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Self-Assembled Dimers of Copper(II) Complexes of Tripodal Dianionic Ligands, 2-Pyridyl-2,2′-dipyrrolylmethanes

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Introduction

Nitrogen heterocycles such as imidazole, pyrazole, and pyridine have frequently been assembled into polydentate ligands, and their metal complexes have been extensively studied to mimic structures and functions of non-heme metalloenzymes from a bioinorganic point of view.[1] Since ligation of pyrrole requires deprotonation of the NH proton that is not acidic under physiological conditions,[2] there have been reported only a few metal complexes with ligation of pyrrole nitrogens not only in Nature but also in coordination chemistry.[3] As is known for Cu−Zn superoxide dismutase (Cu_2Zn_2SOD)[4] and stellacyanin,[5] anionic nitrogen base ligands may provide strong ligand fields for the metal center to regulate its reactivity. Such anionic ligands can be generated by the deprotonation of an imidazole residue of histidine, an indole residue of tryptophan, and amide moieties of a protein backbone. In this regard, metal complexes with pyrrole ligands are of particular importance. In addition to the great interest in tripodal ligands in bioinorganic chemistry,[1] polypyrrolylmethanes have received considerable attention recently in relation to the structure of bacterial pigments.[6] Furthermore, tripyrrolylmethane-like compounds made of three bipyrrole units were published by Sessler and co-workers while this work was being completed.[7]

As an attempt to focus on the structures, spectroscopic properties, and reaction behaviors of metal complexes with polyanionic tripodal ligands, we have designed new ligands having pyrrole moieties. In this paper is described the first synthesis of metal complexes of pyrrole-containing tripodal ligands: Cu(II) complexes of 2-pyridyl-2,2′-dipyrrolylmethanes having carbonyl groups at the 5- and 5′-positions of the pyrrole rings. These neutral complexes turned out to be self-assembled dinuclear complexes with each Cu ion sharing two ligand molecules as evidenced by ESR, FABMS, and X-ray crystallographic analysis.

Experimental Section

Synthesis of the Ligands 1a−c. 2-Pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dicarbethoxy-2,2′-dipyrrolylmethane (**1a**) and 2-pyridyl-3,3′-dimethyl-4,4′-bis(trifluoromethyl)-5,5′-dicarbethoxy-2,2′-dipyrrolylmethane (**1b**) were prepared through the condensation of pyridine-2-carboxaldehyde with ethyl 3-ethyl-4-methylpyrrole-2-carboxylate and ethyl 3-(trifluoromethyl)-4-methylpyrrole-2-carboxylate, respectively, according to the reported methods.[8,9] The hydrolysis−decarboxylation[8b] (94% yield based on **1a**) and benzoylation[10] (39% yield) sequence according to the reported methods converted **1a** into 2-pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dibenzoyl-2,2′-dipyrrolylmethane (**1c**).

Reaction of the Ligand 1c with $Cu(ClO_4)_2$·$6H_2O$. In a typical procedure, a mixture of the ligand **1c** (23.8 mg), $Cu(ClO_4)_2$·$6H_2O$ (16.4 mg), CH_2Cl_2 (3.0 cm^3), MeOH (0.7 cm^3), and Et_3N (0.023 cm^3) was stirred at room temperature for 2 h under argon. Purification by chromatography on alumina with CH_2Cl_2 afforded a green colored Cu(II) complex, $(C_{34}H_{31}N_3O_2Cu)_2$ (**2c**), in an 82% yield based on **1a**. Methoxy-2-pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dibenzoyl-2,2′-dipyrrolylmethane (**3c**) was obtained in a 77% yield from the reaction of **1c** under air by using 2-fold molar amounts of $Cu(ClO_4)_2$·$6H_2O$ (32.8 mg) followed by column chromatography on alumina with CH_2Cl_2.

X-ray Crystallographic Analysis. Recrystallization of **2c** from chloroform−diethyl ether gave dark blue prisms of 1:1 composition of Cu and diethyl ether. Crystal data for **2c**·$2(C_4H_{10}O)$: $C_{76}H_{82}N_6O_6Cu_2$, $M = 1302.61$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.203(2)$ Å, $b = 15.032(2)$ Å, $c = 8.576(3)$ Å, $\alpha = 98.319(19)°$, $\beta = 104.804(18)°$, $\gamma = 70.549(12)°$, $V = 1665.7(6)$ Å^3, $Z = 1$, $D_{calc} = 1.299$ g/cm^3, μ(Mo Kα) = 6.96 cm^{-1}, $T = 296$ K, crystal size 0.30 × 0.20 × 0.15 mm. A total of 3289 reflections were collected ($4° < 2\theta < 40.1°$) on a Rigaku AFC5R diffractometer using graphite-monochromated Mo Kα radiation, and 3122 were unique. The unit cell parameters were obtained from least-squares refinements of 19 reflections (22.0−24.8°). The 1963 reflections with $I > 5\sigma(I)$ were used for structure solution and refinement with a linear correction factor being applied to the data to account for the decay (8.73%) of the three periodically measured standard reflections over the course of data collection. The data were corrected for Lorentz and polarization effects and absorption based on azimuthal scans. The structure was solved by the direct method and refined by the full-matrix least-squares method (Texsan[11]) on a Hewlett-Packard A4032A work station. All non-hydrogen atoms except the C(35) methyl carbon atom of diethyl ether were refined anisotropically. Hydrogen atoms were included at standard positions (C−H = 0.95 Å) but not refined. The refinement converged at $R = 0.070$, $R_w = 0.070$, and GOF = 3.73.

