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Inorganica Chimica Acta 305 (2000) 14-18

Inorganica Chimica Acta

Syntheses, crystal structures and nonlinear optical properties of $MS_4Pd(dppp)$ (M = Mo, W)

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Received 10 November 1999; accepted 28 February 2000

Abstract

The title compounds $[MS_4Pd(dppp)]$ $[M = Mo (1), W (2); dppp = Ph_2PCH_2CH_2CH_2CH_2PPh_2]$ were synthesized for nonlinear optical studies by the reaction of $(Et_4N)_2MS_4$ (M = Mo, W) and $(dppp)PdCl_2$ in the $CH_2Cl_2-CH_3CN$. Single-crystal X-ray analyses revealed that the two compounds consisted of a distorted tetrahedral MS_4 (M = Mo, W) unit with a Pd atom and two S atom bridges. The Pd atom has a *cis*-quasisquare coordination geometry with two P donors of dppp and two S donors of MS_4 . The nonlinear optical properties of 1 and 2 were investigated by a *Z*-scan technique with 7 ns laser pulses at 532 nm. It was observed that the nonlinear absorption for 1 is very small, but it has considerable large nonlinear refractive index; no nonlinear optical behavior was observed for 2, although it shows a similar structure to that of compound 1. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Optical properties; Palladium complexes; Thiometallate complexes

1. Introduction

The chemistry of Mo (W)–Cu (Ag)–S cluster compounds have been of interest for the past two decades [1]. Many of these compounds have been extensively studied because of their relevance to biological systems and catalytic processes [2,3]. Up to now, a number of Mo(W)–Cu (Ag)–S compounds have been synthesized from the reactions of MS_4^{2-} (M = Mo, W) anions with soft cations Cu⁺, Ag⁺, Au⁺ in the presence of Ph₃P, Ph₃As and Py ligands [4–6]. In our laboratory, we discovered that some Mo(W)–Cu(Ag)–S clusters display very strong nonlinear optical (NLO) effects [4–10]. In order to explore this field further, we have synthesized a series of new Mo(W)–Pd–S cluster compounds. In this article, we report the synthesis, X-ray crystal structures and NLO properties of two new palladiumcontaining cluster compounds: $[MoS_4Pd(dppp)]$ (1) and $[WS_4Pd(dppp)]$ (2).

2. Experimental

2.1. Materials

All solvents were AR grade. $(Et_4N)_2MS_4$ (M = Mo, W) were synthesized according to the literature methods [11], and (dppp)PdCl₂ was prepared similar to the literature method [12].

2.2. Physical measurements

IR spectra were recorded on a Fourier Nicolet FT-170SX spectrophotometer with pressed KBr pellets and the electronic spectra of the two clusters were measured

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with a Hitachi U-3410 spectrophotometer. Carbon and hydrogen analyses were performed on a PE 240C Elemental Analyser.

2.3. Nonlinear optical (NLO) measurements

The dimethylformanide (DMF) solutions of clusters 1 and 2 were contained in a 1-mm thick quartz cuvette with concentrations of 5.0 and 2.7×10^{-4} M for clusters 1 and 2, respectively. The samples were irradiated by a Q-switched frequency-doubled Nd:YAG laser, which produced linearly polarized 7 ns (FWHM) optical pulses at 532 nm. The laser was operated at pulse repetition rate of 10 Hz. The spatial profiles of the optical pulses were nearly Gaussian after passing through a spatial filter. The laser beam was then divided by a beam splitter into two parts: one was used as a reference for the incident energy and the other was focused onto the sample by a focusing mirror of 25-cm focal length. The minimum beam radius of the focused laser beam was measured to be $30 + 5 \mu m$. Both incident and transmitted pulse energies were measured simultaneously by two energy detectors (Rjp-735 energy probes, Laser Precision), which were link to a computer by an IEEE interface. The NLO properties of the samples were determined by performing the Z-scan measurements [13]. The samples were mounted on a

