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Unsymmetrical Oxygenation Products of $[Pd(mnt)_2]^{2-}$: Syntheses and Crystal Structures of $(Bu_4N)_2[Pd(mnt)\{O_2S_2C_2(CN)_2\}]$ and One-Dimensional Coordination Polymer $(Bu_4N)_2[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2$ (mnt = 1,2-Dicyano-1,2-ethylenedithiolato)

Kunihisa Sugimoto, Takayoshi Kuroda-Sowa,* Masahiko Maekawa,† and Megumu Munakata

Department of Chemistry, Kinki University, Higashi-Osaka, Osaka 577-8502

†Research Institute for Science and Technology, Kinki University, Higashi-Osaka, Osaka 577-8502

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Oxidation of $[Pd(mnt)_2]^{2-}$ by H_2O_2 produces a sulfonyl-containing $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ ($\mathbf{1}^{2-}$). Addition of $AgClO_4$ to $\mathbf{1}^{2-}$ results in the formation of $[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2{}^{2-}$ ($\mathbf{2}^{2-}$). Both compounds crystallize with a bulky cation Bu_4N^+ to form $(Bu_4N)_2\mathbf{1}$ and $(Bu_4N)_2\mathbf{2}$, which are characterized by single crystal X-ray analyses. $\mathbf{1}^{2-}$ retains a planar structure except for the sulfonyl oxygen atoms. The electronic absorption band observed at 387 nm (sh) is assigned to d–d transition. $\mathbf{2}^{2-}$ has a double-decker structure consisting of two $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ anions bridged by two Ag(I) ions through Ag–S bonds. Two terminal CN groups in $\mathbf{2}^{2-}$ coordinate to the neighboring Ag(I) ions, forming a one-dimensional chain structure. Crystallographic data are as follows. $(Bu_4N)_2\mathbf{1}$: $PdS_4O_2N_6C_{40}H_{72}$, triclinic, $P\bar{1}$, $a = 12.145(2)$, $b = 10.991(3)$, $c = 10.156(2)$ Å, $\alpha = 65.09(2)$, $\beta = 88.93(2)$, $\gamma = 84.97(2)^\circ$, $Z = 1$. $(Bu_4N)_2\mathbf{2}$: $Ag_2Pd_2S_8O_4N_{10}C_{48}H_{72}$, monoclinic, $P2_1/c$, $a = 9.649(2)$, $b = 13.235(2)$, $c = 25.107(2)$ Å, $\beta = 91.03(1)^\circ$, $Z = 2$.

Metal dithiolenes $[M(mnt)_2]^{n-}$ (mnt = 1,2-dicyano-1,2-ethylenedithiolato; $n = 1,2$) are well-known as planar electron acceptors and have been widely used for the synthesis of charge-transfer complexes with unusual magnetic properties.[1] We have recently reported[2] that they can also function as bridging ligands for copper(I) coordination polymers. Two of four terminal CN groups in $[M(mnt)_2]^{2-}$ (M = Ni, Pd, Pt) coordinate to the neighboring copper(I) ions to form one-dimensional polymer compounds $(Bu_4N)_2[M(mnt)_2Cu_4I_4]$ with an eight-membered Cu_4I_4 ring.[2] Although the attempts to obtain analogous Ag(I) coordination polymers resulted in failure, we could obtain a different type of an Ag(I) coordination polymer when H_2O_2-treated $[Pd(mnt)_2]^{2-}$ was used as a starting material. Here we report the syntheses and crystal structures of a one-dimensional Ag(I) coordination polymer $(Bu_4N)_2[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2$ together with the corresponding discrete monomer $(Bu_4N)_2[Pd(mnt)\{O_2S_2C_2(CN)_2\}]$. The structural analyses of them reveal that one of the four thiol units is doubly oxygenated to give a sulfonyl unit ($-SO_2-$).

Experimental

General Procedures and Materials. All chemicals and solvents used were reagent grade purchased from Wako Chemicals Co. Ltd., Tokyo Kasei Kogyo Co. Ltd., and Aldrich Co. Ltd. Most of manipulations were carried out under argon with Schlenk-type flasks. Solvents were dried and purified before use and stored under argon.

