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The Molecular Structure of $[Mo(S_2P(OEt)_2)_3]_2$-(μ-*p*-NC_6H_4N), a Derivative of *p*-Phenylenediamine

KATHERINE L. WALL, K. FOLTING, J. C. HUFFMAN* and R. A. D. WENTWORTH*

The Molecular Structure Center and Department of Chemistry, Indiana University, Bloomington, Ind. 47405, U.S.A.

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Introduction

A previous study of compounds containing arylimido ligands and Mo(V) led to a report [1] of the preparation and remarkable ESR spectra of $Mo(NC_6H_4X)(S_2P(OEt)_2)_3$(X = H and *p*-$CH_3$). Although seven atoms (6 S and 1 N) are available for binding to the metal, an X-ray study of the *p*-CH_3 derivative has shown [2] that the coordination geometry consists of a distorted octahedron in which one of the dithiophosphate ligands is monodentate.

An attempt to prepare a *p*-NO_2 derivative by the oxidation of Mo(III) with *p*-nitrophenyl azide in the presence of $S_2P(OEt)_2^-$ ions resulted in a crystalline substance whose analysis indicated the presence of nitrogen but whose infrared spectrum indicated the absence of the nitro group. A structural study which is described herein indicates that the compound is $[Mo(S_2P(OEt)_2)_3]_2$ (μ-*p*-NC_6H_4N). The bridging ligand is a deprotonated derivative of *p*-phenylenediamine and results from abstraction of oxygen from the aromatic nitro group.

Experimental

Preparation of $[Mo(S_2P(OEt)_2)_3]_2(\mu\text{-}p\text{-}NC_6H_4N)$

A combination of $MoCl_3(THF)_3$ (4.5 mmol) and *p*-$C_6H_4(NO_2)(N_3)$ (4.5 mmol) were stirred in 20 ml of THF at room temperature until a complete solution was obtained (~48 hr). The addition of $[Et_2NH_2](S_2P(OEt)_2)$ (13.5 mmol) caused the color of the solution to change from orange-brown to red with the precipitation of some $[Et_2NH_2]Cl$. After about 20 min, the solvent was removed under reduced pressure, diethyl ether was added, and the solution was filtered. Ether was then removed from the filtrate under reduced pressure. The residue was triturated with methyl alcohol and filtered again. Recrystallization was accomplished from CH_2Cl_2/CH_3OH and afforded red-brown crystals. *Anal.* Calcd.: C, 25.6; H, 4.6; N, 2.0; S, 27.3. Found: C, 25.6; H, 4.6; N, 2.0; S, 27.3. The magnetic moment in CH_2Cl_2 [3] at 30 °C is 2.3 μ_B (calculated on the basis of two molybdenum atoms).

TABLE I. Crystal Data.

Space group	$P\bar{1}$
Temp. (°C)	−165
a (Å)	15.279(11)
b (Å)	17.019(11)
c (Å)	11.640(8)
α (deg)	90.17(3)
β (deg)	95.51(3)
γ (deg)	74.65(3)
V (Å^3)	2904.4
d_{calc} (g/cm^3)	1.609
Z	2
Crystal size (mm)	0.05 × 0.13 × 0.20
Radiation	MoK_α (0.71069 Å)
Number of unique data	7637
Number of data with $F > 3\sigma(F)$	5772
R(F)	0.063
R_w(F)	0.056
Goodness of fit	1.144
Largest Δ/σ	0.05

X-ray Crystallography. Collection of Data

General operating procedures and computational techniques have been described previously [4]. Crystal data are given in Table I. A total of 8045 reflections were collected in a range of $6° \leqslant 2\theta \leqslant 45°$. The data were corrected for absorption, Lorentz, and polarization effects and reduced to a unique set.

Solution and Refinement of the Structure

The structure was solved by a combination of Patterson and Fourier techniques. All non-hydrogen atoms were located and refined by full-matrix least-squares using anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with each having an isotropic thermal parameter which is equivalent to the parent carbon atom plus one. The final difference Fourier map was essentially featureless with the largest peak equal to 0.86 e/Å^3. Final positional parameters are given in Table II.

Results and Discussion

The structure of $[Mo(S_2P(OEt)_2)_3]_2(\mu$-*p*-$NC_6H_4N)$ is shown in Fig. 1. The *p*-phenyldiimido ligand

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*Authors to whom correspondence should be addressed.

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TABLE II. Final Positional Parameters ($\times 10^4$).

