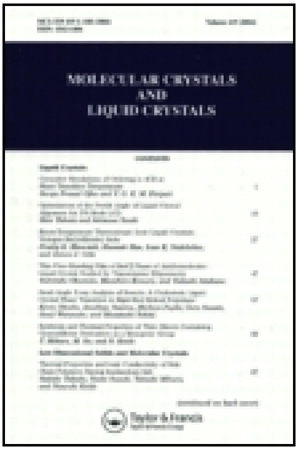


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Silver(I) Coordination Complexes of 1,10-Phenanthroline-5,6-dione with 1D Chain and 2D Network Structure

Ming Wen [a] [b], E. Kejia [a] [b], Megumu Munakata [c], Yusaku Suenaga [c], Takayoshi Kuroda-Sowa [c], Masahiko Maekawa [d] & Sheng Gang Yan [e]

[a] Department of Chemistry, Tongji University, Shanghai, China

[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, China

[c] Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka, Japan

[d] Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka, Japan

[e] Department of Chemistry, School of Chemistry and Engineering, DaLian University of Technology, DaLian, China

Version of record first published: 31 Jan 2007

To cite this article: Ming Wen, E. Kejia, Megumu Munakata, Yusaku Suenaga, Takayoshi Kuroda-Sowa, Masahiko Maekawa & Sheng Gang Yan (2006): Silver(I) Coordination Complexes of 1,10-Phenanthroline-5,6-dione with 1D Chain and 2D Network Structure, Molecular Crystals and Liquid Crystals, 457:1, 203-213

To link to this article: http://dx.doi.org/10.1080/15421400600598768

Mol. Cryst. Liq. Cryst., Vol. 457, pp. 203–213, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600598768

Silver(I) Coordination Complexes of 1,10-Phenanthroline-5,6-dione with 1D Chain and 2D Network Structure

Ming Wen
E. Kejia
Department of Chemistry, Tongji University, Shanghai, China;
State Key Laboratory of Coordination Chemistry, Nanjing University,
Nanjing, China

Megumu Munakata
Yusaku Suenaga
Takayoshi Kuroda-Sowa
Department of Chemistry, Kinki University, Kowakae,
Higashi-Osaka, Osaka, Japan

Masahiko Maekawa
Research Institute for Science and Technology, Kinki University,
Kowakae, Higashi-Osaka, Osaka, Japan

Sheng Gang Yan
Department of Chemistry, School of Chemistry and Engineering,
DaLian University of Technology, DaLian, China

*Two silver(I) coordination complexes of 1,10-phenanthroline-5,6-dione (pdon), $[Ag_2(pdon)_2(ClO_4)_2]$ (**1**) and $[Ag(pdon)_2](CF_3SO_3)$ (**2**), have been synthesized and characterized by elemental analysis, IR, and X-ray diffraction analysis. Using $AgClO_4$ with pdon, the central silver(I) is bridged by ligand pdon with two N and one O atoms and lead to the one-dimensional (1D) chain structure in **1**. When triflate anion is used as a counter ion in **2**, the silver(I) is chelated by two ligands with four N atoms, and then the molecular unit is linked by intermolecular hydrogen bond to afford a novel two-dimensional (2D) network architecture.*

Keywords: hydrogen bond; 1,10-phenanthroline-5,6-dione; silver(I) complex

Address correspondence to Ming Wen, Department of Chemistry, Tongji University, 1239# Siping Road, Shanghai 200092, China. E-mail: m_wen@mail.tongji.edu.cn

1. INTRODUCTION

The transition-metal complexes with polypyridyl bridging ligands are of considerable interest because of their potential as building blocks for supramolecular assemblies and their photophysical and redox properties, which make them useful as light-harvesting complexes and photonic molecular devices and particularly desirable for solar energy conversion schemes [1–4].

The coordination chemistry of the chelating ligand 1,10-phenanthroline-5,6-dione (pdon) has been examined in several studies [5]. 1,10-Phenanthroline-5,6-dione can carry an O-quinone and N-pyridine moiety and form stable complexes with a variety of metal ions. The solution chemistry of its transition-metal complexes between pdon and Co^{2+}, Fe^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{+} has been extensively studied [6].

