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Synthesis, optical nonlinearity and crystal structure of a novel mixed-chalcogen, thiolato-bridged complex $[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}S)(\mu\text{-}Te)(\mu\text{-}SPh)_2]$

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Abstract

A novel dimolybdenum complex in which the metal atoms are bridged by two different chalcogens and two thiolato ligands has been synthesised and structurally characterised. This complex shows a large third-order optical nonlinearity as measured by degenerate four-wave mixing with picosecond excitation at 532 nm. A hyperpolarisability (γ) of 1.2×10^{-30} esu has been obtained. The structure of the complex was established by the single-crystal X-ray diffraction method. It consists of a Mo–Mo unit, which is bridged by one S, one Te and two (SPh) groups. Each Mo atom also has a (η^5-C_5H_5) group attached to it. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Sulfur; Tellurium; Thiolato; Complex

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1. Introduction

The strategy of using certain main group elements as bridges in cluster growth reactions has been successfully used for obtaining a large number of transition metal, nonmetal cluster compounds [1]. Group 16 elements have been widely used for such purpose and the compounds $[Fe_2(CO)_6(\mu\text{-}EE')]$ and $[Fe_3(CO)_9(\mu_3\text{-}E)(\mu_3\text{-}E')]$ (E, E′ = S, Se or Te) have been recognised as convenient starting materials for synthesis of numerous chalcogen bridged cluster compounds [2]. In recent times, optical properties of some inorganic clusters have attracted attention, both in the linear and nonlinear regimes, not only for the fundamental aspects of optical excitation in these materials but also due to their potential for device applications. Interest in the nonlinear regime has stemmed from possibilities for obtaining materials with large nonlinear susceptibilities under nonresonant excitation [3,4]. Some of the chalcogen-bridged clusters synthesised by us display interesting NLO properties [5].

Although chalcogens are now recognised to serve as important ligands towards systematic cluster growth, their influence as stabilising ligands is also being investigated with interest. From the thermolysis of $[Fe_3(CO)_9(\mu_3\text{-}E)(\mu_3\text{-}E')]$ and $[Cp_2Mo_2(CO)_6]$, mixed Fe/Mo carbonyl clusters with one to three bridging chalcogen ligands can be isolated [6]. One such type of cluster, $[Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}E)(\mu_3\text{-}E')]$, contains a tetrahedral metal framework in which two faces are bridged by chalcogen ligands. Our studies indicate that this cluster undergoes fragmentation reaction under facile conditions to produce chalcogen bridged dimolybdenum compounds, $[Cp_2Mo_2(CO)_2(\mu\text{-}E)(\mu\text{-}X)]$ (E = S or Te, X = O; E = Te, X = NPh) [7]. Also, we recently reported that thermolysis of $[Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}S)(\mu_3\text{-}Te)]$ with PhSH, forms the μ_3-hydride, μ-thiolato bridged dichalcogenide mixed metal cluster $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ [8].

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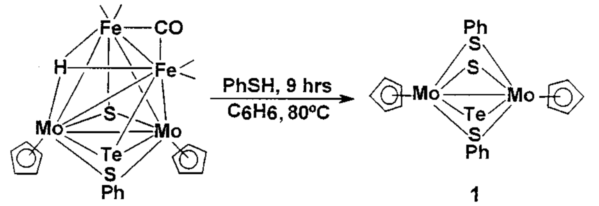

Scheme 1.

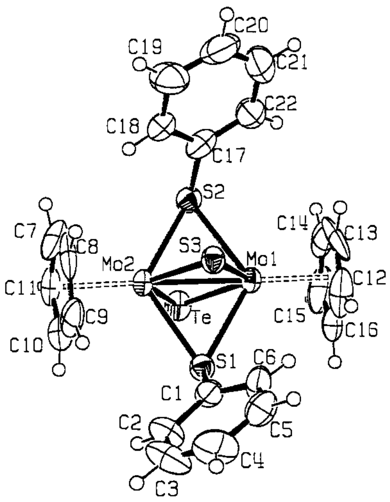

Fig. 1. Molecular structure of $Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}Te)(\mu\text{-}SPh)_2$ (**1**).