Table 1					
Crystal data	and	data	collection	parameters	

Formula	$Mo_1Pd_1S_4P_2C_{27}H$	$W_1Pd_1S_4P_2C_{27}H$
Formula weight Crystal system Space group a (Å) b (Å) c (Å) β (°) V (Å ³) Z T (K) D_{role} (g cm ⁻³)	26 743.03 monoclinic $P2_1/c$ (no. 14) 10.884(5) 11.473(2) 23.527(3) 94.63(2) 2928(1) 4 293 1.685	P_{1}^{26} 830.96 monoclinic $P_{2_1/c}$ 10.863(2) 11.485(1) 23.595 94.71(1) 2933.9(9) 4 293 1.881
$\mu \text{ (mm}^{-1)}$ Crystal size (mm)	1.423 0.85×0.25 $\times 0.08$	5.01 0.36×0.25 $\times 0.22$
Scan type No. of observations	$\omega - 2\theta$ 4495 $(I > 3.0\sigma(I))$	$\omega - 2\theta$ 4630 (<i>I</i> >3.0 σ (<i>I</i>))
No. of variables R R_{w} Goodness-of-fit Maximum shift in final cycle Largest peak in final difference map (e Å ⁻³)	$\begin{array}{c} 316 \\ 0.033 \\ 0.041 \\ 1.05 \\ 0.001 \\ 0.46, \ -0.67 \end{array}$	316 0.035 0.043 1.10 0.002 1.32, -1.26 (near to W atom)

translation stage that was controlled by the computer to move along the Z axis with respect to the focal point. For determining both the sign and magnitude of the nonlinear refraction, a 1.0-mm diameter aperture was placed in front of the transmission detector and the transmittance was recorded as a function of the sample position on the Z axis (closed-aperture Z-scan). For measuring the nonlinear absorption, the Z-dependent sample transmittance was taken without the aperture (open-aperture Z-scan).

2.4. Syntheses of compounds 1 and 2

2.4.1. Preparation of $[MoS_4Pd(dppp)]$ (1)

 $({\rm Et}_4{\rm N})_2{\rm MoS}_4$ (0.242 g, 0.5 mmol) and ${\rm Pd}({\rm dppp}){\rm Cl}_2$ (0.250 g, 0.5 mmol) were added to 30 ml of ${\rm CH}_2{\rm Cl}_2$ and ${\rm CH}_3{\rm CN}$ (1:1 v/v). The obtained mixture was stirred for 12 h at room temperature (r.t.) and then filtered. The solid was dried in air after washing with ${\rm CH}_2{\rm Cl}_2$, distilled water, EtOH and ether, respectively. Single orange crystals were obtained by diffusing ethyl ether into the DMF solution (0.297 g, yield 80%). Anal. Calc. for ${\rm C}_{27}{\rm H}_{26}{\rm MoPdP}_2{\rm S}_4$: C, 43.65; H, 3.53; Found: C, 43.1; H, 3.85%. IR spectra (KBr pellet): Mo–S_t, 488.0; Mo–S_b, 442 cm⁻¹.

2.4.2. Preparation of $[WS_4Pd(dppp)]$ (2)

The method was similar to that for **1**, $(Et_4N)_2WS_4$ (0.286 g, 0.5 mmol) and Pd(dppp)Cl₂ (0.250 g, 0.5 mmol) were added to 30 ml of CH₂Cl₂ and CH₃CN (1:1 v/v). The obtained mixture was stirred for 12 h at r.t. and yellow crystals were obtained (0.316 g, yield 76%). *Anal.* Calc. for C₂₇H₂₆P₂S₄WPd: C, 39.03; H, 3.15; Found: C, 39.09; H, 3.20%. IR spectra (KBr pellet): W–S_t, 484.0; W–S_b, 452 cm⁻¹.

2.5. Crystal data and structure determination

Suitable crystals of compounds **1** and **2** were mounted in random orientation on a glass fiber for X-ray determination. Data were collected on a Enraf– Nonius CAD4 diffractometer using Mo K α radiation at 296 K. Details concerning the intensity and data collection are given in Table 1. The data were corrected for Lorentz and polarization factors, and the absorption was corrected by using empirical scan data and DIFABS. The structures of the compounds were determined by direct methods. The structures of the compounds were refined by full-matrix least-squares fits with isotropic temperature factors for the remaining non-hydrogen atoms to final R = 0.033, $R_w = 0.041$ for compound **1** and R = 0.035, $R_w = 0.043$ for compound **2**. All calculations were carried out on a MICRO-VAX II computer with a TEXSAN program package [14].



Fig. 1. Crystal structure of [WS₄Pd(dppp)].

