2430 *Inorg. Chem.* **2001,** *40,* 2430−2433

# Coordination Polymers from M(hfac)$_2$ [M = Cu$^{II}$, Mn$^{II}$] and 4,4′-Dipyridyldisulfide

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*Received October 25, 2000*

## Introduction

The syntheses and characterization of supramolecular coordination compounds is a subject of current investigation.[1] Among them, the structure, electronic properties, and inclusion phenomena of the self-assembled coordination polymers have attracted special interest.[2] These compounds have been constructed mainly by combining metals with bidentate ligands of pyridine derivatives[3−5] bridged by −N═N−,[6] −CH═CH−,[7] −C≡C−,[8] −C≡C−C≡C−, or alkyl groups.[9] Although coordination polymers from rigid and planar ligands have been well documented, those with twisted ones are rather few.[10] Employing nonrigid ligands may lead to the construction of topologically interesting molecular assemblies, exhibiting unique inclusion phenomena. In this respect, we focus on 4-PDS (=4,4′-dipyridyldisulfide; Chart 1) as a ligand, which may assume a twisted conformation because of the flexible −S−S−bridging group. The C−S−S−C torsion angles in aromatic disulfides are known to be generally within about 20° of 90°.[11] Another interesting aspect of this ligand is that the bridging S atom also has coordinating ability.[12] Though various complexes are known for the isomer 2-PDS (=2,2′-dipyridyldisulfide),[11] no metal complexes seem to be reported for 4-PDS. The 2-PDS complexes are chelate compounds with seven-membered rings,[13] while the present ligand, being unable to form chelate coordination, may afford unique coordination polymers. Here we describe the complexation of 4-PDS with M(hfac)$_2$ (M = Cu, Mn), affording simple N-coordinated 1:1 polymer complexes 4-PDS·Cu(hfac)$_2$ (**1**) and 4-PDS·Mn(hfac)$_2$ (**2**).

**Chart 1.** 4,4′-Dipyridyldisulfide (4-PDS)

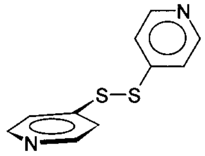

**Table 1.** Crystallographic Data for **1** and **2**

| | 4PDS·Cu(hfac)$_2$ (**1**) | 4PDS·Mn(hfac)$_2$ (**2**) |
|---|---|---|
| chemical formula | $C_{20}F_{12}H_{10}N_2O_4S_2Cu$ | $C_{20}F_{12}H_{10}N_2O_4S_2Mn$ |
| $a$/Å | 7.934(6) | 6.456(7) |
| $b$/Å | 16.029(6) | 20.235(4) |
| $c$/Å | 20.394(5) | 20.242(3) |
| $\beta$/deg | 91.27(4) | 92.62(3) |
| $V$/Å$^3$ | 2593(2) | 2641(3) |
| $Z$ | 4 | 4 |
| fw | 697.96 | 689.35 |
| space group | $P2_1/c$ (No.14) | $P2_1/c$ (No.14) |
| $T$/°C | 23 | 23 |
| $\lambda$/Å | 0.710 69 | 0.710 69 |
| $\rho_{calcd}$/g cm$^{-3}$ | 1.788 | 1.490 |
| $\mu$/cm$^{-1}$ | 11.21 | 7.69 |
| $R_1$ $^a$ | 0.051 | 0.046 |
| $R_w$ $^a$ | 0.150 | 0.138 |

$^a$ $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

## Experimental Section

**General Methods.** All chemicals and solvents used for the syntheses were commercially available. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets in the 4000−400 cm$^{-1}$ range. Elemental analyses were performed by using a Yanagimoto C−H−N recorder (MT-3). DSC analyses were performed under nitrogen at a heating rate 10 °C/min on a MAC Science DSC 3100, in the temperature range 20−300 °C.

**X-ray Structure Analyses.** All the X-ray data were collected using Mo Kα radiation on a Rigaku AFC-7R four-circle diffractometer. Crystal data, data collection parameters, and analysis statistics for **1** and **2** are listed in Table 1. Selected interatomic distances and angles are given in Tables 2 and 3. All calculations were performed using the teXsan crystallographic software package.[14] The structures were solved by direct methods (SIR92)[15] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Absorption correction was applied ($\psi$ scan). Though some of the hydrogen was shown by means of direct methods, all hydrogen atoms were inserted at the calculated positions and refined isotropically using a rigid model.