Transition metal complexes containing thiolato ligands continue to be the focus of considerable research activity. Mitsudo and co-workers [9,10] have reported on the use of a thiolato complex of ruthenium, $[Cp^*RuCl(\mu\text{-}SPh)]_2$, as a promising catalyst for the transformation of sulfur-containing organic compounds. The reactions of cationic class of compounds Mo(IV)/sulfide clusters containing Mo and a Group 8 metal are particularly interesting as models for hydrodesulfurisation (HDS) catalysts. Moreover, there is a continuing importance of molybdenum complexes containing thiolate, thioether or sulfide as models for the molybdenum centre in nitrogenase [11–13]. Recently, Baker et al. [14] have reported on the synthesis and crystallographic characterisation of a series of new 16-electron dithiolate complexes $[W(SPh)_2(CO)_2(PEt_3)_2]$ and $[M\{S(CH_2)_nS\}(CO)_2(PEt_3)_2]$ ($M = Mo$ or W, $n = 2$; $M = W$, $n = 3$). In continuation of our interest in the synthesis of chalcogen-bridged species, we report here on the synthesis and structure of a dimolybdenum compound containing different bridging chalcogens and thiolato bridges.

2. Results and discussion

2.1. Synthesis and characterisation of $[Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}Te)(\mu\text{-}SPh)_2]$

When a benzene solution containing $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ [8] and a large excess of PhSH was subjected to reflux for 9 h, the new blue compound $[Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}Te)(\mu\text{-}SPh)_2]$ (**1**) was obtained in 53% yield (Scheme 1). There was substantial decomposition in the reaction mixtures and the fate of any Fe-containing products is unknown.

^{1}H-NMR spectroscopy confirmed the presence of (η^5-C_5H_5) and (C_6H_5) groups in **1**. Also, the presence of tellurium was confirmed by observation of a single peak in the ^{125}Te-NMR spectrum. Its unambiguous structural assignment is based on a single-crystal X-ray structure analysis.

The molecular structure of **1** is shown in Fig. 1. It consists of a Mo–Mo unit, which is bridged by one S, one Te and two (SPh) groups. Each Mo atom also has a (η^5-C_5H_5) group attached to it. The Mo–Mo bond length of 2.6263(18) Å is slightly longer than the Mo–Mo bond distances in $Cp_2Mo_2S_4$ derivatives, which are normally in the range 2.59–2.61 Å [15], but is comparable with the metal–metal distance of 2.635(1) Å in $[(CpMo)_2(S_2CH_2)\text{-}(S_2CCH_3)Br]$ [16]. It is, however, shorter than the Mo–Mo bond distance in the precursor $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ (2.669(1) Å) or in $[Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}S)(\mu_3\text{-}Te)]$ (2.783(1) Å) and is considerably shorter than the bond distance of 3.073(1) Å observed in $[\{CpMo(S)(S_2C_6H_5)\}]_2$ [6,8]. The Mo–Mo bond length in **1** is longer than the Mo=Mo double-bonded distances reported for the *trans*/*anti* and *trans*/*syn* isomers of $(\eta^5\text{-}RC_5H_4)_2M_2(CO)_2(\mu\text{-}SePh)_2$ (2.609(1) and 2.598(1) Å, respectively) [17], as also for the *trans*/*anti* and *trans*/*syn* isomers of $Cp_2Mo_2(CO)_2(\mu\text{-}SPh)_2$ (2.616(2) and 2.569(6) Å, respectively) [18,19] and in $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_2(CF_3)_2SCH_3)](BF_4)$ (2.604(1) Å) [20]. The average Mo–S(1)–Ph distance (2.484 Å) and Mo–S(2)–Ph distance (2.495 Å) is comparable to other such Mo–SR bond distances found in literature, for instance, Mo–S–Me (2.411(4) Å) in $[Cp_2Mo_2(S_2CH_2(\mu\text{-}SMe)(\mu\text{-}Cl))]$ or the average Mo–S–Me distance (2.453 Å) in $[CpMo(CO)_2(S_2CH_2)(\mu\text{-}SMe)]^+$ or the Mo–S(Pr)^i distance (2.536 Å) in $[Mo_2Ru_2(\mu_3\text{-}S)_2(\mu\text{-}SPr^i)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ [16,21]. The Mo–S and Mo–Te distances in **1** are unexceptional.

