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A Novel Molybdenum(0) Dinitrogen Complex Containing Crown Thioether as the Sole Auxiliary Ligand: *trans*-$Mo(N_2)_2Me_8[16]aneS_4$ ($Me_8[16]aneS_4$ = 3,3,7,7,11,11,15,15-Octamethyl-1,5,9,13-tetrathiacyclohexadecane)

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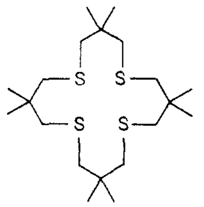
For the past two decades dinitrogen complexes of transition metals have received extensive attention as chemical models to mimic the function of nitrogenase[1] and as potential means of transforming dinitrogen into organonitrogen compounds.[2] Almost all the dinitrogen complexes so far studied carry phosphines as auxiliary ligands. In view of the involvement of sulfur ligands in the nitrogenase cofactor Fe–Mo–S cluster, dinitrogen complexes containing sulfur coligands are of considerable interest.[3] Such compounds are difficult to prepare[4] and those containing sulfur coligands only are unknown. As far as we are aware there are several compounds carrying one or two sulfur ligands,[3,5-9] e.g., *trans*-$Mo(N_2)_2(PMePh_2)_2(Ph_2PCH_2CH_2SMe)$[3] and *mer*-$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$,[5] all of which still contain phosphines as additional coligands. Our synthetic strategy for a molybdenum(0) dinitrogen complex containing only sulfur ligands is to employ a 16-membered quadridentate crown thioether, 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane ($Me_8[16]aneS_4$), as a coligand. This particular crown thioether has been proved to be a potential ligand to stabilize low-valent molybdenum, e.g., Mo(II) in *trans*-$MoX_2Me_8[16]aneS_4$ (X = Cl, Br) and Mo(0) in *trans*-$Mo(CO)_2Me_8[16]aneS_4$.[10] We present here the first example of a well-characterized molybdenum(0) dinitrogen complex containing thioethers as the sole auxiliary ligand, *trans*-$Mo(N_2)_2Me_8[16]aneS_4$ (**1**) together with a reaction of **1** with MeBr affording *trans*-$\{MoBr(N_2Me_2)Me_8[16]aneS_4\}Br$ (**2**). On the basis of electrochemical and structural studies of **1** as well as extended Hückel MO calculations $Me_8[16]aneS_4$ was deduced to act as a p_π donor.



$Me_8[16]aneS_4$

A suspension of *trans*-$MoBr_2Me_8[16]aneS_4$ in THF was stirred with a large excess of 40% Na/Hg under N_2 (5 atm) at room temperature for 4 h. Extraction of the concentrated residue with toluene gave **1** as orange red crystals (36%)[11] together with brown solids (~10%).[12] The former was readily separated from the latter by recrystallization from acetone, in which the latter is sparingly soluble. On prolonged stirring of the reaction mixture (24 h), the yield of **1** decreased to 24%, probably due to C–S bond cleavage of the coordinated $Me_8[16]aneS_4$. In fact, the formation of $MeCH{=}CMe_2$ was confirmed by the GC-MS spectrum. Compound **1** is thermally stable up to 135 °C under N_2 and slightly air sensitive in the solid state.

The complex **1** was fully characterized by spectroscopic data[11] and a single-crystal X-ray structural study.[13] The Mo coordination geometry is slightly distorted octahedral with two N_2 molecules in axial and four S atoms in equatorial sites (Figure 1). The coordinated $Me_8[16]aneS_4$ assumes an all-up conformation where all six-membered $\overline{MoSCH_2CMe_2CH_2S}$ rings adopt the chair form. Thus, the molecule possesses approximately C_{4v} symmetry. The Mo atom is slightly displaced toward the ring C atoms by 0.101 (1) Å from the strict plane defined by the four S atoms, the mean deviation of the S atoms from the 4S plane being 0.002 (2) Å. The displacement of the Mo atom may arise from the particular all-up conformation of $Me_8[16]aneS_4$ and also from the small cavity of $Me_8[16]aneS_4$ for the zero-valent Mo atom. Despite the displacement, the Mo–S bonds seems to be still compressed, and the Mo–S distances (average 2.424(2) Å) are significantly shorter than those (2.483 (8)–2.560 (1) Å) found for Mo(0) thioether complexes.[3,14] The Mo–N (Mo–N(1) 2.008 (5), Mo–N(3) 1.991 (5) Å) and N–N distances (N(1)–N(2) 1.108(7), N(3)–N(4) 1.105(7) Å) of the two mutually trans N_2 ligands are essentially similar.