CAUTION: $AgClO_4$ used in the following preparations is potentially explosive and must be handled with care. Mixtures of H_2O_2 and acetone give peroxides which may explode violently upon impact or friction.[3]

Physicochemical Measurements. Electronic spectra were obtained by a Hitachi 150-20 spectrophotometer. Infrared spectra were recorded on a JASCO FT/IR-8000 spectrometer using KBr disks. FAB-MS spectra were recorded on a JEOL JMS-HX100 spectrometer.

Preparation of $(Bu_4N)_2[Pd(mnt)\{O_2S_2C_2(CN)_2\}]$ ($(Bu_4N)_2\mathbf{1}$). $(Bu_4N)_2[Pd(mnt)_2]$ was prepared by the literature method.[4] To a green solution of $(Bu_4N)_2[Pd(mnt)_2]$ (133 mg, 0.13 mmol) in acetone (10 ml) was added 3 ml of 30 wt% H_2O_2. The color changed to orange and the mixture was stirred for 30 min at room-temperature. After the mixture was filtered, the filtrate was evaporated under reduced pressure to give an orange precipitate (107 mg, 91%). Single crystals of $(Bu_4N)_2[Pd(mnt)\{O_2S_2C_2(CN)_2\}]$ ($(Bu_4N)_2\mathbf{1}$) were obtained by recrystallization from acetone/ether. Anal. Calcd for $C_{40}H_{72}N_6O_2PdS_4$: C, 53.16; H, 8.03; N, 9.30%. Found: C, 52.62; H, 7.81; N, 9.20%. IR (KBr), cm^{-1}: $\nu(SO) = 1207$, 1073; $\nu(CN) = 2195$. UV-vis. (in acetone) 387 nm (sh) $\varepsilon = 540$ $M^{-1} \cdot cm^{-1}$.

Preparation of $(Bu_4N)_2[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2$ ($(Bu_4N)_2\mathbf{2}$). A mixture of $(Bu_4N)_2\mathbf{1}$ (91.7 mg, 0.1 mmol) and $AgClO_4$ (20.7 mg, 0.1 mmol) was stirred in 10 ml of acetone under argon at room-temperature. After few minutes, the resultant solution was filtered and the filtrate was poured into a glass tube. The same amount of ether was added slowly and the tube was sealed. After standing for one week at −5 °C, red crystals of $(Bu_4N)_2[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2$ ($(Bu_4N)_2\mathbf{2}$) were obtained. (12.3 mg, 16% in crystalline form). Anal. Calcd for $C_{48}H_{72}Ag_2N_{10}O_4Pd_2S_8$: C, 37.48; H, 4.72; N, 9.11%. Found: C, 37.26; H, 4.90; N, 9.46%. IR

(KBr), cm^{-1}: ν(SO) = 1263, 1106; ν(CN) = 2195. UV-vis. (in acetone) 454 nm (sh).

Crystallographic Data Collection and Structure Determination. X-Ray measurements of $(Bu_4N)_2$**1** and $(Bu_4N)_2$**2** were performed on a Rigaku AFC7R diffractometer with graphite-monochromated Mo*Kα* radiation (λ = 0.71069 Å). The intensities of three representative reflections were measured after every 150 reflections, showing a good stability of the intensities. An empirical absorption correction based on ψ scan[5] was applied for $(Bu_4N)_2$**2**. The data were corrected for Lorentz and polarization effects. All structures were solved by direct methods[6] and expanded using Fourier techniques.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but not refined. The refinements (on F^2) were performed by using full-matrix least-squares method, where the unweighted and weighted agreement factors of $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ are used. Neutral atomic scattering factors were taken from Cromer and Waber.[8] All calculations were performed using the teXsan[9] crystallographic software package of Molecular Structure Corporation. Crystal data and details of the structure determination for the complexes $(Bu_4N)_2$**1** and $(Bu_4N)_2$**2** are summarized in Table 1.

