

Solid-phase synthesis, crystal structure, and quantum chemical calculation of a molybdenum(II) complex with bis(diethyldithiocarbamate)

Guang-Yu He,⁽¹⁾ Feng-Li Bei,⁽²⁾ Hai-Qun Chen,⁽¹⁾ and Xiao-Qiang Sun^{(1)*}

Received April 7, 2005; accepted December 20, 2005
Published Online June 7, 2006

The complex $\text{Mo}(\text{Et}_2\text{dtc})_2$ [Et_2dtc : bis(diethyldithiocarbamate)] was synthesized by solid-phase reaction at room temperature and characterized by elemental analysis, powder XRD, IR, ^1H NMR and TG/DTA. Its crystal structure was determined by X-ray single crystal diffraction. The crystals are monoclinic with space group $P2_1/c$, $a = 0.61800(12)$ nm; $b = 1.1540(2)$ nm; $c = 1.1610(2)$ nm; $\beta = 95.78(3)^\circ$; $V = 0.8238(3)$ nm³; $D_c = 1.582$ g/cm³; $Z = 2$ $F(000) = 400$; $\mu = 1.285$ mm⁻¹; $R = 0.0703$; $wR = 0.2330$; GOF = 1.060. The coordination geometry of Mo atom, by four S anions from Et_2dtc ligand, is that of a slightly distorted planar square. Furthermore, the optimized geometry, charge distribution, and thermodynamic functions were calculated by quantum chemical method.

KEY WORDS: Mo(II) complex; diethyldithiocarbamate; solid-phase reaction; crystal structure; quantum chemical calculation.

Introduction

Dialkyl-substituted dithiocarbamate (dtc) anions have been proven to be metal chelating agents, which are highly versatile in separating metals with gas chromatography.¹ Their good performance in liquid–liquid extraction and other analytical procedures² makes them very attractive in identifying metals with gas chromatography.³ Some of the dtc salts have shown interesting biological effects including anti-alkylation^{4,5} and anti-HIV properties.^{6,7} They are also used as effective antidotes for cadmium intoxication.^{8,9}

The ability of dtc to bind to metals has been known for many years. They can chelate with virtually all transition elements.¹⁰ Water-soluble dialkyldithiocarbamate complexes have been tested in various medical applications.¹¹ In addition, dialkyldithiocarbamate sodium salts are better extracting agents for many transition metals.¹² They are good floating agents to novel metal ores and copper ores^{13,14} as well. In this paper, we report a solid-phase reaction of molybdenum(II) complex with bis(diethyldithiocarbamate) at room temperature. Infrared and ^1H NMR spectra were acquired. And the crystal structure of molybdenum(II) bis(diethyldithiocarbamate) complex [$\text{Mo}(\text{II})(\text{Et}_2\text{dtc})_2$] has been determined. Furthermore, the optimized geometry, charge distribution and thermodynamic functions of title complex $\text{Mo}(\text{II})(\text{Et}_2\text{dtc})_2$ were calculated by quantum chemical method.

⁽¹⁾ Key Laboratory of Fine Petro-Chemical Engineering, Jiangsu Polytechnic University, Changzhou 213016, P.R. China.

⁽²⁾ Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, P.R. China.

* To whom correspondence should be addressed; e-mail: chtt88@tom.com

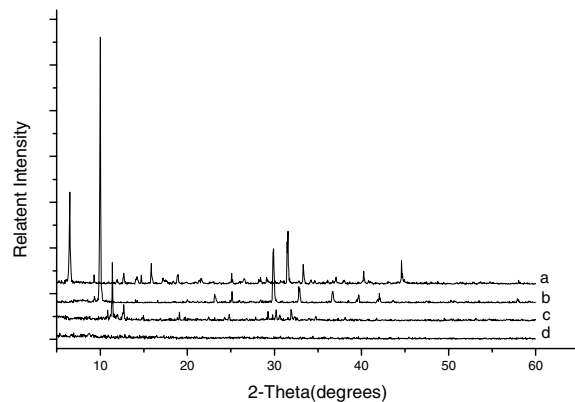
Table 1 Crystal Data and Structure Refinement for Title Complex

