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Six-coordinate molybdenum nitrosyls with a single ene-1,2-dithiolate ligand

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This paper is dedicated to Professor Karl Wieghardt.

Abstract

The synthesis and molecular structures of the (Tp*)Mo(NO)(S–S) family of compounds (where (Tp*) is hydrotris(3,5-dimethyl-1pyrazolyl)borate; (S–S) is an ene-1,2-dithiolate) are reported. The compounds; (Tp*)Mo(NO)(bdt) (1), (Tp*)Mo(NO)(tdt) (2), and (Tp*)Mo(NO)(bdtCl₂) (3) (bdt, 1,2-benzenedithiolate; tdt, 3,4-toluenedithiolate; bdtCl₂, 3,6-dichlorobenzenedithiolate), are the first such structurally characterized {MoNO}⁴ compounds that contain a [(Tp*)Mo(NO)]²⁺ fragment ligated to an ene-1,2-dithiolate. The compounds crystallize in the space groups $P_{2_1/c}$ (1) (a = 11.115(2) Å, b = 13.667(3) Å, c = 16.410(3) Å; $\beta = 98.36(3)^{\circ}$, Volume = 2466.4(8) Å³, Z = 4); $P_{2_1/n}$ (2) (a = 15.579(3) Å, b = 9.942(2) Å, c = 16.527(3) Å; $\beta = 95.79(3)^{\circ}$, Volume = 2546.7(9) Å³, Z = 4); and *Pnma* (3) (a = 17.9879(9) Å, b = 13.2277(7) Å, c = 11.2505(6) Å; Volume = 2676.9(2) Å³, Z = 4). The molecular structures show that the inner coordination sphere remains invariant within this family. A remarkable feature is the fold angle (θ) between the MoS₂ plane and S₂C₂ plane of the ene-1, 2-dithiolate chelate ring. The fold angles (θ) of 42.1° in 1, 41.1° in 2 and 44.4° in 3 are substantially larger than in analogous compounds with a terminal oxo group. Additional insight into the chemistry and properties of complexes 1–3 has been obtained by cyclic voltammetry, IR, NMR, electronic absorption and He I photoelectron (PES) spectroscopies.

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Keywords: Molybdenum nitrosyls; Ene-1,2-dithiolate; Fold angle; Photoelectron spectroscopy

1. Introduction

Mononuclear metal-nitrosyl complexes are of continuing interest [1,2]. Their possible applications include; molecular sensors [3], magnetically-dilute hosts for paramagnetic guests [4], non-linear optical [5] and ferrimagnetic materials [6,7]. Metal-nitrosyls are biologically relevant as they are implicated in the immune system to kill tumor cells [8], as a physiological NO carrier [9], and as intracellular parasites [10]. The metastable linkage isomers of transition metal nitrosyl complexes have potential technological importance which, in principle, could allow the design of a high capacity storage device [11].

The transition metal-nitrosyl complexes reveal a significant mixing between the metal d and π^* (NO) orbitals which led to the development of the {MNO}^{*n*} formalism for describing mononitrosyl complexes [12,13]. In this notation *n* is the total number of electrons contained in the metal d and π^* (NO) orbitals. The title complexes are six-coordinated {MNO}⁴ species, with the metal center coordinated to a bulky tripodal ligand (Tp*). The steric interaction of (Tp*) prevents additional coordination to the metal center, hence, affording stable six-coordinate 16-electron species, which have a formally 4d⁴ electronic configuration (i.e. Mo(II)). The {MNO}⁴ center in (Tp*)Mo(NO)Cl₂ can be reduced by one electron to the corresponding paramagnetic {MNO}⁵ center, and EPR spectroscopy is

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consistent with the unpaired electron being localized in a MO that is predominantly Mo $4d_{xy}$ [3,14,15]. McCleverty and Jones and their coworkers have prepared a series of homo and heterobimetallic complexes in which the redox active (Tp*)Mo(NO)(X, Y) (where X, Y are mono anions) center is linked to a second redox active metal center through polyene bridges [16,17]. These binuclear systems with a reducible {MNO}⁴ center are of general interest due to their possible application as non-linear optical materials.

Numerous metal nitrosyl complexes have been structurally characterized. A Cambridge Crystallographic Database (CSD) search showed 2037 hits of metal– nitrosyl structures, out of which 542 hits were of Group VI transition metal–nitrosyl complexes and 292 hits had molybdenum centers [18]. A total of ten structures containing mononuclear 16-electron [(Tp*)Mo(NO)-(S,S)] cores (where (S,S) = two sulfur donor ligands) including the title complexes, are structurally compared here (Chart 1).

Chart 1. Classification, v(NO) (IR, KBr), and Abbreviations of (Tp*)Mo(NO)(S,S) Compounds ((Tp*): hydrotris(3,5-dimethyl-1-pyrazolyl)borate).

(S,S)	Compound	v(NO)	References
	number	(cm^{-1})	
bdt	1	1670	This work
tdt	2	1660	[19], this
			work
bdtCl ₂	3	1674	This work
S(CH ₂) ₂ CONH(CH ₂) ₂ S	4	1667	[54]
$(1,4-(SCH_2)_2C_6H_4)_2$	5	1653	[46]
$(1,4-(SCH_2)_2C_6H_4)_3$	6	1644	[46]
$(Fe(\eta^{5}-C_{5}H_{4}S)_{2})$	7	1634	[55]
$(SC_{6}H_{5})_{2}$	8	1682	[21,50]
(SCH ₂ CONHCH ₃) ₂	9	1672	[51]
(SC ₂ H ₄ CONHCH ₃) ₂	10	1662	[51]

(bdt) 1,2-benzenedithiolate, (tdt) 3,4-toluenedithiolate, (bdtCl₂) 3,6-dichlorobenzenedithiolate.



Fig. 1. Representation of the $[(Tp^*)Mo(NO)]^{2+}$ system containing equatorial ene-1,2-dithiolate ligands (S–S) coordinated to the Mo center. Structures of the dithiolate dianions (S–S) are also shown.

The synthesis of compound 2 was first reported by McCleverty and coworkers in 1989 [19]. However, this family of compounds has remained essentially unexplored in the intervening years as evident by a recent review of the coordination and organometallic chemistry of metal–NO complexes [1]. Complexes 1–3 (Fig. 1) are the first structurally characterized Mo-nitrosyl complexes containing a single ene-1,2-dithiolate (S_2C_2) chelate. However, it has long been known that the crystal structures of LMo(NO)(SC₆H₅)₂ (where $L = \eta^5$ -C₅H₅, Tp*(8)) exhibit unusual ON-Mo-S-C torsion angles Fig. 2(A) that have been ascribed to $d\pi$ -p π bonding interactions between the thiolate lone pairs, primarily S 3p in character, and the empty Mo $4d_{xy}$ orbitals [20,21]. Molecular orbital calculations by Hoffmann and coworkers suggested that the sulfur atoms can contribute to the stability of 16-electron systems [22,23]. Fourmigué et al. have shown that the fold angle θ , Fig. 2(B) is sensitive to the electronic occupation of metal-dithiolate complexes [24,25]. Here we show that the ene-1,2-dithiolate chelate in compounds 1-3, which have a d_{xy}^0 ground state, exhibit a large fold angle (θ). Similar to $(Tp^*)Mo(NO)Cl_2$, the metal centers in 1–3 can be reduced by one electron to yield the spectroscopically interesting d_{xy}^1 state (formally $(d_{xz}d_{yz})^4 d_{xy}^1$) [14] whose detailed study will be presented elsewhere [29].

