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First optical non-linearity study on Group 6–Group 10 sulfido mixed-metal complexes, synthesis and crystal structure of $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ and $[NEt_4]_2[PdW_2S_8]$

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Two Group 6–Group 10 sulfido mixed-metal complexes, $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ **1** and $[NEt_4]_2[PdW_2S_8]$ **2**, have been synthesized *via* reactions of $[Pd(S_2CNC_4H_8)_2]$ with $[NH_4]_2[WS_4]$ and NEt_4Cl in different molar ratios in dichloromethane. X-Ray crystallographic structure determinations revealed that palladium in **1** is co-ordinated by a pyrrolidinecarbodithioate and a tetrathiotungstate, while in **2** it is co-ordinated by two tetrathiotungstates symmetrically. Both dithiocarbamate and tetrathiotungstate act as bidentate ligands through two sulfur atoms chelating palladium. The Pd–W distances are 2.8669(7) and 2.9008(5) Å in **1** and **2**, respectively. Non-linear optical properties of the compounds were studied with a 7 ns pulsed laser at 532 nm. Compound **1** exhibits mainly optical self-defocusing ($n_2 = -6.8 \times 10^{-18}$ m^2 W^{-1} as measured with a 1.0×10^{-3} mol dm^{-3} acetonitrile solution) with negligible non-linear absorption. Compound **2** exhibits both optical self-defocusing ($n_2 = -7.5 \times 10^{-18}$ m^2 W^{-1}, as measured with a 1.6×10^{-3} mol dm^{-3} acetonitrile solution) and optical non-linear absorption ($\alpha_2 = 3.5 \times 10^{-11}$ m W^{-1}).

Tetrathiomolybdate is a fundamental unit of some molybdenum enzymes and plays an important role in co-ordination chemistry as a ligand for other metals to form analogous compounds of metalloproteins.[1] Recently interesting non-linear optical (NLO) properties have been uncovered for related Group 6–Group 11 sulfido clusters.[2,3] By solution and solid-state synthetic methods, several hundred mixed-metal clusters have been synthesized.[4] As a continuing effort to find inorganic compounds possessing superior NLO properties we turned our attention to Group 6–Group 10 sulfido complexes and clusters.[5]

There are reports on such complexes and clusters containing MS_4 moieties (M = Mo or W).[6] A number of trimeric species of generic formula $[M(M'S_4)_2]^{2-}$ (M = Ni, M′ = Mo or W; M = Pt, M′ = W) were first prepared by Mueller and co-workers[7] and later by Callahan and Piliero,[8,9] who reported the preparation of $[Pd(MoS_4)_2]^{2-}$, $[Pd(WS_4)_2]^{2-}$, and $[Pt(WS_4)_2]^{2-}$ complexes. Their general synthesis involved reactions of aqueous solutions of a metal-(II) or -(IV) species with an excess of the $M'S_4^{\ 2-}$ anionic ligand. They improved the yields by synthesizing the complexes in a mixed-solvent system (acetonitrile–water). To ascertain the fundamental structure of the tetrahedral $M'S_4$ and square-planar MS_4 geometry (M = Ni, Pd or Pt; M′ = Mo or W) the early works had placed emphasis on the IR and Raman spectra.[10] Theoretical work on the electronic structures of $[M(M'S_4)_2]^{2-}$ (M = Ni, Pd or Pt; M′ = Mo or W) species has appeared. Extended Hückel SCCC–MO calculations[11a] showed evidence of strong π bonding between the central metal and ligand orbitals: σ bonding was indicated between M′ and the sulfur ligands.[11b] Raman and resonance-Raman studies imply significant delocalization in the excited states of all $[M(M'S_4)_2]^{2-}$ anions.[12] The ground-state electronic structures of the anions were probed by quasi-relativistic multiple scattering X_α calculations.[13] In the series $[M(M'S_4)_2]^{2-}$ (M = Ni, Pd, or Pt; M′ = Mo or W) only the structures of the two species $[Ni(MoS_4)_2]^{2-}$ and $[Ni(WS_4)_2]^{2-}$ were determined crystallographically, which confirmed the structure proposed for $[M(M'S_4)_2]^{2-}$.[14] Callahan and Cichan[15] had synthesized mixed-ligand complexes $[M(M'S_4)(S_2CNEt_2)]^-$ (M = Ni, Pd or Pt; M′ = Mo or W) by using ligand exchange and redistribution reaction and studied their electrochemical properties. Bowmaker *et al.*[16] investigated the redox properties of $[M(M'S_4)(S_2CNR_2)]^-$ (M = Ni, Pd or Pt; M′ = Mo or W) using d.c. and a.c. cyclic voltammetry to a platinum electrode in dichloromethane solution; ESR spectra were used to identify the species produced after one-electron reduction. In more recent years several phosphino and organometallic bi- and tri-nuclear mixed-metal clusters of the type $[M(WS_4)L^1(L^2)]$ (M = Pt, $L^1,L^2 = PEt_3$;[17] M = Pt, $L^1L^2 = Ph_2PCH_2PPh_2$;[18] M = Pd, $L^1L^2 = Ph_2PCH_2PPh_2$;[19] M = Pt, $L^1L^2 = \eta^4$-cyclooctadiene;[20] M = Ni, $L^1 = PMe_2Ph$, $L^2 = \eta^4\text{-}C_4Me_4$[21]) and $[(L^2)L^1M(WS_4)ML^1(L^2)]$ (M = Pd, $L^1,L^2 = \eta^3\text{-}C_3H_5$ or C_6F_5;[22] M = Ni, $L^1,L^2 = C_6F_5$[23]) have been synthesized and X-ray crystallographically characterized. In the latter case the MS_4 moiety acts as a bridging ligand.