Complete listings of atomic coordinates and bond parameters as well as listings of observed and calculated structure factors have been deposited as Document No. 73013 at the Office of the Editor of Bull. Chem. Soc. Jpn. and are available from the Cambridge Crystallographic Data Centre (deposition Nos. 137065, 137066).

Results and Discussion

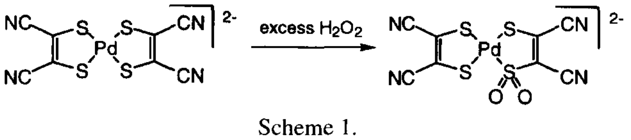
The complex $(Bu_4N)_2$**1** was obtained by a reaction of $(Bu_4N)_2[Pd(mnt)_2]$ and H_2O_2 in acetone (Scheme 1). An excess amount of H_2O_2 was not effective for further oxidation. The observation of a single ion peak at m/z = 209 in the FAB-MS spectrum is reasonable for the formation of a doubly oxygenated $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ species. The crystal structure of $(Bu_4N)_2$**1** was analyzed with $P\bar{1}$ space group (Table 1). The analysis revealed that $\mathbf{1}^{2-}$ has an inversion center at the central Pd atom and that the final structure contains four oxygen atoms with half occupancy factors. The appearance of those four oxygen atoms is ascribed to a disorder of two orientations of $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ having one sulfonyl ($-SO_2-$) group. Figure 1 shows an ORTEP view of the molecular structure of $\mathbf{1}^{2-}$. The selected bond lengths and angles for $\mathbf{1}^{2-}$ are summarized in Table 2. The molecule retains a planarity except for oxygen atoms. A similar oxidation reaction of $[Ni(S_2C_2Ph_2)_2]^{2-}$ by O_2 was reported to form *cis*-$[Ni(O_2S_2C_2Ph_2)_2]^{2-}$ under strong alkaline condition.[10] The difference in two S–O bond lengths in SO_2 moiety (1.468(5) and 1.321(5) Å) probably comes from the disorder. A similar difference in two S–O bond lengths was also reported for a compound containing a $N_2Pd(SO_2)_2$ moiety.[11] The electronic spectrum of $\mathbf{1}^{2-}$ in acetone shows an absorption band at 387 nm (sh, ε = 540 M^{-1}·cm^{-1}), which is shifted from 445 nm (ε = 640 M^{-1}·cm^{-1}) observed for the parent $[Pd(mnt)_2]^{2-}$. The former absorption band is reasonably assigned to d–d transition of $\mathbf{1}^{2-}$ on the basis of the analogy to the S-oxygenated Pd complexes[11] as well as the magnitude of ε. The Pd(1)–S(1) length of 2.276(1) Å is shorter than that of Pd(1)–S(2) (2.292(1) Å), which reflects the difference in valences of S atoms (vide infra).

Red crystals of $(Bu_4N)_2$**2** were obtained by the reaction of $(Bu_4N)_2$**1** with $AgClO_4$ in acetone. An ORTEP view of $\mathbf{2}^{2-}$ is shown in Fig. 2 together with the atom numbering scheme. The selected bond lengths and angles for $\mathbf{2}^{2-}$ are

Table 1. Crystallographic Data for $(Bu_4N)_2$**1** and $(Bu_4N)_2$**2**

	$(Bu_4N)_2$**1**	$(Bu_4N)_2$**2**
Formula	$PdS_4O_2N_6C_{40}H_{72}$	$Ag_2Pd_2S_8O_4N_{10}C_{48}H_{72}$
Fw	903.69	1538.18
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a/Å	12.145(2)	9.649(2)
b/Å	10.991(3)	13.235(2)
c/Å	10.156(2)	25.107(2)
α/deg	65.09(2)	
β/deg	88.93(2)	91.03(1)
γ/deg	84.97(2)	
V/Å^3	1224.6(5)	3205.9(9)
Z	1	2
D_{calc}/ g cm^{-3}	1.225	1.593
μ/cm^{-1}	5.86	14.60
$R1^{a)}$ ($F_o^2 > 2.0\sigma(F_o^2)$)	0.046	0.062
$wR2^{b)}$ (all unique data)	0.121	0.183
GOF	1.05	0.98

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
b) $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.