Incorporating a ligand with two chelating sites into the coordination sphere allows systematic construction of large supramolecular assemblies, capable of acting as antennae in energy-conversion schemes [7], where the photochemical and redox properties of the complexes are strongly dependent on the nature of the ligands [8]. In addition, the silver(I) ion is regarded as an extremely soft acid that favors coordinating to soft bases such as ligands containing O and N donors. Silver(I) complexes with these soft ligands give rise to an interesting array of stereochemistry and geometric configurations with one-dimensional (1D) chains and two- (2D) and three-dimensional (3D) networks all occurring [9]. The final structures and frameworks of these complexes may well depend on a variety of factors such as the ligand structure and the nature of the anions [10].

In our efforts to study the metal complexes of polypyridyl ligands, we describe here the syntheses and structures of two silver(I) coordination complexes with pdon, which led to a 1D chain in **1** and a 2D network formed by hydrogen bond in **2**.

2. EXPERIMENTAL

2.1. General Procedures

All reactions and manipulations were performed under an argon atmosphere using Schlenk techniques. All chemicals were reagent grade and used as supplied without further purification. Solvents were dried and distilled by using standard methods prior to use. Reagent-grade pdon was prepared according to the literature method [11], whereas silver perchlorate and all other chemicals were purchased from Wako Pure Chemical, Inc., and used as received. The IR spectra were measured as KBr disks on a Jasco FT/IR-8000 spectrometer at room temperature. ^1H NMR spectra were measured on a Jeol GSX-270 FT-NMR spectrometer at 23°C. Tetramethylsilane was used as an internal reference. All crystallizations of the silver complexes were performed in the dark.

2.2. Syntheses

2.2.1. $[Ag_2(pdon)_2](ClO_4)_2$ (1)

A THF solution (5 ml) containing $AgClO_4 \cdot H_2O$ (22.5 mg, 0.10 mmol) was added to pdon (21.1 mg, 0.10 mmol). The mixture was stirred at room temperature for 20 min and filtered. A portion of the filtrate (2 ml) was introduced into a glass tube with a diameter of 7 mm and layered with *n*-pentane as a diffusion solvent. After the glass tube was sealed under argon and left standing at room temperature for 2 weeks, yellow brick crystals of **1** suitable for X-ray determination were isolated. The theoretical value of elemental analysis and the isolated yields (24.9 mg, 60%) are based on the formula without THF molecules. Anal. calc. for $C_{24}H_{12}Ag_2Cl_2N_4O_{12}$: C, 34.49; H, 1.44; N, 6.71. Found: C, 34.61; H, 1.44; N, 6.53. Main IR bands (KBr, ν/cm^{-1}): 1692(s), 1569(m), 1460(m), 1423(s), 1295(w), 1079(s), 816(w), 734(m), 624(m). ^1H NMR (300 MHz, CD_3COCD_3): δ 9.18(d, 2H), 8.73(d, 2H), 8.02(d, 2H).

2.2.2. $[Ag(pdon)_2](CF_3SO_3)$ (2)

A solution of pdon (21.1 mg, 0.10 mmol) in THF (5 ml) was treated with $Ag(CF_3SO_3)$ (22.1 mg, 0.10 mmol). This procedure was repeated to yield yellow block single crystals of **2** (20.8 mg, yields 57%). Anal. calc. for $C_{25}H_{12}AgCF_3O_7N_4$: C, 44.30; H, 1.77; N, 8.27. Found: C, 44.12; H, 1.71; N, 8.16. Main IR bands (KBr, ν/cm^{-1}): 1691(s), 1569(m), 1462(w), 1297(m), 1266(s), 1162(w), 1031(m), 736(w), 636(m). ^1H NMR (300 MHz, CD_3COCD_3): δ 9.19(d, 2H), 8.76(d, 2H), 8.03(d, 2H).

2.3. Crystallography

Single-crystal X-ray data for **1** and **2** were measured on a Rigaku/MSC Mercury Charge Coupled Device (CCD) diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71070$ Å). The intensity data were collected at -123 ± 1°C using the ω scan technique, and a total of 19,872 and 6355 reflections were collected for **1** and **2**, respectively. No decay correction was applied. The linear absorption coefficient μ for Mo-Kα radiation is 18.26 and 10.21 cm^{-1}, respectively. In addition, a correction of secondary extinction was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (SAPI91 [12] for **1**, SIR88 [13] for **2**) and expanded using Fourier techniques [14]. All