Atom	x	y	z	Atom	x	y	z
Mo(1A)	2026(1)	7592.5(5)	8586(1)	Mo(1B)	2809(1)	2391.3(5)	6638(1)
S(2A)	1166(2)	7881(2)	6585(2)	S(2B)	3716(2)	1969(2)	8578(2)
S(3A)	3036(2)	8251(2)	7615(2)	S(3B)	1715(2)	1847(2)	7630(2)
P(4A)	2218(2)	8257(2)	6149(2)	P(4B)	2584(2)	1745(2)	9068(2)
O(5A)	1932(5)	9121(4)	5503(5)	O(5B)	2762(5)	906(4)	9722(6)
C(6A)	1465(8)	9837(6)	6095(9)	C(6B)	3127(8)	129(7)	9163(9)
C(7A)	1047(8)	10503(7)	5201(9)	C(7B)	3744(11)	−439(8)	9997(12)
O(8A)	2714(5)	7759(4)	5161(6)	O(8B)	2176(5)	2302(4)	10073(6)
C(9A)	2997(8)	6863(7)	5163(9)	C(9B)	2011(7)	3180(6)	10053(9)
C(10A)	3938(8)	6542(7)	5681(11)	C(10B)	1074(8)	3618(7)	9495(10)
S(11A)	2900(2)	7673(1)	10452(2)	S(11B)	1891(2)	2427(1)	4767(2)
S(12A)	4223(2)	6460(2)	12474(2)	S(12B)	786(2)	3702(2)	2688(2)
P(13A)	3651(2)	6511(2)	10915(2)	P(13B)	1294(2)	3621(2)	4283(2)
O(14A)	3037(4)	5900(4)	10660(5)	O(14B)	1999(4)	4151(4)	4570(5)
C(15A)	2348(6)	5863(6)	11447(8)	C(15B)	2740(7)	4071(7)	3887(8)
C(16A)	1805(7)	5320(6)	10901(9)	C(16B)	3340(7)	4593(7)	4379(9)
O(17A)	4322(4)	6171(4)	9947(5)	O(17B)	609(4)	4021(4)	5191(6)
C(18A)	4969(7)	6617(7)	9686(9)	C(18B)	−242(7)	3785(7)	5202(9)
C(19A)	5590(8)	6121(7)	8895(11)	C(19B)	−488(8)	3835(7)	6417(9)
S(20A)	1107(2)	9072(1)	9081(2)	S(20B)	3451(2)	853(1)	6023(2)
S(21A)	703(2)	7346(1)	9447(2)	S(21B)	4232(2)	2430(1)	5800(2)
P(22A)	219(2)	8554(2)	9682(2)	P(22B)	4362(2)	1277(1)	5302(2)
O(23A)	−791(4)	8880(4)	9117(6)	O(23B)	5378(4)	759(4)	5570(5)
C(24A)	−1056(7)	8660(7)	7943(9)	C(24B)	5837(7)	725(6)	6739(9)
C(25A)	−2018(7)	9148(7)	7643(10)	C(25B)	6554(8)	1170(6)	6772(9)
O(26A)	34(5)	8763(5)	10964(6)	O(26B)	4220(4)	1204(4)	3967(5)
C(27A)	737(9)	8903(10)	11875(12)	C(27B)	4794(7)	1486(6)	3203(9)
C(28A)	969(12)	8271(12)	12684(13)	C(28B)	4302(9)	1625(8)	2042(10)
N(29A)	2410(5)	6567(5)	8305(7)	N(29B)	2560(5)	3412(4)	6952(6)
C(30A)	2459(7)	5766(6)	8008(8)	C(30B)	2513(6)	4212(5)	7286(8)
C(31A)	1666(7)	5554(6)	7609(8)	C(31B)	3327(6)	4399(6)	7673(8)
C(32A)	3307(6)	5187(6)	8031(8)	C(32B)	1682(6)	4802(6)	7249(8)

TABLE III. Selected Distances (A).

Atoms	A End	B End
Mo(1)–S(2)	2.544(3)	2.533(3)
Mo(1)–S(3)	2.486(3)	2.486(3)
Mo(1)–S(11)	2.460(3)	2.466(3)
Mo(1)–S(20)	2.630(3)	2.662(3)
Mo(1)–S(21)	2.471(3)	2.483(3)
Mo(1)–N(29)	1.729(8)	1.723(7)
Mo(1)····S(12)	5.400(3)	5.417(3)
Mo(1A)····Mo(1B)	8.930(6)	

connects the molybdenum atoms with an approximate center of symmetry located at the center of the aromatic ring. Each nitrogen atom from this ligand is adjacent to the sulfur atom from a monodentate dithiophosphate ligand. The distorted octa-

TABLE IV. Selected Bond Angles (Deg).