On account of the interest in the structures and properties of Group 6–Group 10 mixed-metal complexes and clusters, here we report the non-aqueous synthesis, crystal and molecular structure of bi- and tri-nuclear palladium–tungsten sulfido complexes, $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ **1** and $[NEt_4]_2[PdW_2S_8]$ **2**, as well as an investigation of their non-linear optical properties.

Experimental

All reagents and solvents were A.R. or C.P. grade used without further purification. The salt $[NH_4]_2[WS_4]$ was prepared according to the literature.[24] Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyser. Infrared spectra were recorded on a Nicolet 170sx FT-IR spectrometer, UV/VIS spectra on a Shimaduz UV-240 spectrometer with acetonitrile as solvent.

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Preparations

[Pd($S_2CNC_4H_8$)$_2$]. Palladium(II) chloride (0.36 g, 2.0 mmol) was heated in acetonitrile (15 cm^3) to dissolve it. To the resultant cold solution solid $NaS_2CNC_4H_8\cdot 3H_2O$ (0.90 g, 4.0 mmol) was added and stirred. The product precipitating as a yellow powder was filtered off and washed with a large amount of water and then ethanol and diethyl ether and dried in vacuum. Yield 0.67 g (Found: C, 30.2; H, 4.2; N, 7.3. Calc. for $C_{10}H_{16}N_2PdS_4$: C, 30.1; H, 4.0; N, 7.0%).

[NEt_4][$PdWS_4$($S_2CNC_4H_8$)] 1. The compounds [Pd($S_2CNC_4H_8$)$_2$] (0.20 g, 0.5 mmol), [NH_4]$_2$[WS_4] (0.17 g, 0.5 mmol) and $NEt_4Cl\cdot H_2O$ (0.11 g, 0.6 mmol) were mixed and stirred in dichloromethane (15 cm^3) for 30 h. The resultant bright red solution was filtered and Pr^{i}OH (10 cm^3) added to the top of the filtrate, which was then stored at room temperature affording reddish-orange strip crystals. Yield 0.26 g (Found: C, 22.3; H, 4.1; N, 3.8. Calc. for $C_{13}H_{28}N_2PdS_6W$: C, 22.3; H, 4.1; N, 4.0%). IR spectrum (KBr pellets): ν(W–S$_t$) 490.3 and ν(W–S$_b$) 441.2 cm^{-1}.

[NEt_4]$_2$[PdW_2S_8] 2. The compounds [Pd($S_2CNC_4H_8$)$_2$] (0.20 g, 0.5 mmol), [NH_4]$_2$[WS_4] (0.34 g, 1.0 mmol) and $NEt_4Cl\cdot H_2O$ (0.20, 1.1 mmol) were mixed and stirred in dichloromethane (15 cm^3) for over 30 h. The deep red solution was filtered and Pr^{i}OH (10 cm^3) added to the top of the filtrate. The solution was stored at room temperature giving dark red block crystals of **2** and a little amount of **1**, which was rejected mechanically. Yield 0.28 g (Found: C, 19.6; H, 3.7; N, 2.8. Calc. for $C_{16}H_{40}N_2PdS_8W_2$: C, 19.4; H, 4.1; N, 2.8%). IR spectrum (KBr pellets): ν(W–S$_t$) 492.0 and ν(W–S$_b$) 438.4 cm^{-1}.

Crystallography

The crystal data for compounds **1** and **2** are summarized in Table 1, together with some experimental details. Intensity data were collected on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) at 298 K; scan mode ω–2θ. Cell constants were obtained by least-squares fitting to 25 accurately centred reflections (for **1**, $13.7 < \theta < 16.6°$; for **2**, $12.0 < \theta < 17.5°$). All intensity data were corrected for Lorentz-polarization effects. An empirical absorption correction by the ψ-scan method was applied, which resulted in transmission coefficients ranging from 0.561 to 1.000 for **1** and 0.671 to 1.000 for **2**. The structures were solved by direct methods (SIR 92)[25] and refined by full-matrix least-squares analysis on *F*. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and not refined (C–H 0.95 Å). Residuals *R* and *R′* are quoted on *F* at convergence; weighting scheme, $w = \{\sigma_c^2(F_o) + [p^2/4(F_o^2)]\}^{-1}$, $p = 0.0030$ for **1** and 0.0040 for **2**. Calculations were performed on a Silicon-Graphics computer using the TEXSAN program package.[26] The scattering factors for non-hydrogen elements were taken from Cromer and Waber.[27] Selected bond lengths and angles are given in Tables 2 and 3, respectively.