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**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations in Parentheses for **1**

| | | | |
|---|---|---|---|
| Cu−O(1) | 2.343(3) | Cu−O(2) | 1.995(3) |
| Cu−O(3) | 1.975(3) | Cu−O(4) | 2.252(3) |
| Cu−N(1) | 2.023(4) | Cu−N(2) | 2.026(2) |
| | | S(1)−S(2) | 2.029(2) |
| O(1)−Cu−O(2) | 83.2(1) | O(1)−Cu−O(3) | 92.9(1) |
| O(1)−Cu−O(4) | 168.9(1) | O(2)−Cu−O(3) | 87.9(1) |
| O(2)−Cu−O(4) | 85.8(1) | O(3)−Cu−O(4) | 88.2(1) |
| N(1)−Cu−N(2) | 92.5(1) | O(1)−Cu−N(1) | 97.9(1) |
| O(2)−Cu−N(1) | 176.9(1) | O(3)−Cu−N(1) | 89.2(1) |
| O(4)−Cu−N(1) | 93.1(1) | O(1)−Cu−N(2) | 88.3(1) |
| O(2)−Cu−N(2) | 90.3(1) | O(3)−Cu−N(2) | 177.7(1) |
| O(4)−Cu−N(2) | 90.2(1) | | |

**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations in Parentheses for **2**

| | | | |
|---|---|---|---|
| Mn−O(1) | 2.153(7) | Mn−O(2) | 2.133(1) |
| Mn−O(3) | 2.134(7) | Mn−O(4) | 2.135(9) |
| Mn−N(1) | 2.283(10) | Mn−N(2) | 2.294(9) |
| | | Mn−N(2) | 2.029(2) |
| O(1)−Mn−O(2) | 84.4(5) | O(1)−Mn−O(3) | 178.9(1) |
| O(1)−Mn−O(4) | 96.4(4) | O(2)−Mn−O(3) | 94.8(5) |
| O(2)−Mn−O(4) | 178.57(9) | O(3)−Mn−O(4) | 84.3(5) |
| N(1)−Mn−N(2) | 177.6(1) | O(1)−Mn−N(1) | 91.8(1) |
| O(2)−Mn−N(1) | 88.1(5) | O(3)−Mn−N(1) | 89.0(4) |
| O(4)−Mn−N(1) | 93.0(5) | O(1)−Mn−N(2) | 85.9(4) |
| O(2)−Mn−N(2) | 91.3(5) | O(3)−Mn−N(2) | 93.3(4) |
| O(4)−Mn−N(2) | 87.6(5) | | |

**Preparation of 4-PDS·Cu(hfac)$_2$ (1).** A solution of Cu(hfac)$_2$·H$_2$O (50 mg; 0.10 mmol) in 4 mL of methanol was slowly layered on a solution of 4-PDS (22 mg; 0.10 mmol) in 4 mL of methanol. The solution was allowed to stand at room temperature for a day. Emerald-green crystals were obtained in a yield of 73%. IR (KBr, cm$^{-1}$): 3097.6(w), 1650.3(s), 1596.8(s), 1549.5(s), 1524.5(s), 1496.0(s), 1422.7(s), 1255.0(s), 1190.8(s), 1137.3(s), 793.6(s), 715.9(s), 668.7(s), 583.4(s). Anal. Calcd for $C_{20}F_{12}H_{10}N_2O_4S_2Cu$: C, 34.41; H, 1.44; N, 4.01. Found: C, 34.66; H, 1.57; N, 4.45. DSC traces for **1** do not show any peak until the onset of melting at 192.5 °C, followed by decomposition.

**Preparation of 4-PDS·Mn(hfac)$_2$ (2).** A solution of Mn(hfac)$_2$·$n$H$_2$O (49 mg; 0.10 mmol) in 4 mL of methanol was slowly added to a solution of 4-PDS (22 mg; 0.10 mmol) in 4 mL of methanol. The solution was allowed to stand at room temperature for a few weeks. Light-orange crystals were formed as the solvent slowly evaporated. The product was obtained in a yield of 83%. IR (KBr, cm$^{-1}$): 3139.5(w), 1645.5(s), 1588.1(s), 1549.5(s), 1532.2(s), 1489.7(s), 1413.1(s), 1258.8(s), 1201.9(s), 1139.2(s), 801.0(s), 710.6(s), 663.9(s), 584.8(s). Anal. Calcd for $C_{20}F_{12}H_{10}N_2O_4S_2Mn$: C, 34.84; H, 1.46; N, 4.06. Found: C, 34.82; H, 1.48; N, 4.21. DSC traces for **2** do not show any peak until the onset of melting at 249.2 °C, followed by decomposition.