TABLE 1 Crystallographic Data for Complexes **1** and **2**

Parameter	**1**	**2**
Formula	$C_{24}H_{12}Ag_2Cl_2N_4O_{12}$	$C_{25}H_{12}AgSF_3O_7N_4$
Formula weight	835.02	677.32
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$(#14)	$P2_1/n$(#14)
a(Å)	16.840(5)	9.7042(5)
b(Å)	10.672(3)	17.260(1)
c(Å)	14.646(5)	14.1321(8)
β(Å)	105.152(4)	92.988(3)
V(Å^3)	2540(1)	2363.8(2)
Z	4	4
F(000)	1632.00	1344.00
T(°C)	−123.0	−123.0
ρ(g/cm^3)	2.183	1.903
λ(Å, MoKα)	0.71070	0.71070
μ(cm^{-1})	18.26	10.21
No. reflections measured	19872 (total) 5649 (unique)	6355 (total) 5369(unique)
No. observed reflections [I > 2σ(I)]	4988	4068
No. of variable parameters	451	370
Residuals: R, Rw	0.040, 0.087	0.099, 0.287
Goodness of fit	1.08	1.23

$R = \sum \| F_o| - |F_c \| / \sum |F_o|$ $R_\omega = [\sum_\omega (F_o^2 - F_c^2)^2 / \sum \omega (F_o^2)^2]^{1/2}$.

nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom coordinates were refined but their isotropic Bs were fixed. The final cycle of full-matrix least-squares refinements [15] was based on 4988 and 4068 observed reflections and 451 and 370 variable parameters for **1** and **2**, respectively, converged with the unweighted and weighted agreement factors of and $R = \sum \| F_o| - |F_c \| / \sum |F_o|$ and $R = [\sum_w (F_o^2 - F_c^2)^2 / \sum_w (F_o^2)^{2^{1/2}}]$. All crystallographic computations were performed using the teXsan package [16]. Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and angles for the two complexes are given in Table 2.

3. RESULTS

3.1. Syntheses and General Characterization

Two silver(I) coordination polymers were prepared by the reactions of $AgClO_4$ and $AgCF_3SO_3$ with pdon in THF. Here, the molar ratio of

TABLE 2 Selected Bond Distances (Å) and Bond Angles (°) for Complexes **1** and **2**

Bond	Distance	Bond	Angle
Complex **1**			
Ag(1)-O(3)	2.348(3)	O(3)-Ag(1)-N(1)	144.8(1)
Ag(2)-O(1)	2.328(3)	O(1)-Ag(2)-N(3)	145.9(1)
Ag(1)-N(1)	2.394(3)	Ag(1)-O(3)-C(17)	121.6(2)
Ag(2)-N(3)	2.363(3)	Ag(1)-N(1)-C(12)	115.8(2)
Ag(1)-N(2)	2.326(3)	Ag(2)-N(3)-C(13)	125.4(2)
Ag(2)-N(4)	2.342(3)	Ag(2)-N(4)-C(23)	117.1(2)
		O(3)-Ag(1)-N(2)	141.8(1)
		O(1)-Ag(2)-N(4)	141.8(1)
		Ag(2)-O(1)-C(5)	124.4(2)
		Ag(1)-N(2)-C(10)	123.4(2)
		Ag(2)-N(3)-C(24)	116.8(2)
		N(1)-Ag(1)-N(2)	70.8(1)
		N(3)-Ag(2)-N(4)	70.9(1)
		Ag(1)-N(1)-C(1)	126.1(2)
		Ag(1)-N(2)-C(11)	118.2(2)
		Ag(2)-N(4)-C(22)	124.7(2)
Complex **2**			
Ag(1)-N(1)	2.241(4)	N(1)-Ag(1)-N(2)	71.6(1)
Ag(1)-N(4)	2.349(4)	N(2)-Ag(1)-N(3)	116.0(1)
Ag(1)-N(2)	2.405(4)	Ag(1)-N(1)-C(1)	119.2(3)
Ag(1)-N(3)	2.272(4)	Ag(1)-N(3)-C(13)	115.6(3)
		Ag(1)-N(4)-C(15)	127.3(4)
		N(1)-Ag(1)-N(3)	157.4(2)
		N(2)-Ag(1)-N(4)	98.0(1)
		Ag(1)-N(1)-C(12)	123.6(3)
		Ag(1)-N(3)-C(24)	124.8(3)
		N(1)-Ag(1)-N(4)	129.6(2)
		N(3)-Ag(1)-N(4)	72.0(2)
		Ag(1)-N(2)-C(2)	114.5(3)
		Ag(1)-N(4)-C(14)	113.4(3)

metal: ligand = 1:1 was used in the syntheses of these two complexes. The mixed solution of the complexes was stored in aluminum foil–wrapped containers, and air-stable yellow crystals were found in the solution. Counter anions in the synthesis of these coordination polymers can be thought of as the keys to assembling these polymeric architectures. The perchlorate counter anion leads to a 1D chain in complex **1**. When triflate counter anion was employed in the reaction, silver(I) is chelated by two ligands with their N atoms, and then the molecular units are linked by hydrogen bond and afforded the 2D network architecture in complex **2**.