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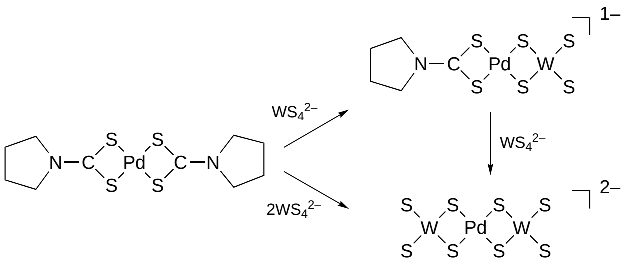
NLO measurements

For optical measurements acetonitrile solutions of samples were placed in a 1 mm (*L*) quartz cuvette. The *Z*-scan[28,29] measurements were carried out with a Q-switched frequency-doubled Nd : YAG laser, which produced linearly polarized, 7 ns, 532 nm optical pulses. The spatial profiles of the optical pulses were nearly Gaussian after passing through a spatial filter. The laser beam was divided by a beam splitter into two parts. The reflected part was taken as a reference representing the incident light energy and the transmitted beam was focused onto the sample with a mirror of 25 cm focal length. The spot radius of the laser beam waist at the focus was measured to be 35 ± 5 μm (ω_0) (half-width at $1/e^2$ maximum in irradiance). The incident and transmitted pulse energies were measured simultaneously by using two energy detectors (Laser Precision, RjP-735 energy probes). The detectors were linked to a computer *via* an IEEE interface. The sample was mounted on a translation stage which was controlled by the computer to adjust the sample position along the *Z* axis with respect to the focal point. To avoid any effect from possible photochemical degradation, the interval between the laser pulses was set to be 20 s so that the experiments were effectively single shots on fresh molecules. To measure the non-linear refraction, an on-axis aperture ($S = 0.40$ for complex **1**, 0.33 for **2**) was positioned right in front of the transmission detector. To test the apparatus the third-order refractive non-linearity (n_2) of CS_2 was measured. A value of $(5 \pm 2) \times 10^{-14}$ cm^2 W^{-1} or $(2.0 \pm 0.8) \times 10^{-11}$ esu was obtained, in good agreement with the reported value of 1.2×10^{-11} esu.[28,29] We also conducted similar measurements on CH_3CN to assess the solvent contribution to the observed non-linearities. The nearly flat lines in the *Z* scans confirmed that the solvent played an insignificant role under the experimental conditions.



Scheme 1

Results and Discussion

Synthesis

Callahan and Cichon[15] had demonstrated the ligand-exchange and -redistribution reaction to obtain mixed-ligand complexes of the type [M(WS_4)(S_2CNEt_2)]$^-$ (M = Ni, Pd or Pt). Owing to the thermal stability of [Pd(WS_4)$_2$]$^{2-}$, in this work no efforts were made to obtain [Pd(WS_4)($S_2CNC_4H_8$)]$^-$ from the ligand-redistribution reaction of [Pd(WS_4)$_2$]$^{2-}$ and [Pd($S_2CNC_4H_8$)$_2$]. The synthetic routes to **1** and **2** are based on the ligand-exchange reaction. The reactant [Pd($S_2CNC_4H_8$)$_2$] was presynthesized and then treated with [NH_4]$_2$[WS_4]; [Pd($S_2CNC_4H_8$)$_2$] is expected to have low thermal stability and the dithiocarbamates could be replaced by the strong ligand WS_4^{2-}.

Compounds **1** and **2** were produced by using different molar ratios of the reactants, [Pd($S_2CNC_4H_8$)$_2$] and [NH_4]$_2$[WS_4] (Scheme 1). When a appropriate amount of [NH_4]$_2$[WS_4] is used only one dithiocarbamate ligand is replaced and the reaction gives a binuclear complex **1**. The product is easily obtained as good-quality single crystals without further recrystallization. When double the amount of [NH_4]$_2$[WS_4] is used two thiocarbamate ligands are substituted and a trinuclear cluster, **2**, is achieved. When the diethyldithiocarbamato complex was used as starting material the diethyldithiocarbamate ligand was more easily replaced by tetrathiotungstate. Also in that case the binuclear product crystallizes with solvent molecules and the crystals readily effloresce.

Crystal structure

Complex **1** is an example of a new type of binuclear palladium–tungsten complex containing thiotungstate as ligand. Compound **2** had been synthesized and characterized by Callahan and Cichon,[15] but its crystal structure was not known. Among the known mixed-metal sulfides containing the moiety MoS_4^{2-} (WS_4^{2-}), there are examples of binuclear complexes such as [RMM′S_4] (R = PhS or CN, M = Cu or Ag, M′ = Mo or W)[30]

Table 1 Crystallographic data for complexes **1** and **2***

	1	**2**
Chemical formula	$C_{13}H_{28}N_2PdS_6W$	$C_{16}H_{40}N_2PdS_8W_2$
M	694.99	991.09
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbca*
a/Å	13.727(1)	13.804(2)
b/Å	8.294(2)	18.138(4)
c/Å	20.009(2)	12.262(2)
β/°	94.072(8)	
U/Å^3	2272.3(5)	3070.0(8)
μ(Mo-Kα)/cm^{-1}	64.07	86.17
F(000)	1344	1888
Crystal size/mm	0.22 × 0.24 × 0.34	0.23 × 0.26 × 0.32
D_c/g cm^{-3}	2.031	2.144
Scan range, ω/°	0.94 + 0.14 tan θ	1.05 + 0.14 tan θ
h, *k*, *l* Ranges	0–14, 0–8, −21 to 21	0–14, 0–20, 0–12
Unique reflections	3217	2308
Observed reflections [$I > 3\sigma(I)$]	2265	1559
R, *R′*	0.024, 0.023	0.030, 0.030
Maximum shift in final cycle	0.05	0.05
Peaks and holes in final difference map/e Å^{-3}	0.37 to −0.45	0.69 to −0.73

* Details in common: $Z = 4$; $2\theta_{max} = 45.0°$; scan speed 16.0° min^{-1} (in ω).

