Synthesis and structural characterisation of a new μ_2-Te bridged complex of molybdenum with oxo and imido ligands

Pradeep Mathur [a,*], Sanjukta Ghose [a], Md. Munkir Hossain [a], Heinrich Vahrenkamp [b]

[a] *Chemistry Department, Indian Institute of Technology, Bombay 400 076, India*
[b] *Institut für Anorganische und Analytische Chemie der Universitat Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany*

Abstract

Reflux of a benzene solution of $Cp_2Mo_2Fe_2(CO)_7Te_2$ and PhN_3 in the presence of air afforded the new compound $Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-}NC_6H_5)$ in 33% yield. It was characterised by IR and ^1H and ^{125}Te NMR. spectroscopy. Crystallographic analysis established its structure. The structure can be described as consisting of a CpMo–MoCp unit, bridged by a μ-Te atom and an imido ligand. Also bonded to each Mo atom is a terminally bonded oxo group.

1. Introduction

Transition metal complexes involving imido and oxo ligands are of much current interest [1]. Imido groups have been widely used as stabilising ligands in high oxidation state transition metal complexes and to provide steric protection about the metal centre [2], the latter being an important property of the imido complexes that is not true of analogous oxo complexes [3]. They have played an important role in the development of well defined olefin metathesis [4] and ring opening metathesis polymerisation (ROMP) catalysis [5]. Transition metal imido species have also been postulated to be important intermediates in a number of industrial processes [6]. For example, surface molybdenum imido species have been suggested to be key intermediates in the industrial 'ammoxidation' of propylene to acrylonitrile [2,7]. They are also believed to be involved in such enzymatic pathways as nitrogen fixation and the metabolism of certain hydrazines [8].

Like the imido ligand, the oxo ligand is also known to stabilise high oxidation state transition metal centres. This stabilisation has been applied to the synthesis of both σ and π organotransition metal derivatives of V(V), Mo(VI), W(VI), etc. [2]. Metal oxo derivatives have long been used as oxidants in organic synthesis

[9]. Besides being utilised in industrial processes involving homogeneous catalysis, metal oxo species are also present on the surface of industrially important heterogeneous catalysts, as in the use of iron molybdate catalysts for the oxidation of methanol to formaldehyde [10]. A variety of evidence suggests that it is the terminal oxo groups on the catalyst surface that are directly involved in the catalytic chemistry [11]. Nature also utilises metal oxo complexes in an ubiquitous series of important enzymes like the Mo- or W-containing 'oxo-transferases'. These compounds play a variety of roles in living systems and are involved in both oxidative and reductive processes [12].

The use of S, Se and Te as versatile bridging and stabilising ligands in cluster chemistry is widely recognised [13]. In general, the dinuclear compounds $(CO)_6Fe_2(\mu\text{-}E_2)$ and the trinuclear compounds $(CO)_9M_3(\mu_3\text{-}E)_2$ (E = S, Se, Te; M = Fe, Ru, Os) have been employed as useful starting materials for cluster growth reactions [14]. In the dinuclear compound the addition of various organic and inorganic moieties occurs across the reactive E–E bond, whereas in the trinuclear starting material it is the lone pair of electrons on the μ_3-E ligands that act as the initial point of contact. These compounds also serve as precursors for the preparation of heterochalcogen atom stabilised mixed-metal clusters of higher nuclearity, under facile conditions. Recently, we have synthesised a new class

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* Corresponding author.
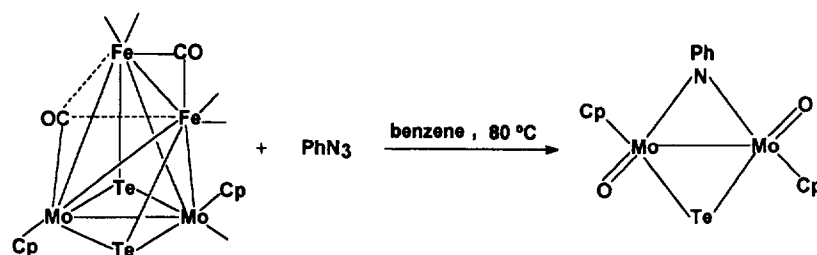
Scheme 1.

of mixed-metal clusters, $Cp_2Mo_2Fe_2(CO)_7(\mu_3$-E$)(\mu_3$-E$')$ and found these to be starting materials for cluster growth reactions [15].