Compounds 1-3 are of further interest because the active sites of sulfite oxidase and xanthine oxidase have a molybdenum atom coordinated by a single ene-1,2-dithiolate at the active site [27,28,30-32]. This pyranopterin-dithiolate unit coordinated to molybdenum is postulated to function as an electron transfer conduit and modulator of the redox potential of the enzyme active site [33]. The electronic structure of these active sites and their relationship to electron transfer is not yet understood; however, the metal-sulfur interaction appears to play an important role [34]. The inner coordination-sphere of the small molecular models of the active site seems invariant, even though large differences are observed in the reduction potentials [35-37]. It has been suggested that modulation of the



Fig. 2. (A: left and B: right): Orbital interaction diagram in $(Tp^\ast)Mo(NO)(SPh)_2$ and $(Tp^\ast)Mo(NO)(S-S)$ complexes.

2. Experimental

2.1. General

All reactions and manipulations were carried out under an inert environment of argon gas using standard Schlenk techniques, a high-vacuum/gas double line setup, and an inert atmosphere glove bag. The argon was predried by passing the high-purity-grade gas through a series of drying towers. All glassware was dried in an oven at 150 °C and Schlenk ware was further purged by repeated evacuation and inert gas flushes prior to use. Tetrahydrofuran (THF) and toluene were distilled from Na-benzophenone; triethylamine was distilled from Na-K amalgam [38]. The prepurified solvents were subsequently transferred and stored under N₂ over fresh drying agents. These solvents were freshly distilled under nitrogen prior to use, thoroughly degassed by repeated freeze-thaw-pump cycles, and transferred to reaction vessels via steel cannulae under a positive pressure of inert gas. Dichloromethane, 1,2-dichloroethane (DCE), cyclohexane, toluene (EM Science, Omnisolv), *n*-hexane and *n*-pentane (Burdick and Jackson) were used as received and deoxygenated by bubbling with argon. Molybdenum hexacarbonyl (Mo(CO)₆, Aldrich) was dried in vacuum prior to use. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KTp*), the precursor complexes $(Tp^*)Mo^V(NO)(CO)_2$ and $(Tp^*)Mo^V(NO)I_2 \cdot C_6H_5CH_3$ and the ligands H₂bdt (1,2-benzenedithiol) were prepared according to literature procedures [26,39,40]. The ligand H₂tdt (4-methyl-1,2-benzenedithiol) and H₂bdtCl₂ (3,6-dichloro-1,2-benzenedithiol) employed in the syntheses of the $(Tp^*)Mo^{V}(NO)(S-S)$ compounds (2, 3) were used as received from Aldrich.

TLC analysis was carried out on silica gel 60 F₂₅₄ plastic sheets (EM Science) and column chromatography was carried out in glass columns with silica gel (Merck, grade 9385, 230–400 mesh, pore diameter 60 Å) as the stationary phase. Mass spectra were recorded on a JEOL HX110 high-resolution sector instrument utilizing fast atom bombardment (FAB) ionization in a matrix of 3-nitrobenzyl alcohol (NBA). IR spectra (4000-400 cm^{-1}) were collected on a Nicolet Avatar ESP 360 FT IR spectrophotometer in KBr disks or as dichloromethane solutions (between NaCl plates) at room temperature (r.t.). Electronic absorption spectra of samples dissolved in 1,2-dichloroethane solutions were recorded with a 1 cm pathlength Helma quartz cell equipped with a teflon stopper, on a Cary 300 (250-900 nm) spectrophotometer. Solvent background corrections were made in all cases. ¹H NMR (CDCl₃) spectra

were acquired on a Bruker DRX-500 spectrometer operating at a ¹H frequency of 500.13 MHz using a 5 mm Nalorac triple-resonance 3-axis gradient probe. Chemical shifts were referenced to residual CHCl₃ at 7.24 ppm.

2.2. Synthesis of $(Tp^*)Mo(NO)(bdt)$ (1)

In a 100 ml round bottom evacuated Schlenk flask, highly purified (Tp*)Mo(NO)I₂·C₆H₅CH₃ (0.38 g, 0.5 mmol) was added to H₂bdt (0.1 g, 0.7 mmol) in 50 ml of dry, degassed toluene in a 100 ml round bottom Schlenk flask for synthesis of 1. The mixture was deoxygenated thoroughly with argon saturation while being stirred at ~80 °C. Dry, degassed Et₃N (0.4 ml, 2.2 mmol) was added slowly dropwise via a gas tight syringe to this rigorously stirring solution. The solution changed color to greenish and later to deep blue. The reaction mixture was refluxed for 16 h, and the reaction progress was monitored by IR spectroscopy (shift of v(NO) stretching frequency) and TLC analysis (disappearance of $(Tp^*)Mo^V(NO)I_2$ precursor). Upon completion of the reaction, the blue-green precipitate, primarily $Et_3N \times$ HI resulting from the proton abstraction and ligand exchange processes, was removed by filtration from the hot solution under dry argon. The filtrate was cooled to r.t. and evaporated to dryness with a rotorary evaporator. The solid dark-purple residue was re-dissolved in toluene, concentrated under vacuum, and layered with *n*-pentane. The dark-purple powder precipitate was collected by filtration and washed with *n*-pentane until the filtrate was clear. The powder was then dissolved in dichloromethane, filtered to remove any insoluble materials, and evaporated to dryness in vacuum. The solid was pumped on for several hours to assure dryness and the complete removal of excess triethylamine. The solid material was re-dissolved in dichloromethane, concentrated, and loaded on a silica gel chromatographic column under a positive pressure of argon. A dark-purple fraction (band 1) eluted off the column using dichloromethane:cyclohexane (1:3) as the eluant. Band 1 was further purified by a second silica gel column using dichloromethane:cyclohexane (1:1) as the eluant. The purity of compound was confirmed by TLC analysis. The dark-purple solution, which was deemed pure by TLC was evaporated to dryness in vacuum, redissolved in dichloromethane, and layered with npentane to yield a dark-purple crystalline material. This material was filtered, washed with pentane and then dried in vacuum. The product was characterized by IR, UV-Vis and mass spectroscopy. Slow vapor diffusion of *n*-pentane into a saturated dichloromethane solution of 1 afforded diffraction quality crystals. Characterization: HRMS $[M+H]^+$ peak gives m/z =565.0798 (calculated, 565.0792) and corresponds to the formula $[{}^{12}C_{21}H_{27}N_7^{11}B^{32}S_2^{35}O^{98}Mo]$, IR data (KBr)

ν(B−H) = 2551 cm⁻¹, ν(NO) 1670 cm⁻¹, UV−Vis data λ(nm)(E(cm⁻¹)); ∈(M⁻¹ cm⁻¹)):732(13700; 1576), 579(17300; 4527), 370(27000; 3154), 326(30700; 3645), 292(34200; 5898).¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ (ppm) 8.057, 7.274 (2H, dd, ³J_{HH} = 4.5, 3.0 Hz; 2H, dd, ³J_{HH} = 4.5, 3.0 Hz), 5.992, 5.623 (2H, s; 1H, s), 2.485, 2.404, 2.308 (7H, s; 4H, s; 7H, s).