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

W–Pd	2.8669(7)	W–S(1)	2.153(2)
W–S(2)	2.148(2)	W–S(3)	2.235(2)
W–S(4)	2.236(2)	Pd–S(3)	2.342(2)
Pd–S(4)	2.336(2)	Pd–S(5)	2.322(2)
Pd–S(6)	2.319(2)	S(5)–C(1)	1.712(7)
S(6)–C(1)	1.725(7)	N(1)–C(1)	1.287(9)
N(1)–C(2)	1.474(9)	N(1)–C(5)	1.493(9)
S(1)–W–S(2)	108.81(9)	S(1)–W–S(3)	110.49(9)
S(1)–W–S(4)	110.32(9)	S(2)–W–S(3)	110.31(9)
S(2)–W–S(4)	111.37(10)	S(3)–W–S(4)	105.51(7)
S(3)–Pd–S(4)	99.10(8)	S(3)–Pd–S(5)	92.58(7)
S(3)–Pd–S(6)	167.38(8)	S(4)–Pd–S(5)	167.50(8)
S(4)–Pd–S(6)	93.29(7)	S(5)–Pd–S(6)	75.27(7)
W–S(3)–Pd	77.54(6)	W–S(4)–Pd	77.63(6)
C(1)–N(2)–C(2)	125.2(6)	C(1)–N(1)–C(5)	124.9(7)
C(2)–N(1)–C(5)	109.9(6)	S(5)–C(1)–S(6)	111.1(4)
S(5)–C(1)–N(1)	125.3(6)	S(6)–C(1)–N(1)	123.6(6)
N(1)–C(2)–C(3)	104.1(6)	N(1)–C(5)–C(4)	104.6(7)
C(2)–C(3)–C(4)	106.0(7)	C(3)–C(4)–C(5)	104.1(7)

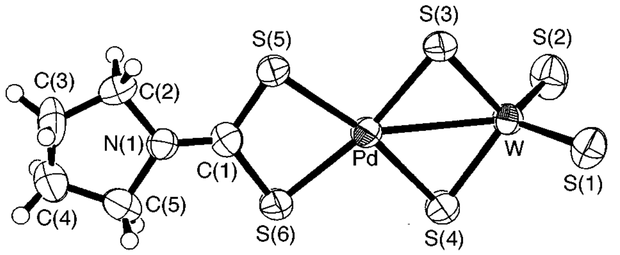


Fig. 1 An ORTEP drawing of the molecular structure and labelling scheme for the anion portion of $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ **1**

and trinuclear clusters such as $[M(M'S_4)_2]^{n-}$ (M = Cu, Ag, Ni, Pt, Hg, Pb,[31] Zn[32] or Mn;[33] (M′ = Mo or W).

The ORTEP[34] diagram of the anion $[PdWS_4(S_2CNC_4H_8)]^-$ of compound **1** is shown in Fig. 1. The palladium atom is co-ordinated by a pyrrolidinecarbodithioate and a tetrathiotungstate, which both act as bidentate ligands with two sulfur atoms as chelates. The configuration of the dithiocarbamate is similar to that found in $[Pd(S_2CNC_4H_8)(PEt_3)\{\eta^1\text{-}CH(CN)CH_3\}]$[35] and $[Pd(S_2CNC_4H_8)(PEt_3)\{CH(CH_3)_2\}]$.[36] The S(5)–C(1)–S(6) angle of 111.1(4)° is smaller than the average S–C–S angle of 114.2(2)° found in the above two complexes, while the S(5)–Pd and S(6)–Pd distances are shorter than the average S–Pd distance of 2.384(1) Å. This indicates that a much tighter connection between thiocarbamate ligand and palladium atom is formed in **1** than that in the above two organopalladium complexes. The S(5)–Pd–S(6) bond angle is restricted by the chelate ring to 75.27(7)° and is much smaller than the other three S–Pd–S angles. Owing to the interaction between palladium and tungsten atoms, the S(3)–Pd–S(4) angle is opened to 99.10(8)°, which is much bigger than the square planar four-co-ordinate angle of 90°. All the Pd–S bonds are in the range of 2.319(2)–2.342(2) Å, which are comparable to those found in $[Pd(i\text{-}mnt)_2]^{2-}$ (i-mnt = isomaleonitrile dithiolate).[5] The configuration of the WS_4 moiety is tetrahedral similar to that in $[Ag(WS_4)(CN)]^{2-}$.[30] The two terminal W–S_t distances are near to those of 2.153(3) and 2.158(3) Å found in $[Ag(WS_4)(CN)]^{2-}$. The two bridging W–S_b bonds are a little longer than the W–S_t bonds as is usually observed in related compounds.[19,30] The S(3)–W–S(4) angle is 4° smaller than the other five S–W–S angles. This is opposite to the case of $[Ag(WS_4)(CN)]^{2-}$, in which the S_b–W–S_b angle is bigger than the others.