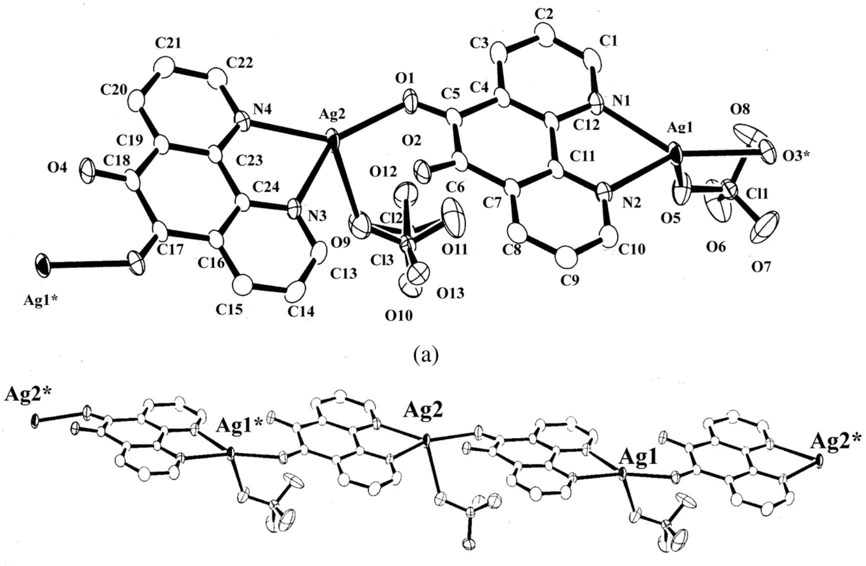
In the infrared spectra of **1** and **2**, a broad strong absorption occurs in the region of 624–1692 cm^{-1}, and their peaks are shifted slightly to different frequencies compared with the normal absorption of $AgClO_4$ at 1140, 1109, 1087, and 629 cm^{-1} and of $AgCF_3SO_3$ at 1256, 1179, 1037, and 648 cm^{-1}. This suggests that the perchlorate groups in complexes **1** are present not as ionic species, but as coordinated ones [17], whereas the IR spectra of triflate groups in complex **2** are close to normal ones. The coordination of silver(I) ions with O and N atoms of pdon can also be seen by comparing the spectra of **1** and **2** with those of the free ligand. (Main IR bands of pdon (KBr, ν/cm^{-1}): 1688, 1565, 1460, 1418, 1299, 1208, 928, 807, 738.)

The ^{1}H NMR chemical shifts of free ligands are δ H 9.04(d, 2H), 8.45(d, 2H), and 7.69(d, 2H). From observed ^{1}H NMR chemical shifts of silver(I) complexes **1** and **2**, the coordination chemical shifts of complexes have some changes with slight shift to low field compared with free ligands, in which the chemical shift change of the meta-position proton of the ligand N atom is larger than that of the para-positon proton and that of the para-positon proton is larger than that of the ortho-position proton. The structure of final products are 1D linear in **1** and 2D network in **2**.

3.2. Structure Characterizations

3.2.1. 1D Chain Complex of $[Ag_2(pdon)_2](ClO_4)_2$ (1)

The molecular structure of complex **1** together with the numbering scheme is shown in Figure 1a. The center silver(I) in this complex is chelated by two N atoms from one ligand and then coordinates with the O atom of the other ligand; each ligand group employs its two N and one O atoms to bridge silver(I) ions from end to end in turn. The polymeric 1D chain of the silver(I) ions is bridged sequentially by the ligand moieties, as shown in Figure 1b. The distorted tetrahedral environment about the silver(I) ion in **1** is completed by further coordination with one O atom of perchlorate counter anions, which is over the ligand parallel. The bond distances of Ag-O are 2.348(2) and 2.328(2) Å, respectively, which are well within the normal range of 2.17–2.61 Å observed in silver(I) complexes [18]. The Ag-N bond distances vary from 2.326(3) to 2.394(3) Å, all being within the normal range observed in the polypyridyl silver(I) complexes [19]. In five members of the chelating ring of **1**, the average chelating bond angles of N-Ag-N is 70.85(1)°, which is smaller than that in reported silver(I) polypyridyl complexes. The remaining one O atom of the ligand is not involved in coordination, and the perchlorate ion plays charge-balance and space-filling roles.