The cyclic voltammogram of **1** measured in THF (0.2 M *n*-Bu_4NBF_4, scan rate 100 mv/s, 20 °C) showed an irreversible oxidation at −0.52 V versus SCE due to Mo(0/I). This value is more negative than the corresponding reversible oxidation potential of *trans*-$Mo(N_2)_2(R_2PCH_2CH_2PR_2)_2$ (−0.16 V versus SCE for R = Ph (dppe),[15a] −0.43 V for R = Et).[16a] Thus, **1** is more electron rich than the diphosphine analogues. Consistent with this, the Mo–N(3) distance of the N_2 ligand located on the same side as the Mo atom with respect to the 4S plane is slightly shorter than that (2.014 (5) Å) of the dppe analogue.[17] Probably due

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(11) Anal. Calcd for $C_{20}H_{40}N_4S_4Mo$: C, 42.86; H, 7.19; N, 9.99. Found: C, 42.97; H, 6.98; N, 9.99. ^1H NMR (benzene-d_6) δ 0.73 (s, 3 H, Me), 1.11 (s, 3 H, Me), 2.28 (d, J = 11.0 Hz, 2 H, CH_2), 2.54 (d, J = 11.0 Hz, 2 H, CH_2).

(12) The brown solids were tentatively assigned to be *cis*-$Mo(N_2)_2Me_8[16]aneS_4$ on the basis of the observation of two $\nu(N{\equiv}N)$ bands (1935 s, 1850 s, cm^{-1}) and its quantitative transformation into *trans*-$Mo(CO)_2Me_8[16]aneS_4$[10] on bubbling CO in toluene. Due to the extreme air sensitivity an analytically pure sample could not be obtained.

(13) Crystal data for **1**: orthorhombic, space group $P2_12_12_1$; a = 14.468 (5) Å, b = 10.871 (6) Å, c = 17.140 (14) Å, V = 2696 (3) Å^3, Z = 4, ρ_{calcd} = 1.38 g cm^{-3}. The intensities of 3615 reflections ($3 < 2\theta < 55°$) were collected on a Rigaku AFC-6 diffractometer by using Mo Kα radiation. The data were not corrected for absorption (μ = 8.20 cm^{-1}). The structure was solved by the Patterson method and refined by block-diagonal least-squares by using 2809 unique observed reflections with $|F_o| > 4\sigma(|F_o|)$. Refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms and with fixed positional and thermal parameters for hydrogen atoms to converge R = 0.034 (R_w = 0.033) with GOF = 1.19. The largest peak in the final difference map was 0.50 e/Å^3. The R factor ratio for two possible enantiomers of **1** in crystals was not significant enough to determine its absolute configuration.

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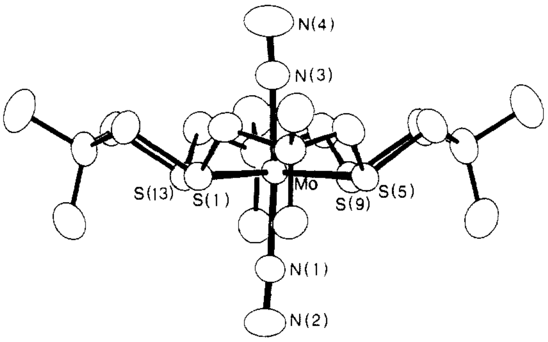

Figure 1. Molecular structure of **1** showing the 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follow: Mo–S(1) 2.424 (2), Mo–S(5) 2.428 (2), Mo–S(9) 2.419 (2), Mo–S(13) 2.424 (2); S(1)–Mo–S(5) 90.4 (1), S(5)–Mo–S(9) 89.3 (1), S(9)–Mo–S(13) 90.2 (1), S(1)–Mo–S(13) 89.7 (1), S(1)–Mo–S(9) 175.1 (1), S-(5)–Mo–S(13) 175.3 (1), N(1)–Mo–N(3) 176.8 (2), Mo–N(1)–N(2) 176.7 (5), Mo–N(3)–N(4) 176.2 (5).