Table 3 Selected bond distances (Å) and angles (°) for complex **2**

W(1)–Pd	2.9008(5)	W(1)–S(1)	2.240(3)
W(1)–S(2)	2.238(3)	W(1)–S(3)	2.148(3)
W(1)–S(4)	2.149(4)	Pd–S(1)	2.359(3)
Pd–S(1*)	2.359(3)	Pd–S(2)	2.347(3)
S(1)–W(1)–S(2)	105.2(1)	S(1)–W(1)–S(3)	110.3(1)
S(1)–W(1)–S(4)	110.7(1)	S(2)–W(1)–S(3)	110.3(1)
S(2)–W(1)–S(4)	111.5(1)	S(3)–W(1)–S(4)	108.9(1)
S(1)–Pd–S(2)	98.2(1)	S(1)–Pd–S(2*)	81.8(1)
W(1)–S(1)–Pd	78.2(1)	W(1)–S(2)–Pd	78.5(1)

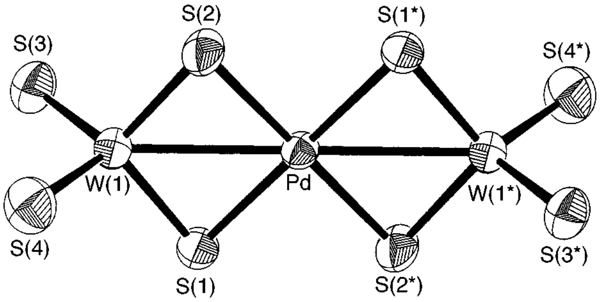


Fig. 2 An ORTEP drawing of the molecular structure and labelling scheme for the anion portion of $[NEt_4]_2[PdW_2S_8]$ **2**

The centrosymmetric $[Pd(WS_4)_2]^{2-}$ anion and the atom numbering scheme of compound **2** is depicted in Fig. 2, and confirms the structure proposed by Callahan and Cichon.[15] The palladium atom disposed at the centre of symmetry is co-ordinated by four sulfur atoms, the five-atom assembly being planar as required by the symmetry. The Pd–S(1), Pd–S(2) distances and S(1)–Pd–S(2) angle are comparable to those found in compound **1** and $[Pd(WS_4)(Ph_2PCH_2PPh_2)]$.[19] The configuration of the tetrathiotungstate is very similar to that in compound **1**. The WS_4 tetrahedron is distorted with angles varying from 105.2(1) to 111.5(1)°. The $Pd(S_b)_2W$ and $W(S_t)_2$ moieties of **2** are planar within 0.0113 and 0.0014 Å, respectively. The dihedral angle between these two planes is 89.75°.

The Pd–W distances 2.8669(7) Å in complex **1** and 2.9008(5) Å in **2** are slightly longer than the sum of the atomic radii for these two metals. Metal–metal bonding might appear to be a logical consequence of placing two metals in close proximity as in **1** and **2**. The formal oxidation states, Pd^{II} and W^{VI}, may mean them having small ionic radii, but the actual oxidation states of the palladium and tungsten centres are still to be confirmed. Metal–metal interactions in bridged thiometalate derivatives can be gauged from the angles about the bridging atoms.[37] A remarkable structural feature of **1** and **2** is the sharply acute

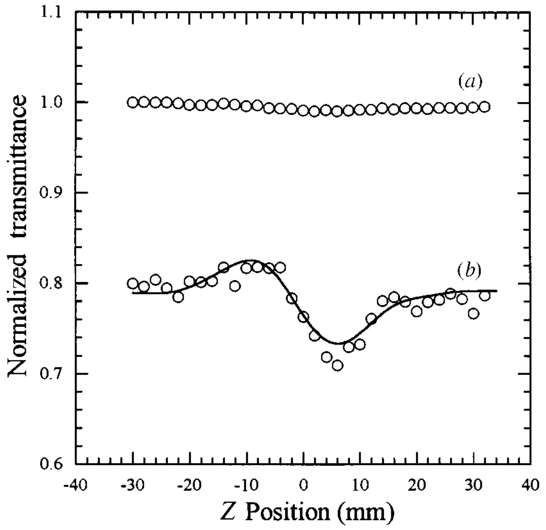


Fig. 3 The Z-scan data of $[NEt_4][PdWS_4(S_2CNC_4H_8)]$ **1** in acetonitrile, concentration 1.0×10^{-3} mol dm^{-3}, at 532 nm with incident energy of 88 μJ per pulse, $\alpha_0 = 108$ m^{-1}; (*a*) collected in the open-aperture configuration and showing small NLO absorption; (*b*) the Z-scan data and curve (displaced downward by 0.2 from 1.0 for clarity) obtained by dividing the normalized Z-scan data at closed-aperture configuration by the normalized Z-scan data in (*a*)

$Pd-S_b-W$ angles as shown in Tables 2 and 3, accompanied by the opened-up S_b-W-S_b and S_b-Pd-S_b angles as mentioned above. More significantly the observed distortion of the $Pd(S_b)_2W$ rhombus may imply a direct, transannular Pd–W bonding interaction. Such a interpretation has been applied in thiometalate systems such as $[(Ph_3P)_2Ag(\mu\text{-}WS_4)Ag(PPh_3)]$ [metal–metal bond distances 3.056(2) and 2.886(2) Å],[38] $[\{Pd(C_6F_5)\}_2(\mu\text{-}WS_4)]$ [2.848(1) Å],[22] $[NPr^n_4]_2[Ag(WS_4)(CN)]$ [2.890(1) Å],[30] $[NPr^n_4]_2[Cu(MoS_4)(CN)]$ [2.624(1) Å],[30] and $[\{Au(PMePh_2)\}_2(\mu\text{-}WS_4)]$ [2.836(1) and 2.843(1) Å].[39]

The structures of the NEt_4 cations in compounds **1** and **2** are unremarkable, and there are no short anion–cation contacts.