Empirical formula	C ₁₀ H ₂₀ MoN ₂ S ₄
Formula weight	288.22
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> -1
Unit cell dimensions	<i>a</i> = 13.861(3), <i>b</i> = 10.142(2), and <i>c</i> = 8.7320(17) Å; β = 103.70(3)°
Volume (Å ³)	1192.6(4)
Z	4
Calculated density (mg/m ³)	1.605
Absorption coefficient (mm ⁻¹)	0.129
<i>F</i> (000)	592
Crystal size (mm ³)	0.30 × 0.14 × 0.10
Theta range for data collection (deg)	2.51–24.97
Limiting indices	−16 ≤ <i>h</i> ≤ 15, −12 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 10
Reflections collected	1118
Independent reflections	1118 [<i>R</i> (int) = 0.0000]
Completeness to theta = 24.97°	99.9%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on <i>F</i> ²
Goodness-of-fit on <i>F</i> ²	1.114
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.1125
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.1175
Largest diff. peak and hole	0.358 and −0.237 e. Å ⁻³

Experimental

Physical measurements

Elemental analysis for carbon, hydrogen, and nitrogen were performed on Perkin-Elmer 240C instrument. The IR spectra were recorded in the 4000–400 cm⁻¹ region using KBr pellets on a Nicolet 170SX FT spectrophotometer. Proton NMR spectra were obtained on a Bruker DRX 300 spectrometer using TMS as internal standard. The TG/DTA data were acquired on a SDT2980 simultaneous for samples of approximately 10 mg under a nitrogen atmosphere (150 ml/min) at a heating rate of 20°C/min. The solid-phase reaction was investigated by Bruker D8 ADVANCE powder XRD diffractometer. The single crystal data were measured on Nonius-CAD-4 diffractometer.

**Fig. 1** The X-ray powder diffraction patterns of reactants and products.

Synthesis

All chemicals were obtained from commercial source and used without further purification.

Preparation of the *N,N'*-diethyldithiocarbamate sodium [Na(Et₂dtc)]. To a stirred solution of diethyl secondary amine (0.05 mol, Et₂NH is 40% aqueous solution) in ethanol (5 ml), carbon disulfide (3.1 ml–0.052 mol), and sodium hydroxide (50% aqueous solution 4 ml) were added dropwise while keeping the temperature below 4°C. After stirring for 4–5 h, volatiles were evaporated without heating. The pure product [Na(Et₂dtc)] was obtained after recrystallization from ethanol. Yield 80–90%. Found: C, 30.19; H, 4.8; N, 7.6. Calcd. for the title compound (C₁₀H₂₀N₂S₄Mo₁): C, 30.60; H, 5.14; N, 7.14.

Solid-phase synthesis of Mo(Et₂dtc)₂. At room temperature, the accurately weighed white ligand *N,N'*-diethyldithiocarbamate sodium [Na(Et₂dtc)](a) and red NH₄MoO₄(b) (2:1) were carefully mixed in an agate mortar, and the mixture was ground for 25 min. The primary product (c) formed after the reaction mixture turned green. The fine product (d) was obtained by washing primary product with water. Crystals, suitable for X-ray structure determination, were prepared after recrystallizing from ethanol.

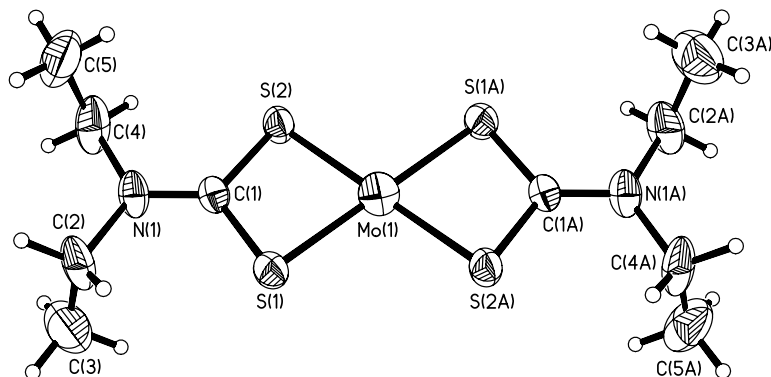


Fig. 2 Molecular structure of the title compound with 50% probability of the thermal ellipsoids.

Crystal structure determination

A green prismatic crystal with approximate dimensions of 0.36 mm \times 0.24 mm \times 0.18 mm was selected for data collection. The XRD data were collected on a Nonius-CAD-4 diffractometer. Reflection data were measured at 293 K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The $\omega - 2\theta$ scan technique was used with θ limit $2.49^\circ < \theta < 24.96^\circ$. A total of 1443 independent reflections were collected, of which 1079 observed reflections ($I > 2\sigma(I)$) were used for the structure

determination. The structure was solved by direct methods using the *SHELXTL* program package.¹⁵ All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares methods. All the hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave $R = 0.0439$, $wR = 0.1125$ for 1035 reflections