to large anisotropic thermal motion of the free N(4) atom, which is common for coordinated N_2,[18] the N(3)–N(4) length is not different from the corresponding value (1.118 (8) Å) of the dppe complex.[17] The electron richness of **1** may be also reflected in the low $\nu(N{\equiv}N)$ frequencies (1955 m, 1890 vs cm^{-1}) compared with those (2020 w, 1970 s cm^{-1}) of the dppe analogue.[19] These electrochemical, spectral, and structural data suggest that the $MoMe_8[16]aneS_4$ moiety is an even stronger π-base than the $Mo(dppe)_2$ fragment. This is confirmed by MO calculations on the hypothetical model compounds, MoL_4 and *trans*-$Mo(N_2)_2L_4$ ($L = SH_2$) of D_{4h} symmetry and the corresponding PH_3 analogues of C_{4v} symmetry.[20] The coordinated thioether differs from the phosphine in having a free-filled p_π (lone pair) orbital. The antibonding interactions of the p_π orbitals with the $d_{xz}(d_{yz})$ orbital of the Mo atom destabilize the e_g orbitals (HOMO) of $Mo(SH_2)_4$, which are 0.78 eV higher in energy than the corresponding e orbitals of $Mo(PH_3)_4$. Consequently, stronger $d_\pi(Mo)-p_\pi^*(N_2)$ back-bonding is expected for *trans*-$Mo(N_2)_2(SH_2)_4$ than for the PH_3 analogue. Indeed, the overlap population of Mo–N π-bonding (0.160) assessed for the SH_2 complex is larger than that (0.133) of the PH_3 analogue. By contrast, the population of σ-bonding for the former (0.444) and the latter (0.437) are comparable. Thus, the above results can be rationalized by postulating that $Me_8[16]aneS_4$ is a p_π donor.

Further evidence for the electron richness of **1** is provided by its ready reaction with MeBr. Thus, reaction of **1** with 2 mol of MeBr in benzene under ambient conditions for 5 h gave quantitatively a dimethylhydrazido complex, *trans*-$\{MoBr(N_2Me_2)Me_8[16]aneS_4\}Br$ (**2**)[24] as brown crystals. No methyldiazenido (—N=NMe) complex was detected in the reaction mixture. Dimethylation of the coordinated N_2 ligand with MeBr has been observed already for the electron-rich *trans*-$Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2$,[16] whereas the corresponding reaction of the dppe analogue stopped at the stage of monomethylation.[25] It is to be noted that the dimethylation of **1** is more facile than that of the $Et_2PCH_2CH_2PEt_2$ complex which took place under photoirradiation.[16b]

We are currently investigating the reaction of **1** with other RX (R = H, acyl), H_2, and π-acids to delineate the p_π character of $Me_8[16]aneS_4$. Thus, **1** gives novel organometallic compounds containing $Me_8[16]aneS_4$, e.g., *trans*-$MoL_2Me_8[16]aneS_4$ ($L = HC{\equiv}CH, CH_2{=}CH_2$).[26] Thioethers have been long ignored as coligands in organometallic chemistry. The successful preparation of **1** as a thermally stable compound and the versatility of its chemistry, however, suggest that quadridentate crown thioethers have great promise as potential ligands at least comparable with tertiary phosphines.[27]

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Supplementary Material Available: Details of X-ray structure determination and listings of atomic coordinates, thermal parameters, and bond distances and angles (10 pages); listings of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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(24) Anal. Calcd for $C_{22}H_{46}N_2S_4Br_2Mo$: C, 36.57; H, 6.42; N, 3.88. Found: C, 36.47; H, 6.32; N, 3.61. ^1H NMR (acetone-d_6) δ 1.18 (s, 6 H, Me_2C), 1.24 (s, 6 H, Me_2C), 2.77 (d, $J = 11.0$ Hz, 4 H, CH_2), 2.86 (d, $J = 11.0$ Hz, 4 H, CH_2), 3.24 (s, 3 H, Me_2N).

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