Scheme 1.

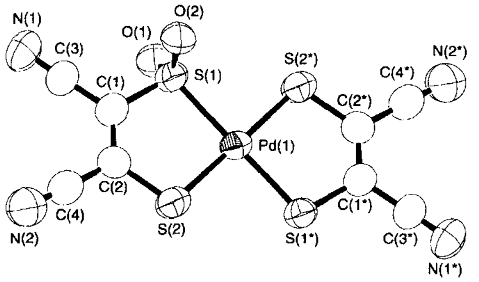


Fig. 1. An ORTEP drawing of the $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ anion ($\mathbf{1}^{2-}$). Disordered oxygen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (°) for $(Bu_4N)_2$**1**

	Bond lengths (Å)		
Pd(1)–S(1)	2.2760(9)	Pd(1)–S(2)	2.292(1)
S(1)–O(1)	1.321(5)	S(1)–O(2)	1.468(5)
	Bond angles (°)		
S(1)–Pd(1)–S(2)	89.91(4)	S(1)–Pd(1)–S(2*)$^{a)}$	90.09(4)
Pd(1)–S(1)–O(1)	117.6(2)	Pd(1)–S(1)–O(2)	110.1(2)
Pd(1)–S(1)–C(1)	103.0(1)	O(1)–S(1)–O(2)	122.4(3)
O(1)–S(1)–C(1)	101.4(3)	O(2)–S(1)–C(1)	97.2(2)

a) $-x$, $-y$, $-z$.

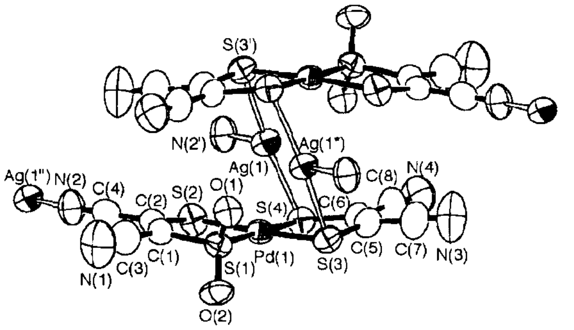


Fig. 2. An ORTEP drawing of the $[AgPd(mnt)\{O_2S_2C_2(CN)_2\}]_2^{2-}$ anion ($\mathbf{2}^{2-}$).

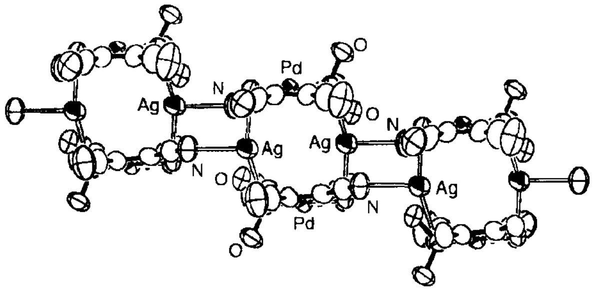


Fig. 3. View of one-dimensional polymer of $\mathbf{2}^{2-}$.

summarized in Table 3. The molecular structure of $\mathbf{2}^{2-}$ consists of two $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ anions bridged by two Ag(I) ions through Ag-S bonds (2.50 Å in average), forming a double-decker type structure. The structure of $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ in $\mathbf{2}^{2-}$ clearly shows one of four thiol sites in the parent $[Pd(mnt)_2]^{2-}$ was oxidized by H_2O_2 to a sulfonyl ($-SO_2-$). It is interesting to compare the geometry of sulfur atoms with different oxidation states. The Pd(1)–S(1) length in $\mathbf{2}^{2-}$ (2.256(2) Å) is clearly shorter than the other Pd–S lengths (2.311 Å in average) and the S(1)–C(1)–C(2) angle of 118.8(7)° is smaller than the other corresponding angles (123.9° in average). These facts can be interpreted by the contraction in size of the sulfur atom due to the change in the formal oxidation state from −2 to +2.[11] The slightly elongated S(1)–C(1) length (1.794(9) Å) compared to the other S–C lengths (1.747 Å in average) is probably due to the balance of bond strengths between Pd–S and S–C bonds. The S(3) and S(4) atoms belonging to the mnt coordinate to Ag(I) ions. The average Ag–S length (2.50 Å) is shorter than those observed in $[M(mnt)_2\{Ag(PR_3)_2\}_2]$ (2.728—3.093 Å).[12] While the discrete molecule of $\mathbf{1}^{2-}$ retains planarity except for the sulfonyl oxygen atoms, the structure of $[Pd(mnt)\{O_2S_2C_2(CN)_2\}]^{2-}$ anion in $\mathbf{2}^{2-}$ bends slightly at four sulfur atoms. The dihedral angle of two planes defined by two mnt moieties is 16°.