The formation of the blue compound, **1**, may be envisaged to occur from decarbonylation and fragmentation of the parent compound under the thermolytic conditions. Several other compounds were observed during chromatographic work-up, but they could not be characterised completely due to insufficient yields. Compound **1** was also obtained by a different route in a slightly lower yield of 34% together with the parent compound $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}$

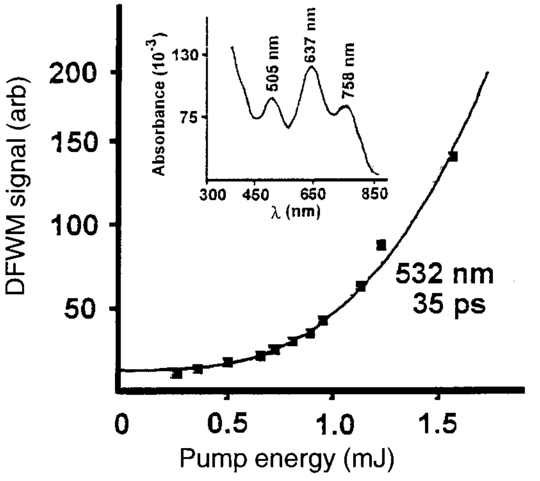

Fig. 2. DFWM signal variation with pump pulse energy. The solid curve is a cubic polynomial fit to the data. The inset shows the linear absorption spectrum of **1**.

Table 1
Comparison of the nonlinear response of the clusters

Cluster	Absorption coefficient (cm^{-1}) at 532 nm	γ (molecular hyperpolarisability) (esu)
$Cp_2Mo_2(\mu\text{-}S)(\mu\text{-}Te)(\mu\text{-}SPh)_2$ (**1**)	0.24	1.21×10^{-30}
$Cp_2Mo_2Fe_2STe(\mu\text{-}SPh)(\mu_3\text{-}H)(CO)_5$	1.05	5.31×10^{-31}
$Cp_2Mo_2Fe_2STe(CO)_7$	1.3	3.64×10^{-31}
C_{60} (Ref. [26])	6 (at 1064 nm)	3×10^{-34}

H)] (yield 41%) when a benzene solution of $[Cp_2Mo_2Fe_2(CO)_7(\mu_3\text{-}S)(\mu_3\text{-}Te)]$ and a large excess of PhSH was subjected to reflux for 9 h.

2.2. *Nonlinear optical properties of* **1**

We find the value of χ^3 for compound **1**, as measured using the degenerate four-wave mixing (DFWM) technique [22] to be large. Fig. 2 shows the DFWM signal at 532 nm as a function of input pulse energy. The inset in the Figure shows the linear absorption spectrum. It is evident that there is insignificant absorption at 532 nm and hence the nonlinearity is mainly nonresonant.

The DFWM signal shows the expected cubic dependence on the energy of one of the pump pulses. From these data, and taking the refractive indices of n-hexane and CS_2 to be 1.372 and 1.628, respectively, a χ^3 of 4.5×10^{-13} esu was obtained for **1**. From this value and the concentration of the solution, the molecular hyperpolarisability γ was found to be 1.21×10^{-30} esu. This value is at least one order of magnitude larger than those reported for other frequently cited, promising materials like phthalocyanine, for which DFWM data under nonresonant excitation are available [23,24]. Among clusters, compound **1** has hyperpolarisability that is four orders of magnitude larger than the well known fullerene, C_{60}, data for which were obtained under similar nonresonant excitation conditions.

It is worthwhile comparing the magnitude of nonlinearity of compound **1** with that of the starting materials from which it was synthesised (Table 1). It is evident that the nonlinearity in either starting material is an order of magnitude lower than in the final compound **1**. The large nonresonant third-order hyperpolarisability of **1** indicates that it is a promising nonlinear optical material.