Atoms	A End	B End
S(2)–Mo(1)–S(3)	79.2(1)	79.5(1)
S(2)–Mo(1)–S(11)	165.1(1)	164.7(1)
S(2)–Mo(1)–S(20)	86.1(1)	86.8(1)
S(2)–Mo(1)–S(21)	93.0(1)	89.7(1)
S(2)–Mo(1)–N(29)	91.3(3)	92.8(3)
S(3)–Mo(1)–S(11)	89.7(1)	91.0(1)
S(3)–Mo(1)–S(20)	86.6(1)	84.3(1)
S(3)–Mo(1)–S(21)	162.8(1)	159.5(1)
S(3)–Mo(1)–N(29)	105.0(3)	105.3(3)
S(11)–Mo(1)–S(20)	83.2(1)	80.3(1)
S(11)–Mo(1)–S(21)	94.8(1)	95.5(1)
S(11)–Mo(1)–N(29)	101.3(3)	101.2(3)
S(20)–Mo(1)–S(21)	77.5(1)	77.8(1)
S(20)–Mo(1)–N(29)	167.5(3)	170.2(3)
S(21)–Mo(1)–N(29)	90.4(3)	92.5(3)
Mo(1)–N(29)–C(30)	163.9(7)	170.3(7)

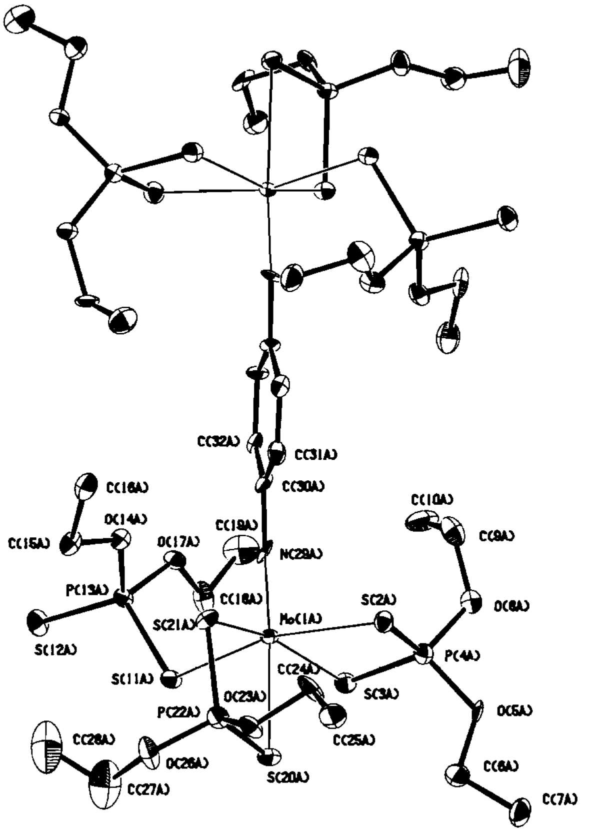

Fig. 1. An ORTEP drawing of $[Mo(S_2P(OC_2H_5)_2)_3]_2(\mu\text{-}p\text{-}NC_6H_4N)$ showing thermal ellipsoids at the 50% probability level. The numbering scheme for the A end of the molecule is shown while the corresponding scheme for the B end can be obtained by inversion through the center of the aryl ring.

hedron about each metal atom is completed by the donor atoms from two bidentate dithiophosphate ligands. Some relevant bond distances and angles are given in Tables III and IV. The structure and dimensions of both ends of this molecule are remarkably similar to those of $Mo(NC_6H_4CH_3)(S_2P(OEt)_2)_3$ [2].

Formation of the *p*-phenyldiimido ligand requires reduction of the original *p*-NO_2 substituent by way of oxygen abstraction. Accompanying oxidation products were not identified. Complete and partial reduction of aromatic nitro substituents by oxophiles has precendent [5, 6] but it should also be noted that this substituent is unscathed during the oxidation of $MoO(S_2CNEt_2)_2$ by *p*-nitrophenyl azide, a reaction which yields $MoO(NC_6H_4NO_2)(S_2CNEt_2)_2$ [7].

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