2.3. Synthesis of $(Tp^*)Mo(NO)(tdt)$ (2)

The preparation of (Tp*)MoNO(tdt) (2) followed from published procedures [19]. A mixture of $(Tp^*)Mo(NO)I_2 \cdot C_6H_5CH_3$ (0.9 g, 1.2 mmol) and H₂tdt (0.33 g, 2.1 mmol) were refluxed for 16 h instead of 24 h as given in the literature [19]. Slight modifications were also made in the work up procedures to obtain the pure compound suitable for growing X-ray diffraction quality crystals. In our work-up procedure the reaction mixture was evaporated to dryness under reduced pressure and the solid obtained was dissolved in a 1:3 CH₂Cl₂:cyclohexane mixture and subjected to column chromatography. The product is contained in a deep blue band that is well separated from other side products, which do not separate well when eluted with CH₂Cl₂ as in the original preparation [19]. Further purification was achieved by a second column chromatography step using 1:1 CH₂Cl₂:cyclohexane as the eluant. Slow diffusion of heptane into a CH₂Cl₂ solution of 2 yielded X-ray diffraction quality crystals. Compound 2 reveals similar spectroscopic features to those reported in the literature [19].

2.4. Synthesis of $(Tp^*)Mo(NO)(bdtCl_2)$ (3)

All the synthetic steps were similar to those described for **1**, except for the stoichiometric ratio of the reagents. Highly purified (Tp*)Mo(NO)I₂·C₆H₅CH₃ (677 mg, 1.00 mmol) was added to a solution of H₂bdtCl₂ (220 mg, 1.1 mmol) in 50 ml of dry, degassed toluene in a 100 ml round-bottom Schlenk flask. Characterization: HRMS [M+H]⁺ peak that gives m/z = 633.0035 (calculated, 633.0002) and corresponds to the formula [$^{12}C_{21}H_{25}N_7^{11}B^{32}S_2^{35}Cl_2O^{98}Mo$] for **3**, IR (KBr) ν (B– H) = ν (B–H) = 2548 cm⁻¹; ν (NO) 1674 cm⁻¹, UV– Vis data λ (mm)(E(cm⁻¹); \in (M⁻¹ cm⁻¹)): 739(13 500; 1583), 573(17 500; 6476), 372(26 900; 3734), 330(30 300; 5186), 294(34 000; 8477). ¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ (ppm) 7.369 (1H, s), 6.017, 5.629 (2H, s; 1H, s), 2.502, 2.415, 2.287 (7H, s; 4H, s; 7H, s).

2.5. X-ray crystal structure determinations

2.5.1. Crystal structures of 1 and 2

Crystals of 1 and 2 were mounted on glass fibers for structure determination using an Enraf-Nonius CAD4 diffractometer. Crystal data and details of structure determinations are given in Table 1. The structures were determined by direct methods and refined on F^2 by fullmatrix least-squares with anisotropic parameters for the non-hydrogen atoms. Scattering factors were taken from Cromer and Waber [41], anomalous dispersion effects were included for all non-hydrogen atoms with the values of $\Delta f'$ and $\Delta f''$ taken from Cromer [42], and the structure was solved by direct methods using SHELXS in the Bruker SHELXTL (Version 5.0) software package. Hydrogen atoms were placed in calculated positions with isotropic displacement parameters.

2.5.2. Crystal structure of 3

A dark-purple cuboid of 3 was mounted on a glass fiber for structure determination using a Bruker SMART 1000 CCD detector X-ray diffractometer. Key parameters for the structure determination are also summarized in Table 1. Empirical absorption and decay corrections were applied using the program SADABS. The structure was solved by direct methods using SHELXS in the Bruker SHELXTL (Version 5.0) software package. Refinements were performed on F^2 by full-matrix least-squares with anisotropic displacement parameters for all the non-hydrogen atoms (using SHELXL and illustrations were made using XP). Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they are bonded and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. Scattering factors and anomalous dispersion were taken from International tables Vol C, tables 4.2.6.8 and 6.1.1.4 [41,42].

2.6. Photoelectron spectroscopy

He I gas-phase photoelectron spectra (PES) were collected on an instrument with a 36 cm radius hemispherical analyzer (8 cm gap, McPherson) and custom designed sample cells, excitation sources, and detection and control electronics [43,44]. The excitation source was a quartz lamp with the ability to produce He I photons (21.21 eV). The ionization energy scale for the He I experiments was calibrated by using the ${}^{2}E_{1/2}$ ionization of methyl iodide (9.538 eV), with the argon ${}^{2}P_{3/2}$ ionization (15.759 eV) used as an internal calibration lock during the experiment. During data collection the instrument resolution (measured using the FWHM of the argon ${}^{2}P_{3/2}$ ionization peak) was 0.022-0.025 eV. All data were intensity corrected with an experimentally determined instrument analyzer sensitivity function. The He I spectra were corrected for the presence of ionizations from other lines (He Iß line, 1.9 eV higher in energy and 3% the intensity of the He Ia line). All samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. The sublimation temperatures (in $^{\circ}C$, 10^{-4} Torr) were as follows: (Tp*)Mo(NO)(bdt), 209-218°;

Table 1 Crystal data and structure refinement for complexes 1-3

Identification code	1	2	3
Empirical formula	C ₂₁ H ₂₆ BMoN ₇ OS ₂	C ₂₂ H ₂₈ BMoN ₇ OS ₂	C ₂₁ H ₂₄ BCl ₂ MoN ₇ OS ₂
Formula weight	563.36	577.38	632.25
Temperature (K)	298(2)	298(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	Pnma
Unit cell dimensions			
a (Å)	11.115(2)	15.579(3)	17.9879(9)
b (Å)	13.667(3)	9.942(2)	13.2277(7)
<i>c</i> (Å)	16.410(3)	16.527(3)	11.2505(6)
α (°)	90	90	90
β (°)	98.36(3)	95.79(3)	90
γ (°)	90	90	90
V (Å ³)	2466.4(8)	2546.7(9)	2676.9(2)
Ζ	4	4	4
$D_{\text{calc}} (\text{mg m}^{-3})$	1.517	1.475	1.534
Absorption coefficient (mm^{-1})	0.729	0.729	0.872
F(000)	11.52	1160	1252
Crystal size (mm ³)	0.23 imes 0.13 imes 0.03	0.17 imes 0.12 imes 0.08	$0.40 \times 0.10 \times 0.10$
2θ Range for utilized data (°)	1.85 to 24.97	1.71 to 24.97	2.14 to 27.29
Limiting indices	$0 \le h \le 13, \ 0 \le k \le 16,$	$0 \le h \le 18, \ 0 \le k \le 11,$	$-23 \le h \le 23, -16 \le k \le 16,$
	$-19 \le 1 \le 19$	$-19 \le 1 \le 19$	$-14 \le 1 \le 1$
Reflections utilized	4328	4468	26 517
Independent reflections	4328 $[R_{int} = 0.0000]$	4468 $[R_{int} = 0.0000]$	$3004 [R_{int} = 0.0741]$
Completeness to $\theta = 24.97^{\circ}$ (%)	100.0	100.0	95.5
Absorption correction	None	None	Empirical
Max/min transmission	0.9784, 0.8502	0.9456, 0.8893	0.9179, 0.7219
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4328/0/289	4468/0/314	3004/0/177
Goodness-of-fit on F^2	1.043	1.051	1.069
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0630, wR_2 = 0.1218$	$R_1 = 0.0484, wR_2 = 0.1092$	$R_1 = 0.0517, wR_2 = 0.1202$
R indices (all data)	$R_1 = 0.1507, wR_2 = 0.1454$	$R_1 = 0.0922, wR_2 = 0.1222$	$R_1 = 0.0921, wR_2 = 0.1457$
Largest difference peak and hole (e $Å^{-3}$)	0.855 and -0.550	0.631 and -0.327	0.595 and -0.521
RMS difference density (e $Å^{-3}$)	0.106	0.077	0.127