3. Experimental

3.1. *General procedures*

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon. All solvents were deoxygenated immediately prior to use. Infrared spectra were recorded on an Impact 400 FTIR spectrophotometer, as hexane solutions in 0.1 mm path length cells. Elemental analysis was performed using a Carlo–Erba automatic analyser. ^{1}H- and ^{125}Te-NMR spectra were recorded on a Varian VXR-300S spectrometer in $CDCl_3$. The operating frequency for ^{125}Te-NMR spectrum was 94.705 MHz with a pulse width of 9.5 μs and a delay of 1 s. The spectrum was referenced to Me_2Te ($\delta = 0$). The starting materials $[Cp_2Mo_2Fe_2\text{-}(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ and $[Cp_2Mo_2Fe_2STe(CO)_7]$ were prepared as reported in literature [8,6]. Thiophenol was purchased from Fluka and used as such.

3.2. *Reaction of* $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)\text{-}(\mu\text{-}SPh)(\mu_3\text{-}H)]$ *with PhSH*

A benzene solution of $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ (0.80 g, 0.095 mmol) and PhSH (0.4 ml, 3.6 mmol) was refluxed with constant stirring for 9 h. The solvent was removed in vacuo and the residue was subjected to chromatographic work-up using silica gel TLC plates. On elution with hexane–benzene mixture (50:50, v/v), compound **1** was separated (36.1 mg, 53%), together with unreacted $[Cp_2Mo_2Fe_2(CO)_5(\mu_3\text{-}S)(\mu_3\text{-}Te)(\mu\text{-}SPh)(\mu_3\text{-}H)]$ and some other compounds that could not be characterised completely due to insufficient yields. IR for **1** [hexane, ν cm^{-1}]: 1523 (m, br), 1465 (m, br), 1383 (sh), 1231 (vs), 1225 (vs), 1202 (vs), 1024 (m, br), 930 (s), 913 (vs), 806 (s), 767 (vs), 725 (vs). ^{1}H-NMR [$CDCl_3$]: δ 6.51 (s, C_5H_5), 6.92–6.94 (m,

C_6H_5). ^{125}Te-NMR [$CDCl_3$]: δ 761. Anal. Calc. for $C_{22}H_{20}Mo_2S_3Te{\cdot}CH_2Cl_2$: C, 36.8; H, 3.10. Found: C, 36.5; H, 3.34%.

3.3. Thermolysis of [$Cp_2Mo_2Fe_2(CO)_7(\mu_3$-S)(μ_3-Te)] with PhSH

A benzene solution (50 ml) of [$Cp_2Mo_2Fe_2(CO)_7(\mu_3$-S)(μ_3-Te)] (0.15 g, 0.19 mmol) and thiophenol (0.4 ml, 3.6 mmol) was refluxed with constant stirring for 9 h. The solvent was removed in vacuo and the residue was subjected to chromatographic work-up using silica gel TLC plates. Using hexane–benzene (50:50, v/v) mixture as eluent, the new blue compound [Cp_2Mo_2(μ-S)(μ-Te)(μ-SPh)$_2$] (**1**) (0.046 g, 34%) could be isolated together with the red [$Cp_2Mo_2Fe_2$-$(CO)_5$(μ_3-S)(μ_3-Te)-(μ-SPh)(μ_3-H)] (0.066 g, 41%).

3.4. Structural characterisation of 1

Crystal data: $C_{22}H_{20}Mo_2S_3Te.H_2O$, monoclinic, $P2_1/c$, $a = 10.938(2)$, $b = 10.926(2)$, $c = 20.337(4)$ Å, $\beta = 99.24(3)°$, $U = 2398.9(8)$ Å^3, wavelength = 0.71073 Å, $Z = 4$, $\mu(\text{Mo–K}_\alpha) = 2.510$ mm^{-1}, $D_{\text{calc}} = 1.988$ Mg m^{-3} number of reflections collected/unique = 4849/4710. Dark-blue crystals of **1** were grown from dichloromethane–hexane solvent mixtures at −5°C. A dark-blue opaque single crystal was mounted using glue to a thin glass fibre. Diffraction data were collected on Nonius Turbo CAD4 four-circle diffractometer. Of a total of 4849 data collected in the θ-range of 2.65–26.0°, ($-13 < h < 13$, $-13 < k < 0$, $-25 < l < 0$) in ω–2θ-scan mode using graphite monochromatised Mo–K$_\alpha$ radiation, 4710 were independent ($R_{\text{int}} = 0.0746$). These data were corrected empirically for absorption (with maximum 0.5071 and minimum 0.3543 transmission). Hydrogen atoms were fixed on calculated positions. Full-matrix least-squares refinement, based on F^2, of the positional, isotropic, and anisotropic thermal parameters converged at $R_1 = 0.0640$ ($wR_2 = 0.1404$) for 2432 data with $I = 2\sigma(I)$ and $R_1 = 0.1810$ ($wR_2 = 0.1848$) for all data. Despite correction for absorption there are still some rest electron residues near the heavy atoms Te and Mo1 and Mo2. Solution of the structure was performed using direct methods and refinement carried out by least-squares procedures. SHELXS-86 and SHELXL-97 were used as the computing systems. Selected bond lengths and bond angles for **1** are given in Table 2.