(a)

(b)

FIGURE 1 Crystal structure of **1**: (a) molecular structure with numbering scheme and (b) 1D chain structure.

3.2.2. 2D Network Complex of [Ag(pdon)$_2$](CF$_3$SO$_3$) (2)

An ORTEP drawing of complex **2** with the atom numbering scheme is shown in Figure 2a. Each metal center is chelated by two ligands simultaneously, and then the intermolecular hydrogen bonds connect molecular units and give rise to the 2D network packing architecture. In complex **2**, the [Ag(pdon)$_2$] cation tends to be significantly distorted from D_{2d} symmetry, which has been attributed to crystal packing forces [20]. The primary distortion is a flattening of the two ligands relative to one another with a dihedral angle of 85° between the tow ligand planes. The Ag-N bond distances ranging from 2.272(4) to 2.405(4) Å are well within the normal range observed in reported silver(I) polypyridyl complexes [19]. The intermolecular C−H···O hydrogen bond distances, ranging from 2.28 to 2.39 Å, are less than the regular hydrogen bond distance of 3.0 Å. When triflate anion was employed in complex **2**, the O atoms of ligand do not coordinate to silver(I) ions as shown in complex **1**.

4. DISCUSSION

In this work, the ligands of pdon coordinate to silver(I) ions with N atoms, which display different characteristics using different anions.

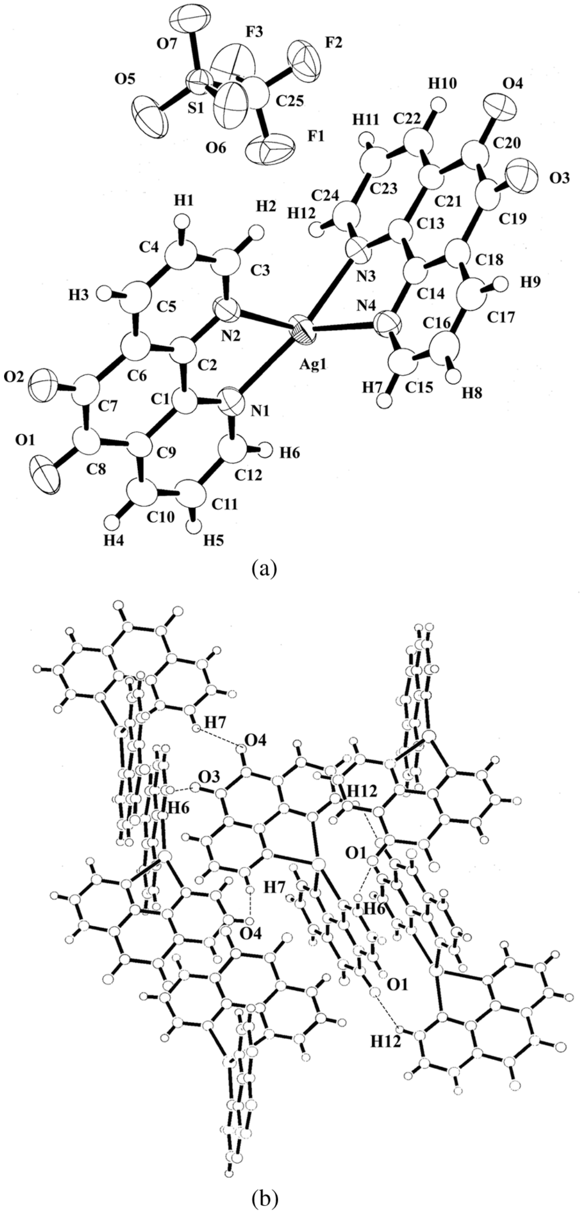


FIGURE 2 Crystal structure of **2**: (a) ORTEP view with an atomic labeling scheme and (b) 2D network formed by hydrogen bond. Hydrogen bond distance: H6-O3, 2.38 Å; H7-O4, 2.28 Å; and H12-O1, 2.39 Å.