 $(Tp^*)Mo(NO)(tdt), 220-229^\circ; (Tp^*)Mo(NO)(bdtCl_2), 218-230^\circ.$

3. Results and discussion

3.1. Synthesis and physical properties of $Tp^*Mo(NO)(S-S)$ compounds

The identities of the reaction products were confirmed by their high resolution mass spectra. The reaction products 1–3 are soluble in dichloromethane, dichloroethane, toluene and benzene. Scheme 1 shows several different routes to the synthesis of Tp*Mo(NO)(S–S) complexes. The Tp*Mo(NO)X₂ precursors (X = Cl, Br, I) are well known; however, partial halogenation of the pyrazole ring at C-4 position has been observed in the preparation of Tp*Mo(NO)Cl₂ and Tp*Mo(NO)Br₂, precursor [45]. In addition, use of the precursor Tp*Mo(NO)Cl₂ can lead to the formation of unexpected



Scheme 1. Synthetic routes to the $(Tp^*)Mo(NO)(S,S)$ compounds [19,39,40,45,49].

products, including disulfide formation during the synthesis of $Tp^*Mo(NO)((SCH_2)_2C_6H_4)$ [46]. The $Tp^*Mo(NO)I_2 \cdot C_6H_5CH_3$ precursor has been primarily used for the synthesis of $Tp^*Mo(NO)(S-S)$ complexes in this work because it is relatively easy to prepare from $Tp^*Mo(NO)(CO)_2$ and the iodide ligand seems to be a very good leaving group in the subsequent substitution reactions [45].

The solid-state IR spectra in KBr exhibited bands characteristic of the (Tp*) ligand ($v(B-H) = 2551 \text{ cm}^{-1}$ for 1, 2550 cm⁻¹ for 2 and 2548 cm⁻¹ for 3). This v(B-H) is similar to that observed in the range of 2543-2549 cm^{-1} for the related chelate complexes (including 5, 6) [46]. The solution IR spectra of the $(Tp^*)Mo(NO)(S-S)$ complexes in dichloromethane showed no significant frequency shifts or additional bands, indicating that the solid phase and solution structures are similar. The purity of the products was also confirmed by the absence of v(CO) and the shift in the v(NO) stretching vibrations of the precursor complexes $(Tp^*)Mo(NO)(CO)_2$ (v(CO) = 1906 cm⁻¹, v(NO) = 1655 cm⁻¹) and (Tp*)Mo(NO)I₂ (ν (NO) = 1700 cm^{-1}) which also served as a diagnostic tool for monitoring the progress of the reaction.

The values of v(NO) range from 1674 for **3** to 1660 cm⁻¹ for **2** and decrease slightly with increasing electron withdrawing properties of the substituents on the benzene rings of the coordinated ene-dithiolates. The reduction potential ($E_{1/2}$) of -723 mV for **3**, -896 mV for **2**, and -862 mV for **1** also follows the trend **3** > **1** > **2** [47]. McCleverty and coworkers have earlier proposed a correlation between $E_{1/2}$ and v(NO) [48]. Our results also show that the more electron withdrawing the ene-dithiolate the higher is the v(NO) stretch. Thus v(NO) is a sensitive indicator of the perturbation of electron density on the Mo center by the remote substitution on the ene-dithiolate ligand.

The diamagnetic $\{MoNO\}^4$ complexes have been probed using ¹H NMR [1,19,39,40,45,49–51]. The 1-D NMR data and X-ray structures show that complexes 1-3 have effective C_s symmetry with two of the three pyrazolyl rings being magnetically equivalent. The ¹H NMR spectrum shows pyrazolyl methyl groups in the (Tp*)-ligand as singlets of relative area 7:4:7 at δ (ppm) 2.308, 2.404, 2.485 in 1 and δ (ppm) 2.287, 2.415, 2.502 in 3. The pyrazolyl 4-H signals appeared as two signals of relative area 1:2 at δ (ppm) 5.623, 5.992 for 1 and δ (ppm) 5.629, 6.017 for 3. These are in the typical range of CH₃ (δ (ppm) 1.5–3.0) and pyrazolyl 4-H (δ (ppm) 5.0-6.5) shifts for other (Tp*)Mo(NO)(S,S) complexes [49]. The aryl protons of the bdt^{2-} ligand in 1 resonate as two doublets of doublets (4.5, 3.0 Hz) at δ (ppm) 7.274 and 8.057 and those protons of the $bdtCl_2^{2-}$ ligand in 3 resonate as one singlet at δ (ppm) 7.369.

3.2. Molecular structure analysis of $(Tp^*)Mo(NO)(S-S)$ compounds

The structures of compounds 1-3, determined by single-crystal X-ray diffraction, are shown in Fig. 3. Tables 2 and 3 show key geometric features of the coordination environment of the Mo atom. Compounds 1-3 are the first structurally characterized six-coordinate {MoNO}⁴ complexes that contain a single ene-1,2dithiolate ligand cis to the terminal nitrosyl group. We have previously reported the structures and properties of the corresponding oxo analogues, $(Tp^*)MoO(S-S)$ [4,35,52,53]. Compounds 1, 2 and 3 crystallize in three different space groups $P2_1/c$, $P2_1/n$ and *Pnma*. No symmetry is imposed on 1 and 2 by their space groups, but C_s symmetry is imposed on **3** by the space group Pnma (Fig. 4). In the crystals of 3, the atoms N1, O1, Mo1, B1, H1A, N31, N32, C33, C34, H34A, C35, C36, H36A, C37, H37A lie on a mirror plane. In these complexes the terminal nitrosyl ligand and the two sulfur atoms of the ene-dithiolate are constrained to be mutually *cis* to each other by the *fac* stereochemistry imposed by the tridentate Tp* ligand. Thus molecules of compounds 1 and 2 also have effective C_s symmetry. All three molecules exhibit a distorted pseudo-octahedral coordination geometry, in which the Mo atom is ligated by a nitrogen atom from the nitrosyl ligand, two sulfur donor atoms of the (S-S) ligands and three nitrogen donor atoms of the tridentate facially coordinated (Tp*) ligand. The maximum angular deviations from ideal octahedral geometry within the N_2S_2 planes of the compounds are: 5.96° in 1 (N(21)-Mo(1)-S(2)); 5.52° in 2 (N(11)-Mo(1)-S(1)) and 4.08° in 3 (N(21)-Mo(1)-S(2), N(11)-Mo(1)-S(1)). The mean deviation of 4.00° in 1, 3.45° in 2 and 3.38° in 3 is consistent with deviations observed in other structures based on $[(Tp^*)Mo(NO)]^{2+}$ fragment [21,46,50,51,54,55]. The N-Mo-N angles between the nitrogen atoms of (Tp*) ligand are always less than 90° .