Table 2 Selected bond lengths (Å) and angles (°) for compound $\boldsymbol{1}$

3. Results and discussion

3.1. Structures of compounds 1 and 2

The two title compounds are isomorphous and crystallize in the monoclinic space group $P2_1/c$. Therefore, the structure of compound 2 will be mainly described in here. The crystal of compound **2** is a neutral compound consisting of a distorted tetrahedral WS4 with a palladium atom and two sulfur atom bridges (Fig. 1). The selected bond lengths and bond angles are given in Tables 2 and 3, respectively. The palladium atom has a cis-quasisquare coordination geometry with two phosphorus donors of dppp and two sulfur donors of WS₄. The terminal W-S distances (average 2.150 Å) are similar to those found in [NEt₄][PdWS₄- $(S_2CNC_4H_8)$ [15], but the W–S bridge distances (2.224 Å) are slightly shorter than those observed in $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ (2.236 Å). The Pd–P distances (2.287 Å) are longer than those for (dppp)PdCl₂ [12]. Pd-S bond lengths (average 2.364 Å) are slight

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Bond lengths					
Pd–P ₁	2.294(1)	Pd–P ₂	2.291(1)	Pd–S ₁	2.351(1)
Pd–S ₂	2.360(1)	Pd–Mo	2.9102(7)	Mo–S ₁	2.219(1)
Mo-S ₂	2.228(1)	Mo–S ₃	2.153(1)	Mo–S ₄	2.134(1)
$P_1 - C_1$	1.819(5)	$P_2 - C_3$	1.826(4)	$C_1 - C_2$	1.516(6)
$C_2 - C_3$	1.514(7)				
Bond angles					
$P_2 - Pd - P_1$	92.00(5)	P ₂ -Pd-S ₁	167.00(5)	P ₂ -Pd-S ₂	87.24(5)
P ₂ -Pd-Mo	133.45(4)	P ₁ -Pd-S ₁	84.30(5)	$P_1 - Pd - S_2$	177.40(5)
P ₁ –Pd–Mo	132.74(3)	$S_1 - Pd - S_2$	96.98(5)	S ₁ -Pd-Mo	48.46(3)
S ₂ -Pd-Mo	48.66(3)	S ₄ -Mo-S ₃	109.78(6)	S ₄ -Mo-S ₁	110.63(6)
S ₄ -Mo-S ₂	110.28(6)	S ₄ -Mo-Pd	121.53(5)	S ₃ -Mo-S ₁	110.71(6)
S ₃ -Mo-S ₂	110.38(5)	S ₃ –Mo–Pd	128.69(4)	S ₁ -Mo-S ₂	104.98(5)
S ₁ -Mo-Pd	52.47(3)	S ₂ -Mo-Pd	52.68(3)	Mo-S ₁ -Pd	79.07(4)
Mo-S ₂ -Pd	78.66(4)			-	

Table 3

Selected bond lengths (Å) and angles (°) for compound 2

Bond lengths					
Pd–P ₁	2.287(2)	Pd–P ₂	2.286(2)	Pd–S ₁	2.360(2)
Pd-S ₂	2.368(2)	Pd–W	2.9259(6)	W-S ₁	2.217(2)
W-S ₂	2.230(2)	W–S ₃	2.163(2)	W-S ₄	2.137(2)
$P_1 - C_1$	1.822(7)	$P_2 - C_3$	1.827(7)	$C_{1} - C_{2}$	1.53(1)
C ₂ -C ₃	1.49(1)				
Bond angles					
$P_2 - Pd - P_1$	91.89(7)	P ₂ –Pd–S ₁	167.18(7)	P ₂ –Pd–S ₂	87.55(6)
P ₂ -Pd-W	133.55(5)	P ₁ –Pd–S ₁	84.63(7)	P ₁ –Pd–S ₂	177.54(7)
P ₁ –Pd–W	132.74(5)	$S_1 - Pd - S_2$	96.43(7)	S ₁ –Pd–W	48.14(5)
S ₂ -Pd-W	48.43(4)	S ₄ –W–S ₃	109.81(8)	S ₄ –W–S ₁	110.56(8)
S ₄ -W-S ₂	110.43(8)	S ₄ –W–Pd	121.49(7)	$S_{3} - W - S_{1}$	110.74(8)
$S_3 - W - S_2$	110.33(7)	S ₃ –W–Pd	128.70(5)	$S_1 - W - S_2$	104.88(7)
S ₁ -W-Pd	52.46(5)	S ₂ –W–Pd	52.59(5)	W-S ₁ -Pd	79.40(7)
$W-S_2-Pd$	78.98(6)				



Fig. 2. Electronic spectrum of [MoS₄Pd(dppp)] (5.0×10^{-4} M) (_) and [WS₄Pd(dppp)] (2.7×10^{-4} M) (- -) in DMF. The optical path is 1 mm.



