure) and a mononuclear complex *trans*- $[\text{PdCl}_2(\text{HL})_2]$ (**2**) were prepared. These complexes were characterized structurally and magnetically; the small intramolecular antiferromagnetic interaction in the latter complex may originate from superexchange through the diamagnetic metal center.