## Results and Discussion

**A. Molecular and Crystal Structure of 4PDS·Cu(hfac)$_2$ (1).** An ORTEP view of a copper center of compound **1** is shown in Figure 1, together with the atom numbering scheme. Selected bond distances and angles are listed in Table 2. The coordination geometry of the copper(II) ion is pseudooctahedral in which the two hfac ligands occupy the cis positions and the N-donor site of the 4-PDS ligand is coordinated to the rest. This is somewhat unusual because a trans geometry is usually found in L$_2$Cu(hfac)$_2$ type complexes, the only exception is a pyridine-coordinated one. The elongation of the Cu−O(1) and Cu−O(4) bonds relative to Cu−O(2) and Cu−O(3) ones may be ascribable to the Jahn−Teller effect; the lobes of the $d_{x^2-y^2}$ orbital are directed toward O(2), O(3), N(1), and N(2), while the $d_{z^2}$ orbital is directed along the O(1)−Cu−O(4) axis. Similar types of distorted coordination geometries are reported for phen·Cu(hfac)$_2$[16] and DMeDPQ·Cu(hfac)$_2$.[17] Consistent with the above structure, the IR spectrum of **1** shows two carbonyl stretching bands[18] at 1650 and 1669 cm$^{-1}$. We assign the former band to the stretching of $C_{(14)}{=}O_{(2)}$ and $C_{(17)}{=}O_{(3)}$, which are more strongly bonded to the Cu(II) ion, and the latter one to that of $C_{(12)}{=}O_{(1)}$ and $C_{(19)}{=}O_{(4)}$. The intramolecular geometry of the 4-PDS ligand shows the C−S−S−C torsion angle of 88.1(2)° and the S−S bond distance of 2.029(2) Å. These values are comparable to those in other typical aromatic disulfides found in the literature, for instance, 87.1° and 2.016(2) Å in 2,2′-dipyridyldisulfide and 90.5° and 2.060(3) Å in 2,2′-diaminodiphenyldisulfide.[11] Thus, the disulfide moiety seems to maintain its characteristic shape even when coordinated to metal ions.

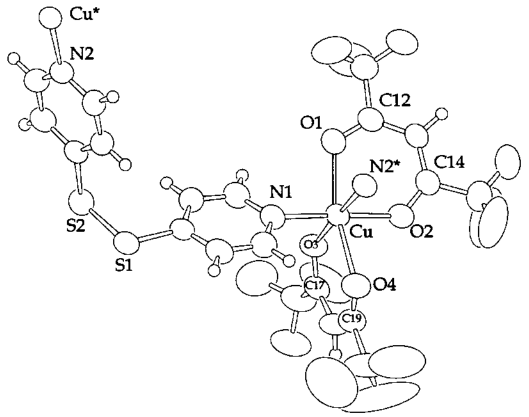

**Figure 1.** ORTEP drawing of **1** with the atom numbering scheme, showing the copper coordination environment. Displacement ellipsoids are shown at the 50% probability level.

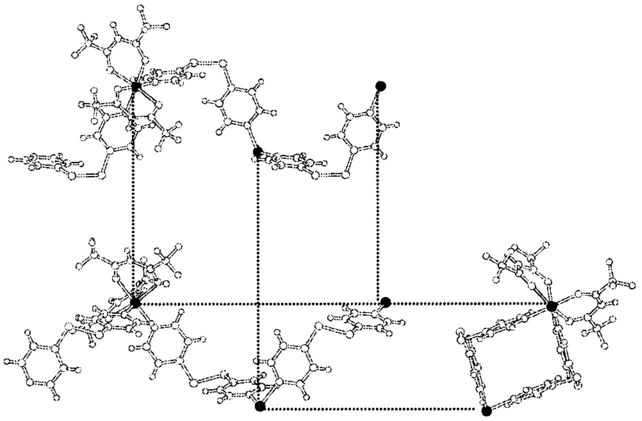

**Figure 2.** One-dimensional helical chain in **1** viewed along the three directions [100] (top), [001] (bottom), and [010] (right). Cu atoms are shaded. Only two hfac ligands are shown for clarity.