Fig. 3. The normalised Z-scan data $[MoS_4Pd(dppp)]$ ($5.0 \times 10^{-4}M$) in DMF solution with 532 nm, 7 ns laser pulses. The optical path is 1 mm. The peak incident irradiance of the pulses at focus is 240 MW cm⁻². The experimental data were measured without (\bullet) an aperture. The open circles (\bigcirc) were obtained by dividing the Z-scan data collected with the aperture by those collected without the aperture; they have been vertically displaced by -0.4 for clarity. The solid curves are the theoretical fits based on the Z-scan theory.

longer than in [{(allyl)Pd}₂WS₄] (average 2.34 Å) [16]. The W–S–Pd angles (average 79.19°) are larger and the W–Pd distance (2.9259 Å) bond length is longer than those in $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ (77.58° and 2.8669 Å, respectively).

3.2. NLO properties of compounds $[MoS_4Pd(dppp)]$ (1) and $[WS_4Pd(dppp)]$ (2)

The electronic spectra of compounds 1 and 2 in DMF are depicted in Fig. 2. It was noted that both compounds have relatively low linear absorption in the visible and near-IR region. The lowest absorption

peaks are located at 486 and 390 nm for compounds 1 and **2**, respectively. The Z-scan results for compounds **1** are shown in Fig. 3, where the filled circles were the Z-scan data measured without the aperture and the open circles were the results obtained from the division of the closed aperture Z-scan data by the open aperture Z-scan data. To obtain the NLO parameters, we employed a Z-scan theory [13], which considers nonlinearities of third-order nature. The total absorption coefficient can be written as $\alpha = \alpha_0 + \alpha_2 I$, where α_0 and α_2 are the linear and nonlinear absorption coefficients, respectively, and I is the irradiance of the laser beam within the sample. The total refractive coefficient can be expressed as $n = n_0 + n_2 I$, where n_0 and n_2 are the linear and nonlinear refractive indices. The good fits between the theory and our experimental data suggest that the observed NLO phenomena are effectively a third-order process. In Fig. 3, it was observed that compound **1** shows a negative sign for n_2 . This indicates that the laser beam propagating in compound 1 undergoes a self-defocusing process. Table 4 lists the measured nonlinear absorption coefficient, α_2 and nonlinear refractive index, n_2 for compound **1**. It should be noted that the Z-scan measurements reported here could not reveal the origin of the measured α_2 and n_2 values for compound 1. Excited state effects, two-photon absorption, third-order bound-electronic effect and nonlinear scattering are the possible mechanism behind the observed nonlinearities [17-19]. The observed self-defocusing property possess by compound 1 shows that it can be a promising material for applications such as protection of optical sensors. It is also interesting to compare this compound with other different structural clusters. Table 4 shows that compound 1 is comparable with most of the other clusters in terms of the effective n_2 value. It should also be pointed out that compound 2 has very weak NLO properties, although it shows a similar structure to that of compound 1.

4. Supplementary material

Supplementary data have been deposited with the Cambridge Crystallographic Data Centre (CCDC Nos. 135112 and 135113). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This research was supported by the National Natural Science Foundation of China and the National University of Singapore.

Table 4					
The NLO	parameters	for	cluster	compounds	a

Compound	Structure	$\alpha_{\rm o}~({\rm cm^{-1}~M^{-1}})~(\times 10^3)$	α_2 (cm $W^{-1}~M^{-1}$) ($\times 10^{-5}$)	$n_2 \ ({ m cm}^2 \ { m W}^{-1} \ { m M}^{-1}) \ (imes 10^{-10})$
[MoS ₄ Pd(dppp)] ^b	linear	5.50	2.0	-1.1
[WS ₄ Pd(dppp)] ^b	linear	7.57		
[MoOS ₃ Cu ₃ I(py) ₅] ^c	nested	0.04	2.5	-1.3
[WOS ₃ Cu ₃ I(py) ₅] ^c	nested	2.10	15.0	16.0
$[Et_4N][Mo_2O_2S_6Cu_6I_6]$ d	twin-nested	0.74	2.0	-3.0
[WOS ₃ Cu ₂ (PPh ₃) ₃] ^e	butterfly	2.50		6.70

^a Note: α_0 is the linear absorption coefficient, α_2 is the nonlinear absorption coefficient and n_2 is the nonlinear refractive index. The dashed lines represent negligible nonlinearity coefficients.

^b This work.

^c Ref. [5].

^d Ref. [20].

e Ref. [21].

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