Seven other structurally characterized complexes with $[(Tp^*)Mo(NO)S_2]$ cores are available in the CSD database (Chart 1) [18]. Of these {MoNO}⁴ complexes, only 1–3 have five-membered ene-1,2-dithiolate chelate rings. The molecular structure of a complex containing similar fragment and an oxygen containing five membered chelate ring (catechol) has been reported earlier, in which boron sequestering resulted in the degradation of the (Tp*) ligand skeleton [49]. Structurally characterized chelate compounds 4, 5 and 6 contain nine, 17 and 25 membered chelate rings, respectively, [46,54]. Compound 7 contains the organometallic chelate ligand 1,1'-dithiaferrocenyl-S,S' [55]. Compounds 8, 9 and 10 possess two mono thiolates [21,50,51].

The structural parameters (bond lengths and angles) for the $[(Tp^*)Mo(NO)]^{2+}$ core reported in Table 2 for compounds 1, 2 and 3 are similar to one another and



Fig. 3. The ORTEP drawing of $(Tp^*)Mo(NO)(bdt)$ (1), $(Tp^*)Mo(NO)(tdt)$ (2), and $(Tp^*)Mo(NO)(bdtCl_2)$ (3). The atoms are drawn as 50% probability ellipsoids. H-atoms have been made arbitrarily small for clarity.

also agree with those found for compounds **4** through **10** (Chart 1). The observed Mo–N1 distance of 1.818(6) Å in **1** is 0.044 Å (8 σ) longer than that of 1.774 (6) Å in complexes **2** and **3**. All three values are between the largest (1.839 Å in **7**) and the smallest (1.730 Å in **5**). Another structural parameter of interest in metal nitrosyl complexes is the M–N–O angle. This angle is 174.2(6)° in **1**, 175.0(4)° in **2** and 174.5(5)° in **3**. The other Mo–N–O angles in Chart 1 range from 179.026° in **8** to 172.431° in **7**. A nearly linear Mo–N–O unit is expected for a six-coordinate {MoNO}⁴ compound [13]. The N–O bond distance is 1.113(7) Å in **1**, 1.171(5) Å in **2**, and 1.181(7) Å in **3**, and shows no correlation with ν (NO).

Additional structural features common in these compounds are the angles between *trans* ligands. The angle involving the nitrosyl nitrogen atom (N1–Mo–N31) is close to 180°, whereas other two *trans* angles (S1–Mo– N11 and S2–Mo–N21) fall in the range 160–166°. Compound **3** shows the strongest *trans* effect from a terminal nitrosyl group of all of the compounds in Table 2. Its Mo–N31 distance (2.258(5) Å) is 0.110 Å longer relative to Mo–N11 and Mo–N21 (both 2.148 Å). This *trans* effect due to the strong σ -donor and π -acceptor properties of the nitrosyl ligand [3] is not as pronounced as the *trans* effect in the corresponding oxo-Mo analogue of complex **3** where the strong π -donor and σ -donor properties of the oxo-ligand lengthen the corresponding Mo–N31 distance (2.391(3) Å) by 0.214 Å relative to Mo–N21 (2.177(2) Å) and 0.225 Å relative to Mo–N11 (2.166(3) Å) [35].

The Mo–S1 and Mo–S2 distances are 2.374(2) Å and 2.3882(19) Å in 1, 2.3773(15) Å and 2.4078(15) Å in 2 and 2.3926(12) Å in 3^1 . The average Mo–S bond lengths of 2.3811 Å in 1 and 2.3926 Å in 3 compares with 2.376 and 2.374 Å in the corresponding oxo-Mo anologues. Thus a slight Mo–S bond lengthening is observed in nitrosyl–Mo family in the chelate complexes which is opposite of the trend observed in non-chelated complexes. A bond reduction is observed from an average value of 2.382 Å in (Tp*)MoO(SPh)₂ to 2.357 Å in (Tp*)Mo(NO)(SPh)₂ (8). It is interesting to note that the

Table 2

Comparison of key bond lengths and parameters for compounds with [(Tp*)Mo(NO)S2) core (all of the bond lengths and *trans* effects are in Å and angles in °)

Compounds	Mo-N1	Mo-N1-O1	Mo-N31	Mo-N21	Mo-N31	Mo-S1	Mo-S2	S1-Mo-S2	N1-Mo-X	ΔT	$\varphi_{\rm d}$
1	1.818(6)	174.2(6)	2.181(6)	2.164(5)	2.260(6)	2.374(2)	2.3882(19)	84.17(8)	86.14(10)	0.088	175.0
2	1.774(4)	175.0(4)	2.187(4)	2.161(4)	2.257(4)	2.3773(15)	2.4078(15)	83.79(5)	87.26(14)	0.080	174.4
3	1.774(6)	174.5(5)	2.148(3)	2.148(3)	2.258(5)	2.3926(12)	2.3926(12)	83.96(6)	87.63(13)	0.110	174.7
4	1.767	175.939	2.230	2.234	2.249	2.342	2.352	105.171	96.547	0.017	164.2
5	1.730	173.309	2.237	2.231	2.256	2.366	2.340	102.612	95.691	0.022	166.6
6	1.759	176.764	2.238	2.234	2.260	2.345	2.339	102.248	94.462	0.024	166.0
7	1.839	172.431	2.202	2.197	2,263	2.375	2.357	90.278	98.165	0.064	167.5
8	1.763	179.026	2.215	2.205	2.244	2.345	2.368	102.957	90.950	0.034	172.7
9	1.763	176.904	2.223	2.219	2.242	2,347	2.349	102.820	95.638	0.020	165.0
10	1.791	177.605	2.209	2.222	2.256	2.337	2.345	104.353	95.794	0.041	166.1

 ΔT = trans effect [(Mn-N31)-(average Mo-N11 and Mo-N21)]. φ_d = dihedral angle between planes Mo-N11-N21 and Mo-S1-S2.

¹ The shortest Mo-S distance in mononuclear group VI transitionmetal-nitrosyl complexes containing at least two sulfur donor ligands is 2.289 Å in (tris(2-thioethyl)amine-N, S, S', S'')-nitrosylmolybdenum [56] and the longest is 2.639 Å in (2,3:8,9-dibenzo-1,4,7,10-tetrathiadecane-S, S', S'', S''') - nitrosyldiphenyl(methyl)phosphineiminato-molybdenum(III) [57].