The reaction of the pdon with silver perchlorate leads to a 1D chain, which is formed by pdon ligands with their N and O atoms bridging silver(I) ions. In complex **2**, the silver(I) ion is chelated by two pdon simultaneously, in which two polypyridyl planes are almost perpendicular to each other. The distorted units then are connected by a C–H ··· O hydrogen bond and give rise to 2D network.

The average Ag-O bond distance of 2.338(3) Å observed in **1** is normal compared with the silver(I) complexes [18]. The average Ag-N bond distance of 2.356 Å in **1** is slightly longer than that of 2.317 Å in **2**; they all are within the reported data [19]. In complex **2**, the Ag(1)-N(2) bond distance of 2.405(4) Å is longer than the others, which would suggest that the four coordination silver(I) had the tetrahedron environment based on the rotation between two polypyridyl planes.

Furthermore, the polypyridyl ligands in this work are not involved in π–π interaction between two polypyridyl planes reported in silver(I)–aromatic complexes [18b,19]. In this work, two polypyridyl ligands chelated silver(I) ions and went near to a perpendicular position in **2**. In addition, triflate anions are not bonded to ligands, which is different with perchlorate anions as shown in complex **1**.

However, counter ions play a key role in framework of the complexes. Here, triflate anions lead easier to a C–H ··· O hydrogen bond compared with perchlorate anions. In complex **2**, the average C–H ··· O hydrogen bond distance is 2.35 Å, less than the regular hydrogen bond distance of 3.0 Å. These intermolecular hydrogen bonds in complex **2** lead the molecular structure to be a 2D network, which is different from the 1D chain structure in complex **1**.

In conclusion, with polypyridyl ligand pdon, two distinct coordination complexes **1** and **2**, have been synthesized in metal: ligand = 1:1 stoichiometry. In the pdon–silver(I) complexes reported here, the ligands of pdon coordinate to silver(I) ions with N atoms to display different characteristics when different anions were employed. When pdon is coordinated with silver perchlorate, each ligand group uses its two N and one O atoms to bridge silver(I) ions from end to end to form a 1D chain complex **1**. However, when a triflate anion is used as counter anion, the silver(I) is chelated by two ligands with four N atoms in **2**, and then the molecular units are linked by hydrogen bond and afford a 2D network without $\pi - \pi$ interaction between polypyridyl planes.

5. SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-220697 and 220696 for complex **1** and complex **2**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk; or http//www.ccdc.cam.ac.uk).

ACKNOWLEDGMENT

This work was partially supported by Grants-in-Aid for Science Research [Nos. 10440201, 11874092, 12440189, and 10016743 (priority area: metal-assembled complexes)] from the Ministry of Education, Science, Culture, Sports of Japan, and the project was sponsored by Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry (No. 1380241005), the Science Fund (No. 1380219042) from the Tongji University of China and the GYT fund [No. 1380219055].

REFERENCES

[1] (a) Blake, A. J., Champness, N. R., Hubberstey, P., Withersby, M. A., & Schröder, M. (1999). *Coord. Chem. Rev.*, *183*, 117; (b) Umemoto, K., Yamaguchi, K., & Fujita, M. (2000). *J. Am. Chem. Soc.*, *122*, 7150; (c) Leininger, S., Olenyuk, B., & Stang, P. (2000). *Chem. Rev.*, *100*, 853; (d) Bu, X. H., Biradha, K., Yamaguchi, T., Nishimura, M., Ito, T., Tanaka, K., & Shionoya, M. (2000). *Chem. Commun.*, 1953.

[2] Moser, J. E., Nonnote, P., & Grätzel, M. (1998). *Coord. Chem. Rev.*, *177*, 245.

[3] (a) Ziessel, R. & Harriman, A. (1998). *Coord. Chem. Rev.*, *171*, 331; (b) Venturi, M., Serroni, S., Juris, A., Campagna, S., & Blazani, V. (1998). *Top. Curr. Chem.*, *197*, 193; (c) Miller, M. T., Gantzel, P. K., & Karpishin, T. B. (1999). *J. Am. Chem. Soc.*, *121*, 4292.

[4] Kalyanasundaram, K. & Grätzel, M. (1998). *Coord. Chem. Rev.*, *177*, 347.

