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Synthesis and Electrochemical Properties of Transition Metal Complexes of 2,2′:6′,2″-Terpyridine 1,1″-Dioxide

Kaname Ito, Toshi Nagata,* and Koji Tanaka

Institute for Molecular Science, CREST − Japan Science and Technology Corporation (JST), and Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan

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Introduction

In recent years, metal complexes of 2,2′:6′,2″-terpyridine (terpy) and their derivatives have been gaining considerable attention as electrochemical catalysts. The reactions catalyzed by metal terpyridine complexes include oxidation of organic substrates, such as alcohols,[1] reduction of CO_2,[2] H^+,[3] NO,[4] NO_2^{-5}, and NAD^+,[6] and cleavage of DNA.[7] Derivatives of terpyridine are particularly suitable for electrocatalytic applications because they are chemically robust and form stable complexes with a wide variety of transition metals. On the other hand, the syntheses of terpyridine derivatives are often so troublesome that it is difficult to tune the electrochemical behavior of the metal complexes.

The *N*-oxides of pyridines are promising ligands that are easily derived from pyridine compounds by one-step peracid oxidation.[8] Metal complexes of pyridine *N*-oxide and 2,2′-bipyridine 1,1″-dioxide are numerous, whereas the *N*-oxides of terpyridine have been much less studied. Only a few reports have been published on the metal complexes of 2,2′:6′,2″-terpyridine 1,1′,1″-trioxide ($terpyO_3$).[9]

Chart 1. The Ligand $TerpyO_2$

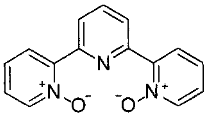

Table 1. Compound Data of the Metal Complexes of $TerpyO_2$

compound	Anal. (calcd) C	H	N	ESI−MS[a] *m/z* (rel int.)	UV−vis[b] λ_{max}/nm (ϵ)
$[Mn(terpyO_2)_2](ClO_4)_2$	45.70 (45.94)	2.95 (2.83)	10.84 (10.71)	292.5 (100)	428 (850)
$[Fe(terpyO_2)_2](ClO_4)_2$	45.82 (45.89)	2.92 (2.82)	10.71 (10.70)	293.0 (100) 201.4 (23)	450 (1100) 600 sh, br (400)
$[Co(terpyO_2)_2](BF_4)_2$	46.98 (47.22)	2.92 (2.81)	11.01 (11.01)	294.5 (100) 202.9 (10)	430 sh (860)
$[Ni(terpyO_2)_2](ClO_4)_2$	45.58 (45.72)	2.86 (2.81)	10.66 (10.66)	294.0 (100)	451 (600)
$[Cu(terpyO_2)(H_2O)](ClO_4)_2$	32.76 (33.01)	2.51 (2.40)	7.63 (7.70)	184.4 (39) 205.0 (100) 296.5 (10) 426.9 (12)	370 sh (2200) 640 br (60)

[a] In CH_3CN solutions, ca. 10 μM. [b] In CH_3CN solutions, ca. 500 μM; sh = shoulder, br = broad. The strong ligand $\pi-\pi$ bands at <360 nm are omitted.

In this short article, we wish to report the synthesis and characterization of metal complexes of 2,2′:6′,2″-terpyridine 1,1″-dioxide ($terpyO_2$). The preparation of $terpyO_2$ was first reported in 1985,[10] but no reports on metal complexes of $terpyO_2$ have been published. Actually, $terpyO_2$ is even more promising than the trioxide $terpyO_3$, because $terpyO_2$ is expected to act as a terdentate ligand with two six-membered chelate rings, which are more stable than the seven-membered rings required in $terpyO_3$ complexes.

Experimental Section

Synthesis of Metal Complexes. (***CAUTION***: Perchlorate salts are potentially explosive. All compounds containing perchlorate should be handled with great care and in small amounts.) A typical procedure is as follows: $terpyO_2$[10] (50 μmol) and a metal salt hydrate (50 μmol for Cu(II) complex; 25 μmol for others) were mixed in appropriate solvents (1 mL) and briefly heated to give a clear solution, which was passed through a membrane filter (Advantec DISMIC-13, PTFE 0.20 μm). The crystalline products were isolated by slow evaporation or vapor diffusion. The starting metal salt, solvents, and yields are listed below for each complex. Other compound data are compiled in Table 1.