Compound **1** assumes a one-dimensional helical chain structure, as shown in Figure 2, which consists of copper(II) ions linked by the twisted ligands of 4-PDS. Thus, the twisted conformation of the ligand may be essential in realizing the helical structure. The helical chain runs along the *b* axis, involving a crystallographic 2-fold screw axis. Such a helical structure is unique because coordination polymers from Cu(II) with N-donor ligands usually form zigzag or linear chain

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**Table 4.** Metal−Oxygen Distances (Å) in Several N-Donor Coordinated M(hfac)$_2$ Complexes [M = Cu, Mn]

| | compound | type of polymer | M−O(1) | M−O(2) | M−O(3) | M−O(4) |
|---|---|---|---|---|---|---|
| | cis configuration | | | | | |
| **1** | 4PDS·Cu(hfac)$_2$[a] | helix | 2.343(3) | 1.995(3) | 1.975(3) | 2.252(3) |
| **3** | (py)$_2$·Cu(hfac)$_2$[b] | (monomer) | 2.266(6) | 2.002(6) | 1.994(5) | 2.300(6) |
| **4** | phen·Cu(pta)$_2$[c] | (monomer) | 2.246(3) | 1.970(3) | 1.970(3) | 2.246(3) |
| **5** | 4,4′-bipy·Mn(hfac)$_2$[d] | zigzag | 2.134(4) | 2.186(4) | 2.186(4) | 2.134(4) |
| **6** | bpe·Mn(hfac)$_2$[e] | zigzag | 2.138(2) | 2.207(2) | 2.207(2) | 2.138(2) |
| **7** | pyim·Mn(hfac)$_2$[e] | screw | 2.166(6) | 2.185(6) | 2.196(7) | 2.159(7) |
| | trans configuration | | | | | |
| **8** | bpp·Cu(hfac)$_2$[f] | zigzag | 2.203(4) | 2.038(6) | 2.166(6) | 2.105(6) |
| **9** | bpe·Cu(hfac)$_2$[f] | linear | 2.129(8) | 2.114(7) | 2.129(8) | 2.114(7) |
| **2** | 4PDS·Mn(hfac)$_2$[a] | zigzag | 2.153(7) | 2.133(10) | 2.134(7) | 2.135(9) |
| **10** | (Him)$_2$·Mn(hfac)$_2$[e] | linear | 2.169(3) | 2.121(3) | 2.169(3) | 2.121(3) |
| **11** | (4NOPy)$_2$·Mn(hfac)$_2$[g] | (monomer) | 2.171(2) | 2.143(3) | 2.171(2) | 2.143(3) |

[a] This work. [b] Reference 19 (py = pyridine). [c] Reference 20 (phen = 1,10- phenanthroline; pta = pivaloyltrifluoroacetone). [d] Reference 22 (4,4′-bipy = 4,4′-bipyridine). [e] Reference 9 (bpe = 1,2-bis(4-pyridyl)ethane; pyim = *N*-(4-pyridylmethyl)imidazole; Him = imidazole). [f] Reference 18 (bpp = 1,3-bis(4-pyridyl)propane). [g] Reference 21 (4NOPy = 4-(*N*-*tert*-butyl-*N*-oxyamino)pyridine).

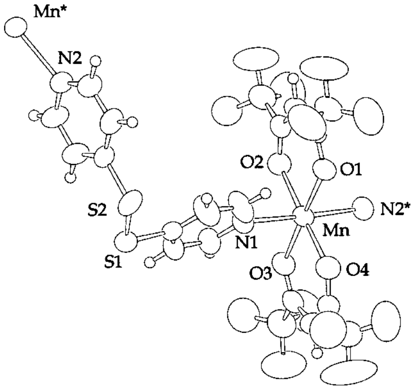


**Figure 3.** ORTEP drawing of **2** with the atom numbering scheme, showing the manganese coordination environment. Displacement ellipsoids are shown at the 50% probability level.

structures,[19] although a somewhat similar structure is found in pyim·Mn(hfac)$_2$.[10] The interchain and intrachain Cu−Cu distances are 10.21 and 11.26 Å, respectively.

**B. Molecular and Crystal Structure of 4PDS·Mn(hfac)$_2$ (2).** The ORTEP drawing of compound **2** with the atom numbering scheme is shown in Figure 3. Selected bond distances and bond angles are shown in Table 3. The manganese(II) ion resides in the center of a pseudooctahedral geometry, which is composed of square-planar Mn(hfac)$_2$ units with the N-donor ligands occupying the trans positions. In the IR spectrum of compound **2**, the carbonyl stretching band at 1650 cm$^{-1}$ shows no splitting.

The polymer structure of **2** is shown in Figure 4. Compound **2** shows a zigzag chain structure consisting of manganese(II) ions and the 4-PDS ligands. The chain runs along the [101] direction. As for the intramolecular geometry of 4-PDS, the C−S−S−C torsion angle is 91.9(6)° and the S−S bond distance is 2.031(5) Å. In this compound, the intrachain Mn−Mn distance (10.26 Å) is shorter than the interchain one (10.64 Å), in contrast to **1**.