Table 3					
Selected bond	lengths (Å) bond	angles (°) and	torsion angl	es (°) (e s d 's in	parentheses)

$\begin{array}{c c c c c c c c c c c c c c c c c c c $		1	2	3
S(1) C(1) 1.75k(6) 1.73k(6) 1.74k(6) S(2) C(2) 1.76k(6) 1.74k(6) 1.74k(5) C(1) C(2) 1.460(11) 1.44k(7) 1.44k(7) N(1)-Mo(1)-S(1) 84.6(2) 87.78(14) 87.63(13) N(1)-Mo(1)-N(2) 87.67(18) 86.75(14) 87.63(13) N(1)-Mo(1)-N(2) 97.6(2) 97.72(17) 96.40(16) N(2)-Mo(1)-N(1) 97.6(2) 97.72(17) 96.40(16) N(2)-Mo(1)-N(1) 81.3(2) 81.42(15) 82.17(19) N(2)-Mo(1)-N(1) 81.3(2) 84.427(16) 85.07(14) N(2)-Mo(1)-N(1) 81.3(2) 84.427(16) 85.07(14) N(2)-Mo(1)-S(1) 175.80(12) 96.80(10) N(1)-Mo(1)-S(2) 174.404(16) 177.80(12) 175.92(10) N(1)-Mo(1)-S(2) 94.37(15) 96.94(11) 96.80(10) N(1)-Mo(1)-S(2) 94.37(15) 96.94(11) 96.80(10) N(3)-Mo(1)-S(2) 94.33(15) 93.98(11) 90.92(11) N(1)-Mo(1)-S(2) 121.6(6) 122.4(4) 120.52(16) C(2)-C(1) 121.6(6) 122.4(4) <t< td=""><td>N(1)-O(1)</td><td>1.113(7)</td><td>1.171(5)</td><td>1.181(7)</td></t<>	N(1)-O(1)	1.113(7)	1.171(5)	1.181(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(1) - C(1)	1.758(9)	1.734(6)	1.743(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(2)-C(2)	1.726(8)	1.751(6)	1.743(5)
$\begin{split} & \text{N(1)} - \text{N(1)} - \text{S(1)} & \text{S(1)} - \text{S(1)} & \text{S(1)} & \text{S(1)} \\ & \text{N(1)} - \text{N(1)} - \text{N(2)} & \text{S(1)} & \text{S(1)} & \text{S(1)} \\ & \text{S(1)} - \text{N(1)} - \text{N(1)} & \text{S(2)} & \text{S(1)} & \text{S(1)} & \text{S(1)} \\ & \text{N(1)} - \text{N(1)} - \text{N(1)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} \\ & \text{N(2)} - \text{N(1)} - \text{N(1)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} \\ & \text{N(2)} - \text{N(1)} - \text{N(1)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} & \text{S(2)} \\ & \text{N(2)} - \text{N(1)} - \text{N(1)} & \text{S(3)} & \text{S(2)} $	C(1)-C(2)	1.406(11)	1.413(7)	1.431(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N(1) = M_0(1) = S(1)$	84 6(2)	87 78(14)	87 63(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1) - Mo(1) - S(2)	87 67(18)	86 75(14)	87 63(13)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1) - Mo(1) - N(21)	97.07(10)	95.06(18)	96.40(16)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(1) M_0(1) N(1)$	97.4(2) 97.6(2)	97.72(17)	96.40(16)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1) - Mo(1) - N(31)	176 7(2)	177.38(17)	178.0(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(21) M_0(1) N(31)$ $N(21) M_0(1) N(11)$	81.3(2)	81 50(15)	82 17(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21) - N(0(1) - N(11)) $N(21) - M_0(1) - N(21)$	81.3(2)	81.39(13)	85.07(14)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21) - N(0(1) - N(01)) $N(21) - M_0(1) - S(1)$	04.2(2) 00.25(16)	07.52(10)	06.80(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(21) - MO(1) - S(1) N(21) - MO(1) - S(2)	99.55(10) 174.04(16)	$\frac{97.32(12)}{177.80(12)}$	90.80(10) 175.02(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21) - MO(1) - S(2) N(11) - MO(1) - S(21)	1/4.04(10)	177.80(12) 84.70(14)	1/3.92(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11) - MO(1) - S(31) $N(11) - M_{-}(1) - S(1)$	03.3(2) 177.(5(1()	64.70(14)	90.80(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11) - MO(1) - S(1) $N(11) - M_{-}(1) - S(2)$	1//.03(10)	1/4.48(11)	1/5.92(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11) - MO(1) - S(2)	94.97(15)	96.94(11)	96.80(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(31) - MO(1) - S(1)	92.32(15)	89.79(11)	90.92(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(31) - MO(1) - S(2)	90.83(15)	93.98(11)	90.92(11)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(1) - C(2) - S(2)	120.1(6)	121.2(4)	120.52(16)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(2) - C(1) - S(1)	121.6(6)	120.3(4)	120.52(16)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1)-Mo(1)-S(1)-C(1)	- 52.9(3)	-52.0(2)	-50.5(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1)-Mo(1)-S(2)-C(2)	49.2(3)	53.5(2)	50.5(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21)-Mo(1)-S(1)-C(1)	-149.6(3)	-146.8(2)	-146.62(19)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21)-Mo(1)-S(2)-C(2)	-162.0(17)	-161.0(3)	-138.3
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(21)-Mo(1)-N(1)-O(1)	178.0(100)	125.0(5)	138.60(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11)-Mo(1)-S(1)-C(1)	104.0(4)	132.8(12)	138.3(14)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11)-Mo(1)-S(2)-C(2)	146.6(3)	150.9(2)	146.6
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(11)-Mo(1)-N(1)-O(1)	-99.0(7)	-153.0(5)	-138.60(10)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(31)-Mo(1)-S(1)-C(1)	125.9(3)	129.0(2)	128.24(19)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(31)-Mo(1)-S(2)-C(2)	-127.8(3)	-124.0(2)	-128.2
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(31)-Mo(1)-N(1)-O(1)	59.0(9)	50.0(7)	0.00(6)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	S(1)-Mo(1)-S(2)-C(2)	-35.5(3)	-34.60(18)	-37.4
$\begin{array}{llllllllllllllllllllllllllllllllllll$	S(1)-Mo(1)-N(1)-O(1)	80.0(7)	28.0(5)	42.02(3)
$\begin{array}{ccccccc} S(2)-Mo(1)-S(1)-C(1) & 35.3(3) & 35.0(2) & 37.41(17) \\ Mo(1)-S(1)-S(2)-C(2) & 138.4(3) & 138.8(2) & 142.6 \\ Mo(1)-S(2)-C(2)-C(1) & 29.0(7) & 29.7(4) & 31.6 \\ Mo(1)-S(1)-C(1)-C(2) & -31.2(7) & -29.5(5) & -31.6 \\ S-S & bite & distance: & 3.192 & 3.195 & 3.201 \\ Mo & distance & from N_2S_2 & plane & 0.069 & 0.071 & 0.063 \\ C36-centroid & of C1 and C2 & 4.185 & 4.159 & 4.198 \\ Fold & angle & (\theta) & 42.0 & 41.1 & 44.4 \\ Dihedral & angle & (between & planes: Mo1-N11-N21 & and Mo1-S1-S2) & 5.0 & 5.6 & 5.3 \\ \end{array}$	S(2)-Mo(1)-N(1)-O(1)	-5.0(7)	-56.0(5)	-42.02(3)
$ \begin{array}{c cccc} Mo(1)-S(1)-S(2)-C(2) & 138.4(3) & 138.8(2) & 142.6 \\ Mo(1)-S(2)-C(2)-C(1) & 29.0(7) & 29.7(4) & 31.6 \\ Mo(1)-S(1)-C(1)-C(2) & -31.2(7) & -29.5(5) & -31.6 \\ S-S & bite & distance: & 3.192 & 3.195 & 3.201 \\ Mo & distance & from N_2S_2 & plane & 0.069 & 0.071 & 0.063 \\ C36-centroid & of C1 and C2 & 4.185 & 4.159 & 4.198 \\ Fold & angle & (\theta) & 42.0 & 41.1 & 44.4 \\ Dihedral & angle & (between & planes: Mo1-N11-N21 & and Mo1-S1-S2) & 5.0 & 5.6 & 5.3 \\ \end{array} $	S(2)-Mo(1)-S(1)-C(1)	35.3(3)	35.0(2)	37.41(17)
$ \begin{array}{cccc} Mo(1)-S(2)-C(2)-C(1) & 29.0(7) & 29.7(4) & 31.6 \\ Mo(1)-S(1)-C(1)-C(2) & -31.2(7) & -29.5(5) & -31.6 \\ S-S & bite distance: & 3.192 & 3.195 & 3.201 \\ Mo & distance from N_2S_2 & plane & 0.069 & 0.071 & 0.063 \\ C36-centroid & Of C1 and C2 & 4.185 & 4.159 & 4.198 \\ Fold & angle (\theta) & 42.0 & 41.1 & 44.4 \\ Dihedral & angle (between & planes: Mo1-N11-N21 & and Mo1-S1-S2) & 5.0 & 5.6 & 5.3 \\ \end{array} $	Mo(1)-S(1)-S(2)-C(2)	138.4(3)	138.8(2)	142.6
$ \begin{array}{c cccc} Mo(1) - S(1) - C(1) - C(2) & -31.2(7) & -29.5(5) & -31.6 \\ S - S \ bite \ distance: & 3.192 & 3.195 & 3.201 \\ Mo \ distance \ from \ N_2S_2 \ plane & 0.069 & 0.071 & 0.063 \\ C36-centroid \ of \ C1 and \ C2 & 4.185 & 4.159 & 4.198 \\ Fold \ angle \ (\theta) & 42.0 & 41.1 & 44.4 \\ Dihedral \ angle \ (between \ planes: \ Mo1 - N11 - N21 \ and \ Mo1 - S1 - S2) & 5.0 & 5.6 & 5.3 \\ \end{array} $	Mo(1)-S(2)-C(2)-C(1)	29.0(7)	29.7(4)	31.6
S-S bite distance: 3.192 3.195 3.201 Mo distance from N ₂ S ₂ plane 0.069 0.071 0.063 C36-centroid of C1 and C2 4.185 4.159 4.198 Fold angle (θ) 42.0 41.1 44.4 Dihedral angle (between planes: Mo1-N11-N21 and Mo1-S1-S2) 5.0 5.6 5.3	Mo(1)-S(1)-C(1)-C(2)	-31.2(7)	-29.5(5)	-31.6
	S–S bite distance:	3.192	3.195	3.201
C36-centroid of Cland C2 4.185 4.159 4.198 Fold angle (θ) 42.0 41.1 44.4 Dihedral angle (between planes: Mo1-N11-N21 and Mo1-S1-S2) 5.0 5.6 5.3	Mo distance from N_2S_2 plane	0.069	0.071	0.063
Fold angle (θ) 42.041.144.4Dihedral angle (between planes: Mo1-N11-N21 and Mo1-S1-S2)5.05.65.3	C36-centroid of C1and C2	4.185	4.159	4,198
Dihedral angle (between planes: $Mo1-N11-N21$ and $Mo1-S1-S2$) 5.0 5.6 5.3	Fold angle (θ)	42.0	41.1	44.4
	Dihedral angle (between planes: Mo1–N11–N21 and Mo1–S1–S2)	5.0	5.6	5.3