$[Mn(terpyO_2)_2](ClO_4)_2$. Red−brown needles (75%), from $Mn(ClO_4)_2\cdot 6H_2O$ (25 μmol) and CH_3CN/*i*-Pr_2O (vapor diffusion).

$[Fe(terpyO_2)_2](ClO_4)_2$. Dark-brown plates (52%), from $Fe(ClO_4)_2\cdot 6H_2O$ (25 μmol) and CH_3OH/H_2O (slow evaporation).

$[Co(terpyO_2)_2](BF_4)_2$. Red−orange microcrystals (75%), from $Co(BF_4)_2\cdot 6H_2O$ (25 μmol) and CH_3CN/*i*-Pr_2O (vapor diffusion).

$[Ni(terpyO_2)_2](ClO_4)_2$. Orange prisms (53%), from $Ni(ClO_4)_2\cdot 6H_2O$ (25 μmol) and CH_3CN/H_2O (slow evaporation).

$[Cu(terpyO_2)(H_2O)](ClO_4)$. Dark green plates (59%), from $Cu(ClO_4)_2\cdot 6H_2O$ (50 μmol) and CH_3OH/H_2O (slow evaporation).

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* To whom correspondence should be addressed.

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Table 2. The Selected Crystallographic Parameters

	$[Cu(terpyO_2)(H_2O)](ClO_4)_2$	$[Ni(terpyO_2)_2](ClO_4)_2$	$[Fe(terpyO_2)_2](ClO_4)_2$
empirical formula	$C_{15}H_{13}N_3O_{11}Cl_2Cu$	$C_{30}H_{22}N_6O_{12}Cl_2Ni$	$C_30H_{22}N_6O_{12}Cl_2Fe$
fw	545.73	788.14	785.29
cryst syst	monoclinic	monoclinic	monoclinic
cell param	$a = 10.431(2)$ Å $b = 16.430(2)$ Å $c = 11.755(2)$ Å $\beta = 107.45(2)°$ $V = 1921.8(6)$ Å^3	$a = 15.304(2)$ Å $b = 10.065(2)$ Å $c = 19.783(2)$ Å $\beta = 97.27(1)°$ $V = 3022.9(8)$ Å^3	$a = 15.320(2)$ Å $b = 9.9900(5)$ Å $c = 19.6900(4)$ Å $\beta = 96.4000(5)°$ $V = 2994.7(3)$ Å^3
space group	$P2_1$/c (No. 14)	$P2_1$/n (No. 14)	$P2_1$/n (No. 14)
Z value	4	4	4
D_{calc} (g cm^{-3})	1.886	1.732	1.742
R; R_w	0.049; 0.065	0.058; 0.105	0.050; 0.076

X-ray Structure Determination. $[Ni(terpyO_2)_2](ClO_4)_2$ and $[Cu(terpyO_2)(H_2O)](ClO_4)_2$. Cell constants and intensity data were collected at 293 K on a Rigaku AFC5S diffractometer equipped with a Mo sealed tube (λ (Mo Kα) = 0.71069 Å) operating at 50 kV 25 mA and a graphite monochromator. The data were corrected for Lorentz polarization effects. Empirical absorption correction based on a ψ scan was applied. Three standard reflections monitored every 150 reflections showed no decay in intensity. The structures were solved by heavy-atom Patterson[11] methods and refined on F by full-matrix least-squares techniques; all calculations were performed by the TEXSAN[12] crystallography software package. The neutral atomic scattering facters and mass attenuation coefficients were taken from references.[13] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at the calculated positions. Selected crystallographic parameters are listed in Table 2; other parameters are available as Supporting Information (Table A).

$[Fe(terpyO_2)_2](ClO_4)_2$. Cell constants and intensity data were collected at 193 K on a Rigaku Mercury diffractometer equipped with a Mo sealed tube operating at 50 kV 25 mA, a graphite monochromator, and a CCD detector. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from −75.0 to 105.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. A second sweep was performed using ω scans from −75.0 to 105.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. The exposure rate was 40.0 s/°, and the detector swing angle was 15.25°. The data were corrected for Lorentz polarization effects. The structure was solved as above, except that the initial phase was obtained by direct methods[14] and the calculations were performed by the CrystalStructure[15] software package. Selected crystallographic parameters are listed in Table 2; other parameters are available as Supporting Information (Table A).