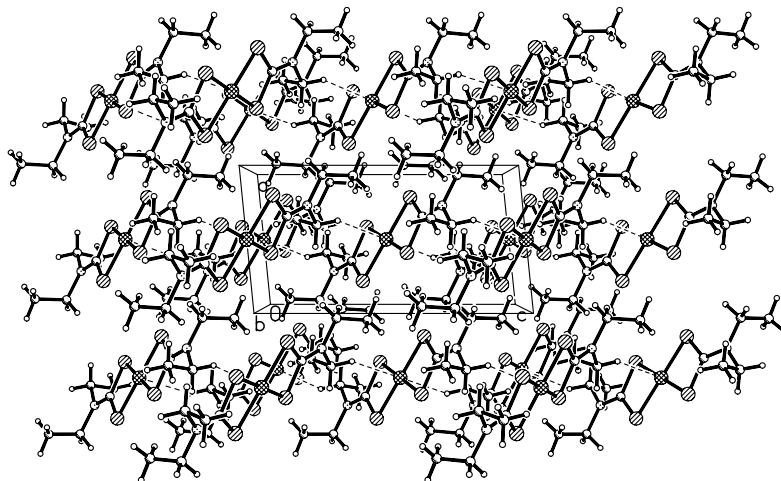


Fig. 3 Crystal packing of the title compound.

Table 2 Bond Lengths (Å) and Angles (°) of the Title Compound

Mo(1)–S(1)	2.1981(16)	S(1)–Mo(1)–S(1)#1	180.00(8)
Mo(1)–S(1)#1	2.1981(16)	S(1)–Mo(1)–S(2)	79.35(6)
Mo(1)–S(2)	2.2013(16)	S(1)#1–Mo(1)–S(2)	100.65(6)
Mo(1)–S(2)#1	2.2013(16)	S(1)–Mo(1)–S(2)#1	100.65(6)
S(1)–C(1)	1.720(6)	S(1)#1–Mo(1)–S(2)#1	79.35(6)
S(2)–C(1)	1.717(6)	S(2)–Mo(1)–S(2)#1	180.00(12)
N(1)–C(1)	1.305(8)	C(1)–S(1)–Mo(1)	85.5(2)
N(1)–C(4)	1.482(9)	C(1)–S(2)–Mo(1)	85.5(2)
N(1)–C(2)	1.499(9)	C(1)–N(1)–C(4)	121.0(5)
C(2)–C(3)	1.494(13)	C(1)–N(1)–C(2)	121.1(6)
C(4)–C(5)	1.453(13)	C(4)–N(1)–C(2)	117.6(6)

with $I > 2\sigma(I)$, $w = 1/[\sigma^2(F_o^2) + (0.1241P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. $S = 1.060$, $(\Delta/\sigma)_{\max} = 0.152$, $(\Delta\rho)_{\max} = 0.831$, $(\Delta\rho)_{\min} = -1.053$. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography.¹⁶ Crystal data and refinement details are given in Table 1.

Calculation method

Molecular modeling of $\text{Mo}(\text{Et}_2\text{dtc})_2$ was started by optimizing the molecular framework obtained from the crystal structure with HyperChem molecular modeling software¹⁷ using MM + force field¹⁸ molecular mechanics. After optimizing geometry, charge distribution and thermodynamic functions were investigated using DFT-BLYP method,^{19,20} with basic set of Double Numerical plus d-functions (DND).²¹ All calculations were performed on Compaq Alpha DS20E server and PIV 1.4G PC.

Results and discussion

Powder XRD characterization

Powder XRD patterns of the ligand N,N' -diethyldithiocarbamate sodium (a), NH_4MoO_4 (b), primary product (c), and fine product of $\text{Mo}(\text{Et}_2\text{dtc})_2$ (d) are shown in Fig. 1. The XRD pattern of product (d) which can be seen in Fig. 1

Table 3 The Atomic Charges

Atom	Charge	Atom	Charge
Mo(1)	0.639	N(1)	-0.289
S(1)	-0.474	C(1)	0.453
C(3)	-0.588	C(2)	-0.284

is different with that of reactants (a and b). This demonstrates that the reaction is brought to completion and the title complex can be synthesized by environment-friendly solid-phase reaction at room temperature.

IR, ¹H NMR spectra, and TG/DTA

The four strong bands in the region from 2830 to 2960 cm^{-1} of IR represent the stretching vibration of C–H for CH_2 . The $\nu_{\text{C}=\text{N}}$ stretching vibration band is slightly shifted from 1610 cm^{-1} for the free ligand to the lower frequency 1600 cm^{-1} for the complex.²² The strong peak of 1202 cm^{-1} shows the stretching vibration of C=S. The ¹H NMR (CDCl_3 , TMS) spectrum of the free ligand gives a triplet within 1.17–1.22 ppm for the protons of the CH_3 and quadruplet around 3.98–4.00 ppm for the protons of the CH_2 . The complex was heated to 800°C in N_2 atmosphere. The figure of TG/DTA analysis shows two weight-loss processes. The complex began to lose 57.43% of its weight at about 74–321°C corresponding to the loss of $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_2$ fragment (Calcd. 59.21%). And finally the 9.80% loss of weight for S (Calcd. 8.10%) from 414 to 798°C left the residue of MoS .