Electronic spectra

The electronic spectra of the complexes exhibit absorption peaks at the wavelengths (with absorption coefficients in dm^3 mol^{-1} cm^{-1}) of 403 (1.0×10^3) and 349 nm (1.9×10^3) for **1**, 398 (2×10^3), 361 (2.1×10^3) and 314 nm (2.7×10^3) for **2**. The assignment of the electronic transitions in simple oxo- thio- and seleno-anions of the transition metals (Mo, W) with T_d and C_{3v} symmetry was studied two decades ago. There is a general consensus that for the simple WS_4^{2-} unit three strong absorption bands, 392, 277 and 216 nm, are attributable to ligand-to-metal charge-transfer transitions $1t_1 \longrightarrow 2e$, $t_1 \longrightarrow 4t_2$ and $3t_2 \longrightarrow 2e$, respectively. Some of the general assignments have proven to be applicable to the Group 6–Group 11 sulfido clusters synthesized later.[4,11b] For Group 10 metal M^{2+} ions having a d^8 electron shell, ligand-to-metal charge-transfer bands are expected to appear, so the electronic spectra of the Group 6–Group 10 sulfido system are more complicated than those of the Group 6–Group 11 sulfido system. Both compounds **1** and **2** have relatively low linear absorptivity at 532 nm. This result is important for the measurements and application of non-linear optical properties.[2a]

Optical properties

The non-linear optical properties of compound **1** and **2** were investigated as the first example of Group 6–Group 10 mixed-metal complexes and clusters, using the Z-scan technique.[28,29] The Z-scan data are given in Figs. 3 and 4. The NLO properties of compound **1** are relatively simple: they are dominated by non-linear refraction; non-linear absorption is negligible. Compound **2** shows both non-linear absorption and refraction. The valley-peak pattern of the normalized transmittance curve obtained in the closed-aperture configuration for compounds **1** and **2** indicates characteristic self-defocusing behaviour of the propagating light in the sample.

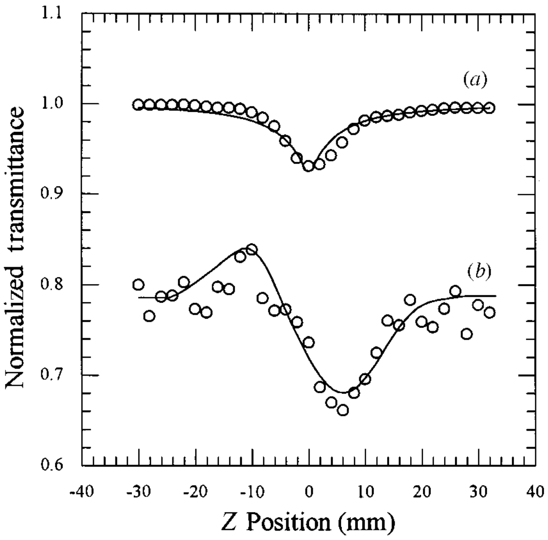


Fig. 4 The Z-scan data of $[NEt_4]_2[PdW_2S_8]$ **2** in acetonitrile, concentration 1.6×10^{-3} mol dm^{-3}, at 532 nm with incident energy of 140 μJ per pulse, $\alpha_0 = 99$ m^{-1}: (*a*) collected in the open-aperture configuration and showing NLO absorption [solid curve is a theoretical fit based on equations (1) and (2)], (*b*) the Z-scan data and curve (displaced downward by 0.2 from 1.0 for clarity) obtained as in Fig. 3

The non-linear absorption component of compound **2** was evaluated by Z-scan experiment in the open-aperture configuration. Theoretical curves of transmittance against the position, equations (1) and (2), were fitted to the observed Z-scan data by

$$T(Z) = [1/\sqrt{\pi}q(Z)] \int_{-\infty}^{+\infty} \ln[1 + q(Z)]e^{-\tau^2}\,d\tau \qquad (1)$$

$$q(Z) = \alpha_2 I(Z)(1 - e^{-\alpha_0 L})/\alpha_0 \qquad (2)$$

varying the effective third-order NLO absorptivity α_2 value, where the experimentally measured α_0 (linear absorptivity), L (the optical path of sample) and $I_i(Z)$ (the on-axis irradiance at position Z) were adopted. The solid line in Fig. 4(*a*) is the theoretical curve calculated with $\alpha_2 = 3.5 \times 10^{-11}$ m W^{-1}.

The non-linear refractive components of complexes **1** and **2** were assessed by dividing the normalized Z-scan data obtained in the closed-aperture configuration by those obtained in the open-aperture configuration. They are plotted in Figs. 3(*b*) and 4(*b*) for **1** and **2**, respectively; the solid curves are an eye guide for comparison where the effective NLO refractivity n_2 values estimated therefore are -6.8×10^{-18} m^2 W^{-1} for **1** and -7.5×10^{-18} m^2 W^{-1} for **2**, respectively.