[5] (a) Hilt, G. & Steckhan, E. (1993). *J. Chem. Soc. Chem. Commun.*, 1706; (b) Lei, Y. & Anson, F. C. (1995). *J. Am. Chem. Soc.*, *117*, 9849.

[6] Bu, X. H., Liu, H., Du, M., Woung, K. M.-C., Yam, V. W.-W., & Shionoya, M. (2001). *Inorg. Chem.*, *40*, 4143.

[7] (a) DeCola, L. & Belser, P. (1998). *Coord. Chem. Rev.*, *177*, 301; (b) Ward, M. D., White, C. M., Barigelletti, F., Aromaroli, N., Calogero, G., & Flamigni, L. (1998). *Coord. Chem. Rev.*, *171*, 481.

[8] (a) Ziessel, R., Hissler, M., EI-Ghayoury, A., & Harriman, A. (1998). *Coord. Chem. Rev.*, *180*, 1251; (b) Waterland, M. R., Flood, A., & Gordon, K. C. (2000). *J. Chem. Soc. Dalton Trans.*, *121*.

[9] (a) Munakata, M., Wu, L. P., & Kuroda-Sowa, T. (1998). *Adv. Inorg. Chem.*, *46*, 173; (b) Munakata, M., Wu, L. P., & Kuroda-Sowa, T. (1997). *Bull. Chem. Soc. Jpn.*, *70*, 1727.

[10] (a) Suenaga, Y., Kuroda-Sowa, T., Maekawa, M., & Munakata, M. (2000). *J. Chem. Soc. Dalton Trans.*, 3620; (b) Maekawa, M., Konaka, H., Suenaga, Y., Kuroda-Sowa, T., & Munakata, M. (2000). *J. Chem. Soc. Dalton Trans.*, 4160; (c) Suenaga, Y.,

Kuroda-Sowa, T., Maekawa, M., & Munakata, M. (1999). *J. Chem. Soc. Dalton Trans.*, 2737; (d) Hirch, K. A., Wilson, S. R., & Moore, J. S. (1997). *Inorg. Chem.*, *36*, 2960.

[11] Yamada, M., Tanaka, Y., Yoshimoto, Y., Yoshimoto, M., Kuroda, S., & Shimao, I. (1992). *Bull. Chem. Soc. Jpn.*, *65*, 1006.

[12] Fan, Hai-Fu. (1991). *Structure Analysis Programs with Intelligent Control*, SAPI91 Rigaku Corporation, Tokyo, Japan.

[13] Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R., & Viterbo, D. (1989). *J. Appl. Cryst.*, *22*, 389.

[14] Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R., & Smits, J. M. M. (1994). *The DIRDIF-94 program system*, Technical Report of the Crystallography Laboratory, University of Nijmegen, the Netherlands.

[15] Sheldrick, G. M. (1997). *Program for the Refinement of Crystal Structures*, (SHELXL-97) University of Goettingen, Germany.

[16] Crystal Structure Analysis Package, (teXsan) Molecular Structure Corporation (1985 and 1999).

[17] Hathaway, B. J. & Underhill, A. E. (1961). *J. Chem. Soc. Dalton Trans.*, 3091.

[18] (a) Wen, M., Munakata, M., Suenaga, Y., Kuroda-Sowa, T., & Maekawa, M. (2002). *Inorg. Chim. Acta.*, *332*, 18; (b) Wen, M., Munakata, M., Suenaga, Y., Kuroda-Sowa, T., & Maekawa, M. (2002). *Inorg. Chim. Acta.*, *338*, 111; (c) Hambley, T. W., Lindoy, L. F., Reimers, J. R., Turner, P., Wei, G., & Widmer-Cooper, A. N. (2001). *J. Chem. Soc. Dalton Trans.*, 614.

[19] (a) Bu, X. H., He, L., & Du, M. (2001). *Inorg. Chem.*, *40*, 4143; (b) Pallenberg, A. J., Marschner, T. M., Barnhart, D., & Barnhart, D. M. (1997). *Poly.*, *16*, 2771; (c) Kaes, C., Hosseini, M. W., Skelton, C. E. F., & White, A. H. (1998). *Angew. Chem. Int. Ed. Engl.*, *37*, 920.

[20] Miller, M. T., Gantel, P. K., & Karpishin, T. B. (1998). *Angew. Chem. Int. Ed. Engl.*, *37*, 1556.