Table 3. Selected Bond Lengths (Å) and Angles (°) for $(Bu_4N)_2\mathbf{2}$

	Bond lengths (Å)		
Ag(1)–S(3′)$^{b)}$	2.494(3)	Ag(1)–S(4)	2.508(3)
Ag(1)–N(2′)$^{c)}$	2.489(9)	Pd(1)–S(1)	2.256(2)
Pd(1)–S(2)	2.305(3)	Pd(1)–S(3)	2.306(3)
Pd(1)–S(4)	2.321(2)	S(1)–O(1)	1.459(7)
S(1)–O(2)	1.453(6)	Ag(1)···Pd(1)	3.016(1)
S(1)–C(1)	1.794(9)	S(2)–C(2)	1.732(9)
S(3)–C(5)	1.755(10)	S(4)–C(6)	1.754(9)
	Bond angles (°)		
S(3′)$^{b)}$–Ag(1)–S(4)	162.33(8)	S(3′)$^{b)}$–Ag(1)–N(2′)$^{c)}$	98.6(2)
S(4)–Ag(1)–N(2′)$^{c)}$	98.9(2)	S(1)–Pd(1)–S(2)	89.40(9)
S(1)–Pd(1)–S(3)	91.75(9)	S(1)–Pd(1)–S(4)	178.26(9)
S(2)–Pd(1)–S(3)	175.9(1)	S(2)–Pd(1)–S(4)	89.31(9)
S(3)–Pd(1)–S(4)	89.62(9)	Pd(1)–S(1)–O(1)	112.7(3)
Pd(1)–S(1)–O(2)	115.3(3)	Pd(1)–S(1)–C(1)	104.2(3)
O(1)–S(1)–O(2)	113.8(4)	O(1)–S(1)–C(1)	104.8(4)
O(2)–S(1)–C(1)	104.6(4)	Ag(1″)$^{c)}$–N(2)–C(4)	142.7(8)
S(1)–C(1)–C(2)	118.8(7)	S(2)–C(2)–C(1)	124.9(8)
S(3)–C(5)–C(6)	123.1(8)	S(4)–C(6)–C(5)	123.6(8)

b) $-x, -y, -z$; c) $-x+1, -y, -z$.

The Ag(I) ion is also coordinated by a terminal CN group of the neighboring molecule with the Ag–N bond length of 2.489(9) Å. The coordination geometry around the Ag(I) ion is a trigonal planar fashion. The C–N–Ag angle of 142.7(8)° is largely deviated from the ideal C–N–M angle (180°): The corresponding angle in $(Bu_4N)_2[Ni(mnt)_2Cu_4I_4]$ is 177.2(5)°. Bent C–N–Ag bond angles have been also reported in the literature.[13] These phenomena illustrate the flexible coordination sphere inherent to Ag(I).[14] Since only one of four CN groups in $\mathbf{1}^{2-}$ participates in coordination to an Ag(I) ion, a double-decker unit of $\mathbf{2}^{2-}$ can function as a building block with two donor and two acceptor sites. As shown in Fig. 3, the Pd_2Ag_2 unit is further associated with two neighboring units to give a one-dimensional chain structure. Each association is supported by two Ag–N(CN) bonds. This is the second example of a terminal CN group in mnt participating in the formation of coordination polymer to give a one-dimensional chain structure (the chain grows along the *a*-axis).

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