Mo–S distances of 2.375 and 2.357 Å in complex 7 do not significantly vary from those in 1 through 3 despite the significant change in the nature of the sulfur donor ligand (1,1'-dithiaferrocenyl-S,S') in 7 [55]. Table 2 shows that there are no significant changes observed in Mo–S distances between chelate rings and non-chelated ligands, however, significant differences are observed in bond angles of S atoms with axial ligands (N1–Mo–S1 or S2). Bond angles N1–Mo–X (X = centroid of S1 and S2) of 86.14(10) Å in 1, 87.26(14) Å in 2, and 87.63(13) Å in 3 are the most acute in all of the structurally characterized mononuclear Group VI transition metalnitrosyl complexes containing at least two sulfur donor ligands².

The dihedral angle (φ_d) (Table 2) between the planes Mo1–N11–N21 and Mo1–S1–S2 groups the ene-1,2dithiolate compounds 1–3 are distinct $(\varphi_d > 174^\circ)$ from the other complexes in Chart 1. The value of $\varphi_d = 175^\circ$ for 1 and 174.7° for 3 is significantly larger than 161.9° and 162.2° in corresponding oxo-Mo complexes. This is due to the longer Mo–NO bond (1.818(6) Å in 1 and 1.774(6) Å in 3) whereas a lone pair interaction of

² This angle has the largest value of 161.862 Å in (1,2-bis(2-mercaptophenylthio)ethane)-nitroso-trimethylphosphine-molybdenum(II) complex [58].



Fig. 4. Compound $(Tp^*)Mo(NO)(bdtCl_2)$ (3) in *Pnma* space group, orientation along *c* axis in a unit cell.

strongly bonded terminal oxo atom (Mo–O = 1.678(4) Å in (Tp*)MoO(bdt) and 1.679(3) Å in (Tp*)MoO(bdtCl₂)) draws the Mo atom out of N₂S₂ (N11–N21–S1–S2) plane. This is also indicated by relatively smaller Mo distances from N₂S₂ plane (Table 3) in the reported complexes (0.069 Å in 1 and 0.063 Å in 3) compared with their oxo analogues (0.264 and 0.258 Å, respectively) [4,35,36,52,53].

The ene-1,2-dithiolate fragment does not show significant structural differences with remote substitution as indicated by the average S-C bond length of 1.742 Å in 1, 1.743 Å in 2 and 1.743 Å in 3 and the C=C bond length of 1.406 Å in 1, 1.413 Å in 2 and 1.431 Å in 3. The significant structural difference most between $(Tp^*)MoE(S-S)$ systems (where, E = NO, O) is the angle (δ) formed between the ene-1,2-dithiolate (S-C= C-S) least-squares plane and the S-Mo-S plane along the line of intersection containing the $S \cdots S$ atoms (see Fig. 2(B)). This angle in 1 is 137.9° , and thus the S–C= C-S plane is folded up toward the terminal nitrosyl group by $\theta = 180^{\circ} - \delta = 42.1^{\circ}$. This fold angle is 41.1° in 2 and 44.4° in 3 and thus increases slightly with respect to the electron withdrawing nature of the remote substituent on ene-dithiolate. The fold angle is in



Fig. 5. The distribution of fold angles (θ) of ene-1,2-dithiolates in Group VI transition metal–ene-1,2-dithiolate complexes.



Fig. 6. The orbital splitting diagram for the molybdenum t_{2g} orbitals of the [Mo(NO)]³⁺ and [MoO]³⁺ cores [62,63].

contrast to what is observed in the oxo-Mo systems where it ranges from 6.9° in (Tp*)MoO(bdtCl₂) to 29.5° in (Tp*)MoO(qdt) [4,35,36,52,53]. The (bdt) ring structure itself is essentially planar in all of the complexes. As mentioned earlier, compounds 1–3 have large fold angles not withstanding their acute ON–Mo–S angles, which are ~ 14° smaller than the O–Mo–S angles in the analogous oxo-Mo compounds [4,35,52,53].