Description of the molecular and crystal structure

A perspective view of the title compound with atomic numbering scheme is shown in Fig. 2. and a perspective view of the crystal packing in the unit cell is shown in Fig. 3. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1.

Table 4 Thermodynamic Properties of Title Complex at Different Temperatures

T (K)	$C_{p,m}^0$ (cal mol ⁻¹ K ⁻¹)	S_m^0 (cal mol ⁻¹ K ⁻¹)	H_m^0 (cal mol ⁻¹ K ⁻¹)	G_m^0 (cal mol ⁻¹ K ⁻¹)
200.00	58.884	128.102	189.921	164.300
298.15	77.125	155.036	196.601	150.377
400.00	95.095	180.251	205.385	133.285
500.00	110.603	203.183	215.691	114.099
600.00	123.648	224.537	227.423	92.701
700.00	134.575	244.443	240.350	69.240
800.00	143.810	263.032	254.282	43.856

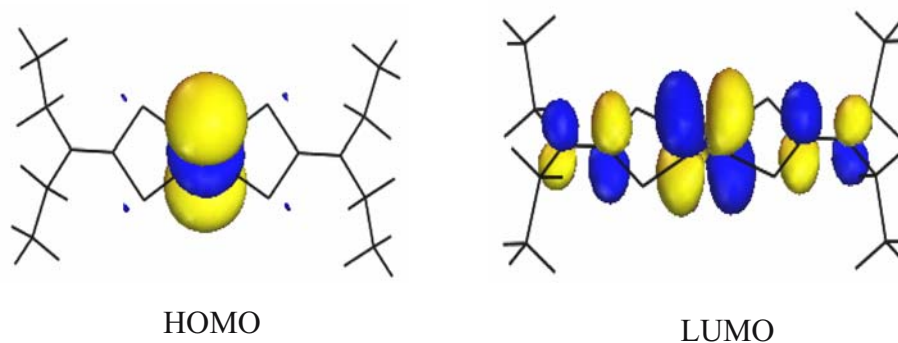
Selected bond lengths and bond angles are listed in Table 2.

The Mo(II) ion is four-coordinated forming a plane-square, i.e. MoS₄. The dithiocarbamate functions as a bidentate ligand coordinating through the S atom with the Mo–S distance of 2.1981(16) and 2.2013(16) Å. The MoS₄ plane is slightly distorted, with dihedral angles ranging from 1.47(3) to –1.97(7). The four-membered MoS₂C ring is planar, with maximum deviation of 0.013 Å for C1 from the plane. The Mo1–S2 and S1–C1 bond lengths are longer than those of Mo1–S1 and S2–C1, respectively. The shorter Mo–S bond length (Mo1–S2) lies adjacent to the C1–S2 bond, which is closer to the normal C=S bond length of 1.69 Å. This characteristic is also found and explained in detail in the similar structure.²³ The bond length

of C1–N1 [1.305(8) Å] has double-bond character, but slightly shorter than those observed in a related structure.²⁴ The other bond distances for the C–C in the ligand ring are in good agreement with those of other corresponding compounds.^{25,26}

Charges distribution, thermodynamic properties, and molecular orbit

The charge distribution of the title complex is listed in Table 3. The charges on the Mo(II) cation of 0.639 indicate that the charges were transferred from the ligands to the Mo(II) cation. Furthermore, the average charges of –1.257 on MoS₄ of the complex demonstrate that the charges on ligands were transferred toward the coordinated center MoS₄. According to vibrational analysis and statistical thermodynamics, the standard thermodynamic functions, heat capacities (C_p^0), entropies (S_m^0), and enthalpies (H_m^0) were obtained and are listed in Table 4. The magnitudes of C_p^0 , S_m^0 , and H_m^0 increase with temperature, but the G_m^0 decreases with temperature. The molecular orbitals HOMO and LUMO were calculated, and their patterns are listed in Fig. 4, which shows that the HOMO orbit mainly appears on the Mo atom, while the LUMO orbit was distributed averagely on ligand atoms and Mo atom, indicating that electrons were transferred from Mo atom to ligand atoms in the process of excitation.