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Table 1. The Yields of the Dinuclear Cu(II) Complexes **2a**−**c** by the Metalation of 2-Pyridyl-2,2′-dipyrrolylmethanes **1a**−**c** with Cu(II) Salts

run	ligand (L)	metal source (M)	molar ratio (M/L)	time (h)	atmosphere	yield (%)
1	**1a**	$Cu(ClO_4)_2$	2	22	air	81
2	**1a**	$CuBr_2$	2	22	air	45
3	**1a**	$CuCl_2$	2	22	air	39
4	**1b**	$Cu(ClO_4)_2$	2	16	air	94
5	**1c**	$Cu(ClO_4)_2$	1	2	Ar	82
6	**1c**	$Cu(ClO_4)_2$	2	2	Ar	28
7	**1c**	$Cu(ClO_4)_2$	1	2	air	46
8	**1c**	$Cu(ClO_4)_2$	2	2	air	0[a]

[a] A 77% yield of methoxy-2-pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dibenzoyl-2,2′-dipyrrolylmethane (**3c**).

Results and Discussion

2-Pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dicarbethoxy-2,2′-dipyrrolylmethane (**1a**), 2-pyridyl-3,3′-dimethyl-4,4′-bis(trifluoromethyl)-5,5′-dicarbethoxy-2,2′-dipyrrolylmethane (**1b**), and 2-pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dibenzoyl-2,2′-dipyrrolylmethane (**1c**) were allowed to react with Cu(II) salts under various conditions as summarized in Table 1 to give binuclear Cu(II) complexes **2a**−**c**, respectively. The complex **2a** was obtained irrespective of the counteranion of the Cu(II) source. The IR spectrum of **2a** showed intense CO stretching vibrations at 1632 and 1588 cm^{-1}. These bands are shifted by 60 and 58 cm^{-1} to lower frequency regions than the corresponding two ν(CO) bands (1692 and 1646 cm^{-1}) of the free ligand **1a**. This fact is indicative of the conjugation of the anionic pyrrole nitrogens to the carbonyl groups in **2a**. The FABMS spectrum of **2a** showed a molecular ion ($m/z = 1026$ for $(C_{26}H_{31}N_3O_4Cu)_2$) that corresponds to the sum of two doubly deprotonated ligands and two Cu ions. ESR spectra of **2a** in benzene solution at room temperature and in benzene glass at 77 K clearly showed a triplet state ESR signal at $g = 4.45$−4.50. Therefore, two Cu(II) ions are located within a short distance, allowing dipolar spin−spin coupling with each other but not strong electron exchange coupling.[12] Similar dinuclear Cu(II) complexes **2b** and **2c** were obtained from the ligands **1b** and **1c**, respectively, and characterized by CHN analysis, IR, FABMS, and ESR.

As is shown in Table 1, the best yield (82%) of the Cu(II) complex **2c** was obtained by using 1.0 molar equiv of $Cu(ClO_4)_2 \cdot 6H_2O$ under argon atmosphere (run 5). Preparation with excess $Cu(ClO_4)_2 \cdot 6H_2O$ (run 6) or under aerobic conditions (run 7) resulted in a serious decrease in the yield of **2c**. The main product (77% yield) under aerobic conditions using excess $Cu(ClO_4)_2 \cdot 6H_2O$ (run 8) was methoxy-2-pyridyl-3,3′-dimethyl-4,4′-diethyl-5,5′-dibenzoyl-2,2′-dipyrrolylmethane (**3c**). The formation of **3c** is explained in terms of the oxidation of **1c** to a triarylmethyl cation followed by addition of MeOH.[1b] Because a methoxy group at the pivot position may cause serious steric constraints on the pyrroles and pyridine, the ligand **3c** seems to have limited conformational freedom in which the ligating atoms are not converged. In fact, any Cu(II) complex of **3c** was not detected. In contrast, the complexes **2a** and **2b** were formed in high yields even when the corresponding ligands were treated with excess $Cu(ClO_4)_2 \cdot 6H_2O$ under aerobic conditions for a long period (runs 1 and 4). It is of interest that the Cu(II)-mediated ligand oxidation is dependent on the electronic and steric factors of the ligands.