As an extension of our interest in the reactivity of metal carbonyls towards phenyl azides, we report here on the reaction of $Cp_2Mo_2Fe_2Te_2(CO)_7$ with PhN_3.

2. Results and discussion

When a benzene solution containing $Cp_2Mo_2Fe_2(\mu_3$-Te$)_2(CO)_7$ and phenyl azide was refluxed for about 36 h in the presence of air, the new compound $Cp_2Mo_2O_2(\mu$-Te$)(\mu$-NC$_6$H$_5)$ was obtained in 33% yield (Scheme 1). The reaction also produced several other compounds which were observed during the chromatographic work-up, but due to instability of some and insufficient amounts of others, characterisation was not possible. The compound $Cp_2Mo_2O_2(\mu$-Te$)(\mu$-NC$_6$H$_5)$ was stable both in the solid state and in solution. It was characterised by IR and ^{1}H and ^{125}Te NMR spectroscopy. The infrared spectrum shows a strong band at 899 cm^{-1}, indicating the presence of terminally bonded oxygen atoms [16–18]. A strong band at 1270 cm^{-1} can be assigned to Mo–N stretching vibrations. The ^{1}H NMR spectrum shows a single peak for the two equiva-

lent Cp ligands (δ 5.9 ppm, s) [1]. The occurrence of multiplet peaks centred at δ 7.6 ppm confirms the presence of the phenyl group. The ^{125}Te NMR spectrum shows a single sharp signal at δ 909 ppm.

Orange crystals of the compound $Cp_2Mo_2O_2(\mu$-Te$)(\mu$-NC$_6$H$_5)$ were grown from a dichloromethane–hexane mixture at -5 °C, and its structure was elucidated by single crystal X-ray diffraction studies. The molecular structure is depicted in Fig. 1. The crystal data and details of measurement are given in Table 1. Fractional atomic coordinates are given in Table 2. Selected bond lengths and bond angles are listed in Table 3. The structure consists of a dimolybdenum unit bridged by a μ-Te atom on one side and by a phenyl imido group on the other. In addition, each Mo atom also has a Cp ligand and a terminally bonded oxo group attached to it. These terminal oxo groups exhibit a trans disposition with respect to each other along the Mo–Mo bond. Disorder in the Cp ring (C(11) to C(15) and C(16) to C(20)) which is attached to Mo(1) prevents its representation in Fig. 1 as a typical planar arrangement of the ring. The average Mo–O bond distance is 1.705 Å, which is similar to other Mo–terminal oxo bond lengths reported in the literature, trans-$Cp_2Mo_2O_2(\mu$-S$)_2$ (1.700(2) Å), trans-$Cp_2Mo_2O_2(\mu$-Se$)_2$ (1.705(4) Å), cis-$Cp_2Mo_2O_2(\mu$-Se$)_2$ (1.691(5) Å) [2,16,19]. The an-
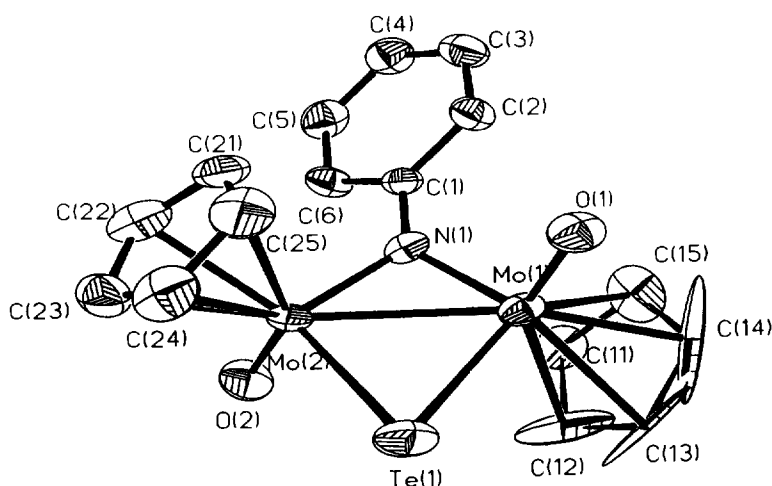
Fig. 1. Molecular structure of $Cp_2Mo_2O_2(\mu$-Te$)(\mu$-NC$_6$H$_5)$.