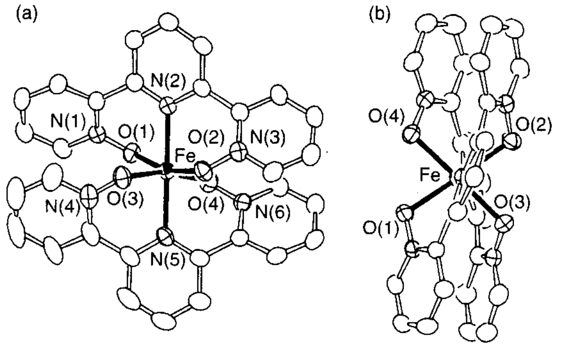

Figure 1. (a) ORTEP view (50% probability ellipsoids) of the complex cation $[Fe(terpyO_2)_2]^{2+}$. Selected bond lengths (Å): Fe−O(1), 2.059(2); Fe−O(2), 2.073(2); Fe−O(3), 2.061(2); Fe−O(4), 2.070(2); Fe−N(2), 2.155(3); Fe−N(5), 2.158(3). Selected bond angles (°): O(1)−Fe−N(2), 81.23(10); O(1)−Fe−O(3), 101.57(10); O(1)−Fe−O(4), 81.27(10); O(2)−Fe−N(2), 82.13(10); O(2)−Fe−O(3), 79.67(10); O(2)−Fe−O(4), 102.22(10); O(3)−Fe−N(5), 82.39(11); O(4)−Fe−N(5), 81.63(10). (b) Viewed from the N(2)−N(5) axis.

Results and Discussion

The complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) were prepared by mixing terpyO$_2$ and metal salt hydrate (1.0 equiv for Cu(II); 0.5 equiv for others) in appropriate solvents. Elemental analyses were consistent with the formula, as shown in Table 1. Interestingly, the bis complex of Cu(II) was not isolated even when an excess amount of terpyO$_2$ was used.

The ESI−MS spectra of the four bis-type complexes in CH_3CN showed the strongest peaks corresponding to $[M(terpyO_2)_2]^{2+}$ (M = Mn, Fe, Co, Ni). In addition to these peaks, the Fe(II) and Co(II) complexes also showed peaks assigned to the solvated mono complex, $[M(terpyO_2)(CH_3CN)_2]^{2+}$. On the other hand, the Cu(II) complex showed two peaks that correspond to the solvated mono complexes, $[Cu(terpyO_2)(CH_3CN)]^{2+}$ and $[Cu(terpyO_2)(CH_3CN)_2]^{2+}$, respectively, as well as a small peak assigned to the bis complex, $[Cu(terpyO_2)_2]^{2+}$. In all cases, the relative intensity of these peaks did not change after 4 h at room temperature. These results demonstrate that in dilute solutions the Fe(II), Co(II), and Cu(II) complexes are in equilibrium between the bis complexes and the solvated mono complexes, whereas the Mn(II) and Ni(II) complexes exist predominantly as the bis complexes.

The solid-state structure of the three complexes $[Ni(terpyO_2)_2](ClO_4)_2$, $[Fe(terpyO_2)_2](ClO_4)_2$, and $[Cu(terpyO_2)(H_2O)](ClO_4)_2$ were examined by X-ray crystallography. The ORTEP drawing of the complex cation $[Fe(terpyO_2)_2]^{2+}$ is shown in Figure 1. The Fe(II) ion is six coordinate in a distorted octahedral environment; the minimum and maximum cis bond angles are 79.7(1)° and 107.2(1)°, respectively. The three donor atoms of each terpyO$_2$ ligand are located in a meridional arrangement. Unlike the bis(terpyridine) complexes,[16] the ligands have nonplanar conformations with an approximate C_2 symmetry. The absence of mirror planes makes the overall symmetry of the complex cation approximately D_2, which is lower than the D_{2d} symmetry of typical bis(terpyridine) complexes.[16] $[Ni(terpyO_2)_2]$-