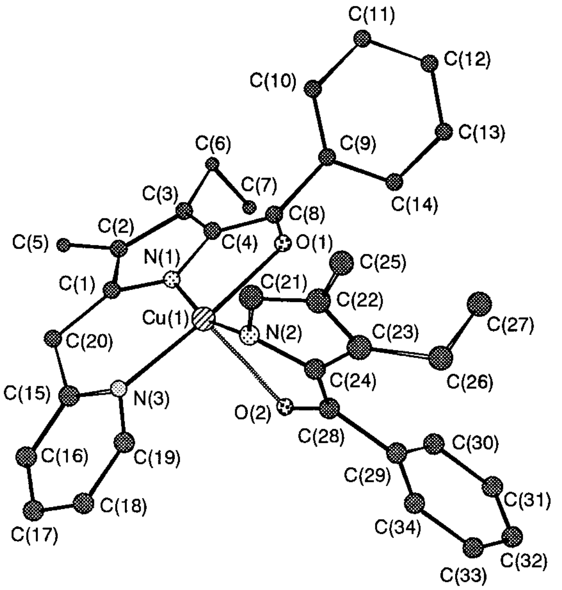
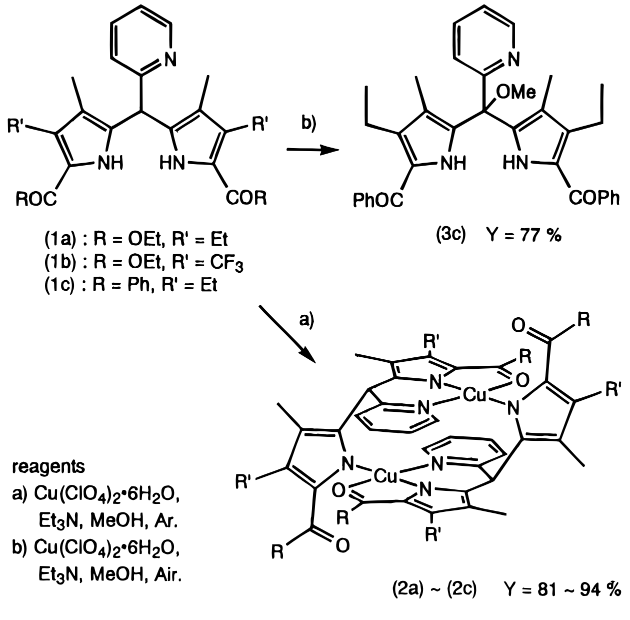


Figure 1. X-ray structure of a half-molecule of **2c**. Atoms (C(35), C(36), O(3), C(37), C(38)) belonging to diethyl ether were omitted. Selected distances (Å) and angles (deg): Cu(1)−N(3) 2.09(1), Cu(1)−N(1) 1.83(1), Cu(1)−N(2) 1.94(1), Cu(1)−O(1) 2.083(9), Cu(1)−O(2) 2.312(8), Cu(1)−Cu(1′) 3.564(4), N(1)−Cu(1)−N(3) 89.6(5), N(2)−Cu(1)−N(3) 103.3(5), O(1)−Cu(1)−N(1) 79.3(5), O(1)−Cu(1)−N(2) 88.0(4), O(1)−Cu(1)−O(2) 87.2(3), O(2)−Cu(1)−N(3) 93.9(4), O(2)−Cu(1)−N(1) 107.8(4), O(2)−Cu(1)−N(2) 79.0(4).

Scheme 1



The single-crystal X-ray analysis of **2c** clearly showed the centrosymmetric dinuclear structure with each Cu(II) ion in a distorted square pyramidal geometry as shown in Scheme 1 and Figure 1. The pyridine nitrogen N(3), the pyrrole nitrogen N(1), and the carbonyl oxygen O(1) occupy three coordination sites in a basal plane of Cu(1). As is seen from a side view in Figure 2, the pyridine ring and the pyrrole ring including its carbonyl plane are approximately coplanar with the basal plane of Cu(1), making a sheet. The pyrrole nitrogen N(2) belonging to the second molecule of the ligand **1c** takes the remaining coordination site in the basal plane of Cu(1). This pyrrole ring (the least-squares plane 2 defined by N(2), C(21), C(22), C(23), and C(24)) is almost perpendicular (97.4°) to the basal plane (the least-squares plane 1 defined by N(1), N(2), N(3), and O(1)). Since the pyrrole nitrogen N(2) cannot take an optimized geometry for the coordination to Cu(1) due to its restricted conformational freedom, the bond length (1.94 Å) of Cu(1)−

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(12) Wilcox, D. E.; Solomon, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 2186−2194.