A series of Group 6–Group 11 sulfido cluster compounds had demonstrated very interesting non-linear optical properties.[1,2] In a number of aspects they are comparable to or even better than the best NLO materials ever reported.[4] Comparatively, compounds **1** and **2** are inferior in NLO properties to most Group 6–Group 11 sulfido cluster compounds. For example the trinuclear cluster $[Cu_2WOS_3(PPh_3)_4]$, the NLO refraction of which is relatively low for Group 6–Group 11 sulfido cluster compounds, at concentration 1.2×10^{-4} mol dm^{-3} has the same magnitude of n_2 value as that of **1** has at a concentration of 1.0×10^{-3} mol dm^{-3}. This may first be attributed to their structures. In the Group 6–Group 11 sulfido cluster compounds Mo^{VI}, W^{VI}, Cu^I and Ag^I are all co-ordinated tetrahedrally. Symmetry matching can enhance the metal–metal interaction. In **1** and **2** the geometry of WS_4 is tetrahedral, while that of PdS_4 is planar. The greater the incorporation of metal atoms, the more sublevels can be introduced into the energy hierarchy, which permits more spin-allowed excited-state to excited-state transitions to take place and hence larger non-linear absorption.[2*a*] Another reason is the low nuclearity. A cluster with larger nuclearity is expected to have more favourable NLO properties.[3*e*] In fact, compounds **1** and **2** are bi- or tri-nuclear clusters and the nuclearities are relatively lower compared to those of Group 6–Group 11 sulfido cluster compounds we studied.[2,3] More work including the synthesis of larger nuclearity clusters should be done before a conclusion can be drawn about NLO properties of Group 6–Group 10 sulfides.

References

1 G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, 1976, **19**, 1.

2 (*a*) S. Shi, W. Ji, S. H. Tang, J. P. Lang and X. Q. Xin, *J. Am. Chem. Soc.*, 1994, **116**, 3615; (*b*) S. Shi, W. Ji, J. P. Lang and X. Q. Xin, *J. Phys. Chem.*, 1994, **98**, 3570; (*c*) S. Shi, W. Ji, W. Xie, T. C. Hong, H. C. Zeng, J. P. Lang and X. Q. Xin, *Mater. Chem. Phys.*, 1995, **39**, 298; (*d*) H. W. Hou, X. Q. Xin, J. Liu, M. Q. Chen and S. Shi, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3211; (*e*) H. W. Hou, X. R. Ye, X. Q. Xin, J. Liu, M. Q. Chen and S. Shi, *Chem. Mater.*, 1995, **7**, 472; (*f*) W. Ji, S. Shi, H. J. Du, S. W. Tang and X. Q. Xin, *J. Phys. Chem.*, 1995, **99**, 17 297; (*g*) D. L. Long, S. Shi, X. Q. Xin, B. S. Luo, L. R. Chen, X. Y. Huang and B. S. Kang, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 2617; (*h*) H. W. Hou, D. L. Long, X. Q. Xin, X. Y. Huang, B. S. Kang, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 5363; (*i*) P. Ge, S. H. Tang, W. Ji, S. Shi, H. W. Hou, D. L. Long, X. Q. Xin, S. F. Lu and Q. J. Wu, *J. Phys. Chem. B*, 1997, **101**, 27; (*j*) H.-G. Zheng, W. Ji, M. L. K. Low, G. Sakane, T. Shibahara and X.-Q. Xin, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 2357.

3 (*a*) S. Shi, W. Ji and X. Q. Xin, *J. Phys. Chem.*, 1995, **99**, 894; (*b*) S. Shi, H. W. Hou and X. Q. Xin, *J. Phys. Chem.*, 1995, **99**, 4050; (*c*) S. Shi, Z. R. Chen, H. W. Hou, X. Q. Xin and K. B. Yu, *Chem. Mater.*, 1995, **7**, 1519; (*d*) Z. R. Chen, H. W. Hou, X. Q. Xin, K. B. Yu and S. Shi, *J. Phys. Chem.*, 1995, **99**, 8717; (*e*) G. Sankane, T. Shibahara, H. W. Hou, X. Q. Xin and S. Shi, *Inorg. Chem.*, 1995, **34**, 4785; (*f*) W. Ji, H. J. Du, S. H. Tang, S. Shi, J. P. Lang and X. Q. Xin, *Singapore J. Phys.*, 1995, **11**, 55; (*g*) S. Shi, Z. Lin, Y. Mo and X. Q. Xin, *J. Phys. Chem.*, 1996, **100**, 10 696; (*h*) H. W. Hou, B. Liang, X. Q. Xin, K. B. Yu, P. Ge, W. Ji and S. Shu, *J. Chem. Soc.*, *Faraday Trans.*, 1996, 2343; (*i*) J. P. Lang, K. Tatsumi, H. Kawaguchi, J. M. Lu, P. Ge, W. Ji and S. Shi, *Inorg. Chem.*, 1996, **35**, 7924.