In summary, the molecular structures of 1, 2 and 3 show that remote substituents on ene-1,2-dithiolate ligand do not significantly alter the structural parameters of the inner coordination sphere of the Mo center. However, a change of axial ligand (E) from oxo to nitrosyl induces significant changes in the fold angle and the E-Mo-X angle (X = centroid of S1, S2). The large fold angle in nitrosyl-Mo complexes despite their smaller E-Mo-X angle is intriguing. A CSD search for the transition metal complexes containing an ene-1,2dithiolate chelate showed a range $(0-52^{\circ})$ of fold angles [59]. A majority of these complexes have planar ($\theta =$ (0.0°) ene-1,2-dithiolate rings but some of them are folded by as much as $52^{\circ 3}$ [59,61]. The fold angle range in the structures of Group VI transition metal enedithiolene complexes is $0-44.4^{\circ}$ (Fig. 5) with the largest value of the fold angle observed in the complexes 1-3reported here.

The geometric structure perturbations in terms of the fold angle has implications with respect to the significant differences between the electronic structures of $(Tp^*)MoE(S-S)$ (E = NO, O). In these compounds the strong covalent bonding of the {MNO}⁴ group leads to an energetically isolated LUMO which is a nonbonding metal d-orbital (d_{xy}) (Fig. 6). The short Mo–O bond in (Tp*)MoO(S-S) complexes, on the other hand, dominates the splitting of t_{2g} orbitals (strong σ and π donor oxo-ligand) [62,63]. The electronic configuration of the oxo-Mo(V) systems is $(d_{xy})^{1}(d_{xz}d_{yz})^{0}$ and the nitrosyl-Mo(II) is $(d_{xz}d_{yz})^4(d_{xy})^0$. The d_{xy} -Sp overlap in LMo(NO)(SC₆H₅)₂ (where $L = \eta^5 - C_6H_5$, Tp*(8)), {MNO}⁴ complexes with filled d_{xz} and d_{yz} orbitals, is maximized by a ON-Mo-S-C torsion angle near 0 and 180° Fig. 2(A), [20,21]. The torsion angle ON–Mo–S–C

³ The most folded ene-1,2-dithiolate ring has been observed in the disordered structure of a uranium complex where $\theta = 76.21^{\circ}$ [60].



Fig. 7. He I PES of $(Tp^*)Mo(NO)(S-S)$ complexes ((S-S) = bdt(1), tdt(2) and $bdtCl_2(3)$.

in the above two LMo(NO)(SC₆H₅)₂ compounds are 12 and -174° in the former and -16 and -168° in the latter and indicate that the electronic structure of L has little influence on the overall stereochemistry of the complex [20,21].

We believe that the fold angle in compounds 1-3 has an electronic origin that may be attributed to the interaction of sulfur lone pairs (Sp_z orbitals) with the metal d-orbitals. The folding of the ene-1,2-dithiolate minimizes the interaction of the filled Sp_z orbitals with the filled metal d_{xz} and d_{yz} orbitals and favors the bonding interaction between the Sp_z orbitals and the empty metal d_{xy} orbital Fig. 2(B). It has been observed that the electronic occupation of d_{xy} orbital has significant effect on the fold angle. The complexes with $(d_{xy})^0$ electronic configuration have the most folded ene-1,2-dithiolate $(1-3: \theta = 41.1-44.4^\circ)$ in related Group VI complexes. We postulate that the fold angle should decrease as the complexes 1-3 are reduced to $(d_{xy})^1$ and the ene-dithiolate should become close to planar $(0 \simeq 0^\circ)$ on further reduction to $(d_{xy})^2$. The metallocene-dithiolene complexes show a fold angle (θ) close to 0° in the 18 electron d^2 complexes; upon oxidation this angle increases to $\theta = 45-50^\circ$ in the 16 electron d^0 complexes [24,25,61,64,65]. The electronic origin of the fold angles in compounds 1-3 and their oxo-analogues is a current active research area in our laboratory [29,37].

3.3. Photoelectron spectroscopy

A stack plot of He I gas phase valence PES of 1, 2 and 3 in the region 5.00-15.00 eV is displayed in Fig. 7. The region from 8.00 to 15 eV is primarily due to the ligand ionizations (Tp*, benzene ring, nitrosyl group). The broad Tp* ionization centered about 9 eV is also observed in analogous compounds with terminal oxo and sulfido groups [43]. In compound 3, chlorine lone pair-based ionization appearing at 10.76 (0.02) eV is easily assigned based on its reduced intensity in the He II excitation source (spectrum not shown). The ionizations appearing at lower energy than 8.00 eV, assigned to the sulfur and the molybdenum based molecular orbitals, are broader in the nitrosyl complexes (1, 2 and 3) than their oxo-Mo analogues [43]. The first ionization energies of 6.95 (0.02) eV for 2, 6.97(0.02) eV for 1, and 7.06 (0.02) eV for 3 (Table 4) suggest that electron withdrawing substituents on the ene-1,2-dithiolate stabilize the HOMO. However, this effect is less than that observed for the oxo-Mo counterparts, where the energy range is 0.8 eV [37]. The details of the PES studies and DFT calculations which probe bonding interactions in $(Tp^*)MoE(S-S)$ (E = NO, O) complexes will be discussed in more detail elsewhere [29,37].

Table 4

First ionization energies in He I gas phase photnelectron spectra for (Tp*)Mo(E)(S-S) systems

Complex	Ionization energy (eV, ± 0.02 eV)					
	$E = NO^{a}$	$E = NO^{a}$			E = O ^b	
	Band 1	Band 2	Band 3	Band 1	Band 2	
(Tp*)Mo(E)(tdt) (1)	6.90	7.56	7.82	6.35	~ 7.50	
(Tp*)Mo(E)(bdt) (2)	6.97	7.64	7.83	7.04	7.53	
$(Tp^*)Mo(E)(bdtCl_2)$ (3)	7.06	7.78	8.43	7.26	7.64	

^a Ref. [29,43].

^b Ref. [35,37,43].

4. Conclusions

The synthesis, structural and physical characterization of three (Tp*)Mo(NO)(S-S) compounds have provided an opportunity to investigate the geometric and electronic structure differences of (Tp*)MoE(S-S) (where E = O, NO) systems as a function of axial ligation and remote substituent effects on the ene-1,2dithiolate ligand. The most significant structural difference is the large fold angle of ene-1,2-dithiolate along S-S axis in the nitrosyl-Mo compounds. It has been postulated earlier that the variation in the fold angle of pyranopterin-ene-1,2-dithiolate may control the electronic structure of the Mo center of enzymes and could play a regulatory role in their catalysis [35,36]. The reduction potential of these (Tp*)Mo(NO)(S-S) compounds is sensitive to peripheral substitution of the ligand, whereas the first ionization energy is not. This diversity is due to the different orbitals involved in each of these processes and supports the electronic structure origin behind the fold angles in Mo-nitrosyls containing an ene-1,2-dithiolate. A more detailed computational analysis of the effect of fold angle on the electronic structures using density functional method is in progress [29,37].

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