**C. Coordination Geometries in N-Donor Coordinated M(hfac)$_2$ Compounds.** The metal−oxygen bond distances in several N-donor coordinated M(hfac)$_2$ [M = Cu, Mn] complexes, including the present compounds, are listed in Table 4. The numbering is shown in Chart 2. The complexes (py)$_2$·Cu(hfac)$_2$[20] (**3**), (phen)$_2$·Cu(pta)$_2$[21] (**4**), and (4NOPy)$_2$·Mn(hfac)$_2$[22] (**11**) are molecular complexes, while the others are coordination polymers; the type of polymer seems to be independent of the coordination scheme.

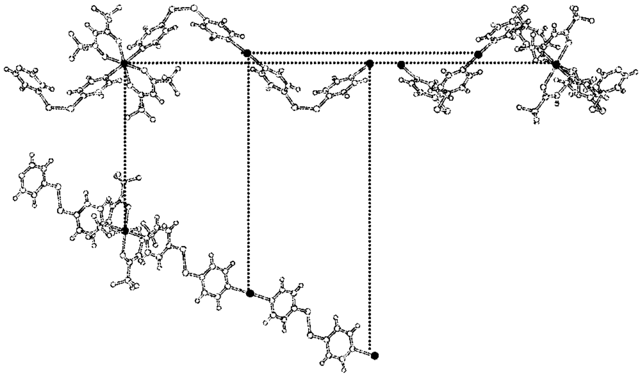
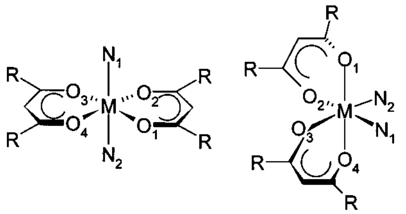


**Figure 4.** One-dimensional zigzag chain in **2** viewed along the three directions [100] (top), [010] (bottom), and [001] (right). Mn atoms are shaded. Only two hfac ligands are shown for clarity.

**Chart 2.** Numbering Scheme of N-Donor Coordinated M(hfac)$_2$ Complexes



The coordination geometry of the present compound **1** is similar to those of **3** and **4**. In these cis coordinated Cu(II) complexes, M−O(2) and M−O(3) are shorter than M−O(1) and M−O(4) because of the Jahn−Teller effect of the Cu(II) ions. This is in contrast to the cis coordinated Mn(II) complexes such as 4,4′-bipy·Mn(hfac)$_2$[23] (**5**), bpe·Mn(hfac)$_2$[10] (**6**), and pyim·Mn(hfac)$_2$[10](**7**), in which the metal−oxygen distances opposite the N-donor sites (M−O(2) and M−O(3)) are slightly longer than the others (M−O(1) and M−O(4)) because of the trans effect of the pyridine nitrogen. Further, we note that in trans coordinated complexes (**8**−**11**),[10,19,22] a bond alternation

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in M−O distances is observed (M−O(1) > M−O(2), M−O(2) < M−O(3), M−O(3) > M−O(4)) both for Cu(II) and for Mn(II) complexes. However, such a tendency is not observed for the present compound **2**.

The coordination scheme and structures in **1** and bpe·Cu(hfac)$_2$[19] (**9**) are markedly different despite the similarity in ligand structure. The bpe (=1,2-bis(4-pyridyl)ethane) ligand, bearing the $-CH_2-CH_2-$ bridging group, is more flexible than 4-PDS. The ligand conformation is affected by intermolecular interactions; the torsional angle of the bridging group in **9** is ca. 180°, and also a twisted ligand structure similar to that of 4-PDS is found in $Cd(NO_3)_2(bpe)_{1.5}$.[24] In contrast, the 4-PDS ligand in **1** and **2** maintains its characteristic conformation as shown above despite the difference in coordination scheme. Thus, the present ligand may be concluded to be rather rigid. Comparison of the structures of **1** and **2** demonstrates that the coordination environment around the metal ion plays an important role in determining the expanded structure. Complexation studies of 4-PDS with simple transition metal salts are underway in these laboratories.

**Acknowledgment.** We thank Prof. T. Sugawara and Dr. H. Terao (The University of Tokyo) for their help in X-ray structure analyses. We also thank Prof. M. Hasegawa and Mr. S. Ebisawa (Toho University) for DSC measurements, and Ms. Y. Sato (School of Pharmaceutical Sciences, Toho University) for elemental analyses.

**Supporting Information Available:** Tables of detailed crystallographic data, atomic positional parameters, anisotropic displacement parameters, and bond lengths and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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