Table 1

Crystal data and refinement details for $Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-NC}_6H_5)$

Empirical formula	$C_6H_{15}Mo_2NO_2Te$
Formula weight	572.77
$F(000)$	1080
Crystal system, space group	monoclinic, Cc
a (Å)	15.8140(10)
b (Å)	16.2400(10)
c (Å)	6.9205(5)
α (°)	90
β (°)	106.036(5)
γ (°)	90
V (Å^3)	1708.2(2)
Z	4
D_{calc} (g cm^{-3})	2.227
Crystal size (mm^3)	0.6×0.4×0.1
Crystal colour	orange
Crystal shape	isometric
μ (mm^{-1})	3.147
Diffractometer	Nonius-Turbo-CAD4
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Temperature (K)	293(2)
Scan type	ω-2θ
Data collection range θ (°)	2.51 to 25.97
No. of reflections collected	1824
No. of independent reflections (R_{int})	1824
Reflections observed	1815
No. of parameters refined	210
Transmission factors: min/max	0.38/0.55
Computing system	SHELXS-86, SHELXL-93
R [a]	0.0406
wR_2 [b]	0.0992
Goodness of fit	1.118
Largest diffracting peak and hole	1.645

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å × 10^3)

Atom	x	y	z	U_{eq}
Te(1)	7169(1)	1406(1)	−1585(1)	47(1)
Mo(1)	7423(1)	2914(1)	−2713(1)	28(1)
Mo(2)	8785(1)	1701(1)	−1760(1)	27(1)
O(1)	6899(4)	2929(4)	−5209(10)	42(1)
O(2)	9391(5)	1713(4)	709(10)	45(2)
N(1)	8664(4)	2864(4)	−2561(11)	30(1)
C(1)	9276(3)	3403(3)	−2980(8)	27(1)
C(2)	9011(3)	3967(3)	−4547(8)	35(2)
C(3)	9627(4)	4486(4)	−5016(9)	44(2)
C(4)	10508(3)	4441(4)	−3918(9)	43(2)
C(5)	10773(3)	3878(4)	−2351(9)	43(2)
C(6)	10157(3)	3359(4)	−1882(8)	36(2)
C(11)	7889(13)	3916(9)	−86(26)	37(7)
C(12)	7354(24)	3391(13)	664(30)	73(15)
C(13)	6508(15)	3411(22)	−663(58)	110(25)
C(14)	6520(14)	3949(20)	−2233(44)	141(28)
C(15)	7374(18)	4261(11)	−1876(22)	42(9)
C(16)	6938(35)	3330(26)	130(65)	85(19)
C(17)	6301(25)	3655(26)	−1505(65)	195(56)
C(18)	6694(35)	4271(19)	−2363(64)	90(17)
C19)	7575(25)	4326(29)	−1258(76)	120(30)
C(20)	7726(27)	3745(36)	282(50)	149(40)
C(21)	9334(5)	1551(5)	−4629(11)	50(2)
C(22)	9933(5)	1182(5)	−2991(12)	54(2)
C(23)	9520(5)	504(4)	−2402(13)	53(3)
C(24)	8666(5)	454(4)	−3676(13)	55(3)
C(25)	8551(5)	1101(5)	−5053(11)	54(3)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

gle Mo–Te–Mo is quite acute (65.68(2)°) in comparison to the Mo–Se–Mo bond angle (75.2(0)°) or the Mo–S–Mo bond angle (77.2(1)°) in *trans*-$Cp_2Mo_2O_2(\mu\text{-Se})_2$ and *trans*-$Cp_2Mo_2O_2(\mu\text{-S})_2$ respectively [16,19]. The approximately trigonal geometry about the bridging N atom implies that the imido moiety has significant π donor character. Although the literature contains several examples of compounds containing the Mo_2-μ-NR moiety [1,20], the compound $Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-NC}_6H_5)$ represents the first example of an Mo_2 compound containing both a μ-Te and a μ-NR group.