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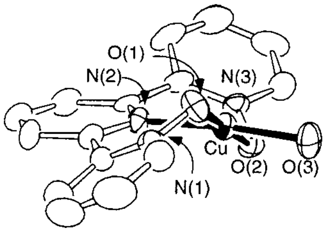

Figure 2. ORTEP view (50% probability ellipsoids) of the complex cation $[Cu(terpyO_2)(H_2O)]^{2+}$. Selected bond lengths (Å): Cu−O(1), 1.916(6); Cu−O(2), 1.945(6); Cu−O(3), 1.988(7); Cu−N(2), 1.987(7). Selected bond angles (°): O(1)−Cu−N(2), 88.4(3); O(1)−Cu−O(3), 91.0(3); O(2)−Cu−N(2), 89.1(3); O(2)−Cu−O(3), 91.5(3).

$(ClO_4)_2$ is isomorphous with the Fe(II) complex, and the overall conformation of the complex cation is similar, except that the metal−ligand bonds are shorter and the distortion of the coordination octahedron is smaller.

The ORTEP drawing of the complex cation $[Cu(terpyO_2)(H_2O)]^{2+}$ is shown in Figure 2. The Cu(II) ion is square planar with the terdentate terpyO$_2$ and one aqua ligand. The terpyO$_2$ ligand has a similar conformation to that of $[Ni(terpyO_2)_2]^{2+}$, and the overall symmetry of the complex cation is approximately C_2.

The electrochemical properties of the new complexes were examined by cyclic voltammetry (Table 3). The four bis complexes showed reversible waves corresponding to the M(III)/M(II) redox couple. Compared with the terpyridine complexes, the M(III)/M(II) redox potentials of the Mn(II), Fe(II), and Ni(II) complexes showed negative shifts (−0.77 to −0.24 V), whereas the potential of the Co(II) complex showed a slightly positive shift (+0.03 V). The reason for this difference is not clear at present. The Fe(II) complex is particularly interesting, because the low $E_{1/2}$ value and the ease of ligand exchange (see the ESI−MS results above) make the complex promising for application as a redox catalyst. Also worth noting is the Mn(II) complex, for which another reversible wave corresponding to the Mn(IV)/Mn(III) couple was observed. A similar behavior was reported for the trioxide complex, $[Mn(terpyO_3)_2]^{2+}$.[9b] Since the terpyridine complexes of manganese are gaining interest as functional mimics of oxygen evolving centers in plant photosynthesis,[17] which inherently require high oxidation states of manganese ions, we expect that the terpyO$_2$ complexes of manganese may offer interesting possibilities in this field. The Cu(II) complexes showed complicated irreversible voltammograms, therefore, only the peak potentials of the first reduction waves are reported.

Table 3. The Electrochemical Data of TerpyO$_2$ and Terpy Complexes

metal	$E_{1/2}$[a,b] terpyO$_2$ complexes	$E_{1/2}$[a,b] terpy complexes[c]	$\Delta E_{1/2}$[d]
Mn(II)	0.37 1.11[e]	0.86	−0.49
Fe(II)	−0.06	0.71	−0.77
Co(II)	−0.09	−0.12	+0.03
Ni(II)	1.02	1.26	−0.24
Cu(II)	−0.19[f]	−0.21[f]	+0.02[f]

[a] In CH_3CN + 0.1 mol dm^{-3} Bu_4NClO_4 solutions, ca. 100 μM, glassy carbon electrodes. [b] The half-wave potentials of the M(III)/M(II) couple (except for Cu(II)) relative to ferrocene/ferrocenium couple. [c] $[M(terpy)_2](ClO_4)_2$ (M = Mn, Fe, Ni), $[Co(terpy)_2](BF_4)_2$, and $[Cu(terpy)(H_2O)](ClO_4)_2$ were used. [d] $\Delta E_{1/2} = E_{1/2}(terpyO_2) - E_{1/2}(terpy)$. [e] The Mn(IV)/Mn(III) couple. [f] The peak potentials of the first reduction waves for Cu(II)/Cu(I).

In summary, five new complexes of first-row transition metals with terpyO$_2$ were characterized and their redox properties examined. Study on the application of these complexes for redox catalysis is currently under way.

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Supporting Information Available: Crystallographic parameters (1 page, PDF) and three tables of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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