4 H. W. Hou, X. Q. Xin and S. Shu, *Coord. Chem. Rev.*, 1996, **153**, 25.

5 D. L. Long, H. W. Hou, X. Q. Xin, K. B. Yu, B. S. Luo and L. R. Chen, *J. Coord. Chem.*, 1996, **38**, 15.

6 M. J. Chetcuti, *J. Cluster Sci.*, 1996, **7**, 225.

7 A. Mueller, E. Ahlbor and H.-H. Heinsoen, *Z. Anorg. Allg. Chem.*, 1971, **102**, 386; A. Mueller and E. Diemann, *J. Chem. Soc. D*, 1971, 65; A. Mueller, M. C. Chakrovorti and H. Dornfield, *Z. Naturforsch.*, *Teil B*, 1975, **30**, 162.

8 K. P. Callahan and P. A. Piliero, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 13.

9 K. P. Callahan and P. A. Piliero, *Inorg. Chem.*, 1980, **19**, 2619.

10 K. H. Schmidt and A. Mueller, *Coord. Chem. Rev.*, 1974, **14**, 115; A. Cormier, K. Nakamoto, E. Ahlborn and A. Mueller, *J. Mol. Struct.*, 1975, **25**, 43; E. Koniger-Ahlborn, A. Mueller, A. D. Cormier, J. D. Brown and K. Nakamoto, *Inorg. Chem.*, 1975, **14**, 2009.

11 (*a*) A. Mueller, R. Jostes, W. Eltzner, C. Nie, E. Diemann, H. Boegge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem.*, 1985, **24**, 2872; (*b*) A. Mueller, E. Diemann, R. Jostes and H. Boegge, *Angew. Chem. Int. Ed. Engl.*, 1981, **10**, 934.

12 R. J. H. Clark and J. R. Walton, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1535.

13 B. D. El-Issa and M. M. Zeedan, *Inorg. Chem.*, 1991, **30**, 2594.

14 I. Søtofte, *Acta Chem. Scand.*, *Ser. A*, 1976, **30**, 157.

15 K. P. Callahan and E. J. Cichon, *Inorg. Chem.*, 1981, **20**, 1941.

16 G. A. Bowmaker, P. D. W. Boyd, G. K. Campbell and M. Zvagulis, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 1065.

17 A. R. Siedle, C. R. Hubbard, A. D. Mighell, R. M. Doherty and J. M. Stewart, *Inorg. Chim. Acta*, 1980, **38**, 197.

18 C. Potevin, J.-M. Manoli, F. Secheresse and S. Marzak, *Inorg. Chim. Acta*, 1987, **134**, 9.

19 B. Wu, W. Zhang, X. Huang, X. Wu and S. Yu, *Polyhedron*, 1997, **16**, 801.

20 K. E. Howard, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1988, **27**, 3561.

21 K. E. Howard, J. R. Lockemeyer, M. A. Massa, T. B. Rauchfuss, S. R. Wilson and X. Yang, *Inorg. Chem.*, 1990, **29**, 4385.

22 J. Ruiz, V. Rodriguez, G. Lopez, P. A. Chaloner and P. B. Hitchcock, *J. Organomet. Chem.*, 1995, **493**, 77.

23 G. Sanchez, G. Momblona, G. Garcia, G. Loepez, E. Pinilla and A. Monge, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2271.

24 J. W. McDonald, G. D. Friesen, L. D. Rosenhein and W. E. Newton, *Inorg. Chim. Acta*, 1983, **72**, 205.

25 A. Altomare, M. C. Burla, G. Camalli, G. Cascarano, C. Giacovazzo, A. Gualiardi and G. Polidori, SIR 92, *J. Appl. Crystallogr.*, 1994, **27**, 435.

26 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985, 1992.

27 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham (Present Distributor, Kluwer Academic Publishers, Dordrecht), 1974, vol. 4, Tables 2.2a and 2.3.1.

28 M. Sheik-Bahae, A. A. Said and E. W. Van Stryland, *Opt. Lett.*, 1989, **14**, 955.

29 M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, *IEEE J. Quantum Electron*, 1990, **26**, 760.

30 S. F. Gheller, T. W. Hambley, J. R. Rodgers, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem.*, 1984, **23**, 2519.

31 A. Mueller, H. Boegge, U. Schimanski, M. Fenk, K. Nieradzik, M. Dartmann, E. Krickemeyer, J. Schimanski, C. Roemer, M. Roemer, H. Dornfield, U. Wienboeker, W. Hellmann and M. Zimmermann, *Monatsh. Chem.*, 1989, **120**, 367.

32 I. Paulat-Boeschen, B. Krebs, A. Mueller, E. Koeniger-Ahlborn, H. Dornfeld and H. Schulz, *Inorg. Chem.*, 1978, **17**, 1440.

33 B. Alessandro, C. Franco, A. G. Carlo, M. Stefano, N. Francesco and O. Amabella, *Inorg. Chem.*, 1992, **31**, 5339.

34 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

35 D. L. Reger, D. G. Garza and L. Lebioda, *Organometallics*, 1992, **11**, 4285.

36 D. L. Reger, D. G. Garza and L. Lebioda, *Organometallics*, 1991, **10**, 902.

37 D. F. Lewis, S. J. Lippard and J. A. Zubieta, *J. Am. Chem. Soc.*, 1972, **94**, 1563.

38 A. Mueller, H. Boegge and E. Koeniger-Albom, *Z. Naturforsch.*, *Teil B*, 1979, **34**, 1968.

39 J. C. Huffman, R. S. Roth and A. R. Siedle, *J. Am. Chem. Soc.*, 1976, **98**, 4340.

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