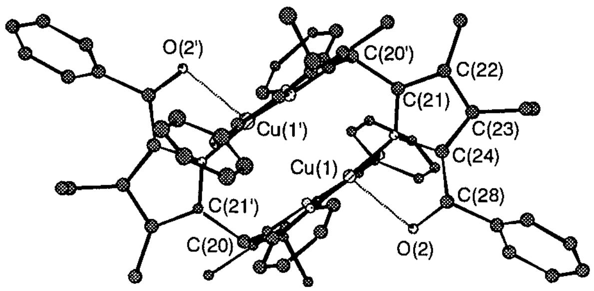

Figure 2. A side view of the whole molecule of **2c**.

N(2) is longer than that (1.83 Å) of Cu(1)−N(1). Moreover, the Cu(1)−N(2) bond tilts with respect to the corresponding pyrrole plane (∠153.1°), whereas the Cu(1)−N(1) bond is almost within the corresponding pyrrole plane (∠175.3°). The carbonyl oxygen O(2) occupies an axial coordination site of Cu(1) with a longer Cu(1)−O(2) bond length (2.312 Å) than the Cu(1)−O(1) bond length (2.083 Å). Two Cu basal planes are arranged in a parallel orientation, making a cavity with an interlayer distance of 2.885 Å (between the two least-squares basal planes). The angle between the basal plane and the Cu(1)−Cu(1′) vector is 56.6°. The Cu(1)−Cu(1′) distance (3.564 Å) is consistent with the observation of a strong triplet state ESR spectrum as shown in Figure 3.[13]

It has recently been shown that a neutral polyimidazole ligand, 1,1-bis(imidazol-2-yl)-4-imidazol-4(5)-yl-2-azabutane (biib), gives dinuclear Cu(II) complexes, $[Cu_2(biib)_2X_2]X_2$, with a coordination structure similar to that of **2c**.[14] An intense half-field ESR transition of **2c** is in remarkable contrast to a very weak signal for $[Cu_2(biib)_2(ClO_4)_2](ClO_4)_2$ in spite of Cu-Cu distances (3.353−3.634 Å) similar to those of **2c**. This points to the unique nature of the anionic ligand in **2c**.

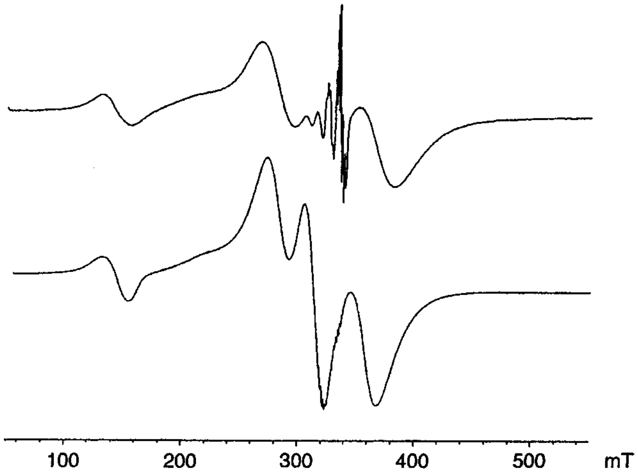

Figure 3. ESR spectra of **2c** in benzene at room temperature (top) and 77 K (bottom). Microwave frequencies are 9.4395 and 9.2250 GHz, respectively. A signal at 322.5 mT ($g = 2.091$; $A_{Cu} = 96$ G; $A_N = 18$ G) at room temperature is due to a mononuclear Cu(II) complex.

In conclusion, the pyrrole-containing tripodal compounds have been shown, for the first time, to serve as polyanionic ligands for metal complexes. The novel structure, unique electronic properties, and unusual stability of **2** are noteworthy, and further studies on metal complexes of related polyanionic ligands are in progress in our laboratory.

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Supporting Information Available: Spectroscopic and analytical data for compounds **1a**−**c**, **2a**−**c**, and **3c** and listings of the details in the structure determination for **2c**, including an ORTEP drawing, crystallographic data, atomic coordinates and *B*(eq), thermal parameters, bond lengths, bond angles, and least-squares planes (15 pages). Ordering information is given on any current masthead page.

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(13) ESR (in benzene glass at 77 K) $g = 4.57$, $g_\perp = 2.07$, $D = 0.072$ cm^{-1}. The ESR spectrum of **2c** shows an additional signal due to a monomeric complex with hfss with one Cu and two nitrogens in benzene solution at room temperature ($g = 2.091$; $A_{Cu} = 96$ G; $A_N = 18$ G).

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