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

Bond distances			
Mo(1)–S(1)	2.480(4)	Mo(1)–S(2)	2.499(4)
Mo(2)–S(1)	2.485(4)	Mo(2)–S(2)	2.490(4)
Mo(1)–S(3)	2.331(4)	Mo(2)–S(3)	2.322(4)
Mo(1)–Te	2.702(2)	Mo(2)–Te	2.700(2)
Mo(1)–Mo(2)	2.626(2)	S(1)–C(1)	1.81(2)
S(2)–C(17)	1.80(2)		
Bond angles			
S(3)–Mo(1)–S(1)	76.32(13)	S(3)–Mo(1)–S(2)	75.52(13)
S(1)–Mo(1)–S(2)	115.64(14)	S(3)–Mo(1)–Mo(2)	55.48(9)
S(1)–Mo(1)–Mo(2)	58.15(10)	S(2)–Mo(1)–Mo(2)	58.08(10)
S(3)–Mo(1)–Te	116.35(10)	Mo(2)–Mo(1)–Te	60.88(5)
S(1)–Mo(1)–Te	71.21(10)	S(2)–Mo(1)–Te	71.89(10)
S(3)–Mo(2)–S(1)	76.39(13)	S(3)–Mo(2)–S(2)	75.84(14)
S(1)–Mo(2)–S(2)	115.79(13)	S(3)–Mo(2)–Mo(1)	55.80(10)
S(1)–Mo(2)–Mo(1)	57.98(10)	S(2)–Mo(2)–Mo(1)	58.40(10)
S(3)–Mo(2)–Te	116.75(10)	S(1)–Mo(2)–Te	71.18(10)
S(2)–Mo(2)–Te	72.05(10)	Mo(1)–S(1)–Mo(2)	63.86(10)
Mo(1)–Mo(2)–Te	60.95(5)	Mo(2)–Te–Mo(1)	58.17(4)
C(1)–S(1)–Mo(1)	116.5(5)	C(1)–S(1)–Mo(2)	108.3(5)
C(17)–S(2)–Mo(2)	113.4(6)	C(17)–S(2)–Mo(1)	111.3(6)
Mo(2)–S(2)–Mo(1)	63.52(10)	Mo(2)–S(3)–Mo(1)	68.73(10)

3.5. Study of nonlinear optical properties of 1

DFWM measurements were performed with 35 ps pulses at 532 nm provided by an Nd–YAG laser at a repetition rate of 10 Hz. The standard backward DFWM geometry [22,25], with strong, equal intensity, counterpropagating pump beams and a weak probe beam, was adopted. The beams were focused to approximately 3 mm diameter spots on the sample. The emitted signal was steered and collected 2 m away from the sample, to eliminate background optical noise. The signal was measured by a sensitive photodiode (Hamamatsu) and fed to a digital storage oscilloscope (Tektronix TDS320). A part of the input laser beam was split off and measured by a similar photodiode, to monitor the input laser energies as well as the fluctuations in them. Both input and emitted light signals were typically averaged over 100 pulses to obtain each data point. The sample dissolved in n-hexane, was contained in an optically polished cuvette of 1 mm path length and its concentration was 2.2×10^{-4} M giving a linear transmission of 95%. The solvent did not produce any signal under the conditions of our experiment. The signals were calibrated with respect to CS_2 whose χ^3 is taken to be 1.62×10^{-12} esu [22].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 119753 for compound **1**. Copies of the information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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