3. Experimental section

3.1. General procedures

The starting materials $Cp_2Mo_2Fe_2(CO)_7Te_2$ [21] and phenyl azide [22] were prepared as reported in the literature. All solvents were dried and distilled immediately prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer as dichloromethane solution in 0.1 mm pathlength NaCl cells. Elemental analyses were performed using a Carlo Erba automatic analyser. ^1H and ^{125}Te NMR spectra were recorded on a Varian VXR-300S spectrometer in $CDCl_3$. The operating frequency for ^{125}Te NMR was 94.705 MHz, with a pulse width of 9.5 μs and a delay of 1 s. The spectrum is referenced to Me_2Te ($\delta = 0$).

Table 3

Selected bond lengths (Å) and bond angles (°)

Te(1)–Mo(1)	2.6341(8)	Te(1)–Mo(2)	2.6353(9)
Mo(1)–O(1)	1.697(6)	Mo(1)–N(1)	1.938(7)
Mo(2)–O(2)	1.713(7)	Mo(2)–N(1)	1.963(7)
N(1)–C(1)	1.393(8)		
Mo(2)–Te(1)–Mo(1)	65.68(2)	O(1)–Mo(1)–N(1)	105.0(3)
O(1)–Mo(1)–C(15)	101.8(5)	N(1)–Mo(1)–C(15)	97.6(7)
O(1)–Mo(1)–C(14)	89.3(7)	N(1)–Mo(1)–C(14)	133.4(8)
C(15)–Mo(1)–C(14)	35.6(6)	N(1)–Mo(1)–C(11)	83.9(6)
C(14)–Mo(1)–C(11)	57.6(6)	O(2)–Mo(2)–N(1)	104.7(3)
O(2)–Mo(2)–Te(1)	103.8(3)	N(1)–Mo(2)–Te(1)	99.7(2)
C(22)–Mo(2)–Te(1)	143.4(2)	C(24)–Mo(2)–Te(1)	86.7(2)
C(25)–Mo(2)–Te(1)	94.2(2)	O(2)–Mo(2)–Mo(1)	113.6(2)
N(1)–Mo(2)–Mo(1)	42.6(2)	Te(1)–Mo(2)–Mo(1)	57.18(2)
C(1)–N(1)–Mo(1)	135.5(5)	C(1)–N(1)–Mo(2)	130.2(5)
Mo(1)–N(1)–Mo(2)	94.2(3)	C(6)–C(1)–N(1)	120.1(4)

3.2. Thermolytic reaction of $Cp_2Mo_2Fe_2Te_2(CO)_7$ and PhN_3

To a benzene solution (50 ml) of $Cp_2Mo_2Fe_2Te_2(CO)_7$ (176.8 mg, 0.20 mmol) was added phenyl azide (36 mg, 0.20 mmol) and the solution was refluxed with constant stirring for about 36 h in the presence of air. The solvent was removed in vacuo. The residue was dissolved in dichloromethane and subjected to chromatographic work-up using silica gel TLC plates. Elution with 30/70 (v/v) ethyl acetate/hexane mixture afforded the orange compound $Cp_2Mo_2O_2(\mu\text{-Te})(\mu\text{-}NC_6H_5)$ (yield 38 mg (33%)) (Scheme 1). Anal. Found: C, 33.4; H, 2.73; N, 2.53. $C_{16}H_{15}Mo_2NO_2Te$ Calc.: C, 33.6; H, 2.62; N, 2.45%.

3.3. Crystallography

Orange crystals of the compound suitable for X-ray diffraction analysis were grown from hexane/dichloromethane solvent mixtures by slow evaporation of the solvents at $-5\,°C$. An isometric crystal of size $0.6 \times 0.4 \times 0.1\,mm^3$ was chosen for data collection. Crystallographic data were measured at 293(2) K on a Nonius-Turbo-CAD4 diffractometer with a graphite monochromator. Solution of the structure was performed using direct methods and refinement was carried out by least-squares procedures. SHELXS-86 [23] and SHELXL-93 [24] were used as the computing system.

Acknowledgements

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