**Fig. 4** Frontier molecular orbit of the title complex.

Supplementary data Further details of crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request. Deposition number CCDC 214324.

Acknowledgement

Financial Support from the National Natural Science Foundation of China (No.21071021) and the Open Foundation of Key Laboratory of Fine Petro-Chemical Engineering of Jiangsu Polytechnic University are gratefully acknowledged

Reference

- Riekkola, M.L.; Makitie, O.; Sundberg, M. *Kem. Kemi.* **1979**, *6*, 525.
- Thorn, G.D.; Ludwing, R.A. *The Dithiocarbamate and Related Compounds*, Amsterdam: Elsevier, 1962.
- Riekkola, M.L.; Pakkanen, T.; Niinisto, L. *Acta Chim. Scand* **1983**, *A37*, 807.
- Gringeri, A.; Keng, P.C.; Borch, R.F. *Cancer Res.* **1988**, *48*, 5708.
- Pannacciulli, I.M.; Lerza, R.A.; Bogliolo, G.U.; Mencoboni, M.P. *J. Cancer* **1989**, *29*, 371.
- Lang, J.M.; Touraine, J.L.; Treppe, C.; Choute, P.; Kirstetter, M.; Falkenrodt, A.; Herviou, L.; Livrozet, J.M.; Retornaz, G.; Tpuraine, F.; Renoux, G.; Renoux, M.; Musset, M. *J. Carauk and the AID-Imuthiol French Study Group*, *Lancet*, **1988**, 702.
- Hersh, E.M.; Brewton, G.; Abrams, D.; Bartlett, J.; Gill, P.; Gorter, R.; Gottlieb, M.; Jonikas, J.J.; Landesman, S.; Levine, A.; Maecel, A.; Petersen, E.A.; Whiteside, M.; zahradnik, J.; Negron, C.; Boutitie, F.; Caraux, J.; Dupuy, J.M.; Saimi, R. *J. Am. Med. Assoc.* **1991**, *265*, 1538.
- Gale, G.R.; Atkins, L.M.; Walker Jr. E.M.; Smith, A.B.; Jones, M.M. *Ann. Clin. Lab. Sci.* **1984**, *14*, 137.
- Shinobu, L.A.; Jones, S.G.; Jones, M.M. *Acta Pharmacol. Toxicol.* **1984**, *54*, 189.
- Allen, F.H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31.
- Bardaji, M.; Connelly, N.G.; Gimeno, M.C.; Jimenez, J.; Jones, P.G.; Laguna, A.; Laguna, M. *J. Chem. Dalton Trans* **1994**, *86*, 1163.
- Xie, J.; Funakoshi, T.; Shimada, H.; Kojima, S. *Res. Commun. Mol. Pathol. Pharmacol.* **1994**, *86*, 245.
- Stary, J. *The Solvent Extraction of Metal Chelate*, Pergamon, 1964, p. 180.
- Jian, F.-F.; Wang, Z.-X.; Bai, Z.-P.; You, X.-Z.; Fun, H.-K.; Chinnakali, K.; Razak, I.A., *Polyhedron* **1999**, *18*, 3401.
- Sheldrick, G.M. SHELXTL 97, Program for Crystal Structure refinement, University of Gottingen, Germany, 1997.
- Wilson, A.J. *International Tables for X-ray Crystallography*, Vol. C, Dordrecht: Kluwer Academic Publishers, 1992; Tables 4.2.6.8 (pp. 219–222) and 6.1.1.4 (pp. 500–502) respectively.
- HyperChem™, Version 4.5 for Windows, Hypercube Inc., Waterloo, Canada, 1994.
- Allinger, N.L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.
- Becke, A.D. *J. Chem. Phys.* **1988**, *88*, 2547.
- Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 786.
- Delley, B. *J. Chem. Phys.* **1990**, *92*, 508.
- Coville, N.J.; Neuse, E.W. *J. Org. Chem.* **1977**, *42*, 3485.
- Lanfredi, A.M.M.; Ugozzoli, F.; Asaro, F.; Pellizer, G.; Marsich, N.; Camus, A. *Inorg. Chim. Acta.* **1992**, *192*, 271.
- Jian, F.F.; Bei, F.L.; Lu, L.D.; Yang, X.J.; Wang, X. et al. *Acta Cryst.* **2000**, *C56*, e288.
- Long, D.L.; Zeng, D.X.; Xin, X.Q.; Huang, X.Y.; Kang, B.S. *Synth. React. Inorg. Met-Org. Chem.* **1996**, *26*, 723.
- Zheng, H.G. Zeng, D.X.; Xin, X.Q.; Wong, W.T. *Polyhedron* **1997**, *20*, 3499.